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**LASER PHYSICS CONFERENCE HELD AT THE CONCORD MOTEL,
DES PLAINES, ILLINOIS, 22-23 MARCH 1965.**

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1965

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LASER PHYSICS CONFERENCE

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ADVANCED RESEARCH PROJECTS AGENCY

at

**CONCORD MOTEL
DES PLAINES, ILLINOIS
22, 23 MARCH 1966**

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PREFACE

The Office of Naval Research sponsored an informal conference on fundamental problems in laser physics at the Concord Motel in Des Plaines, Illinois, on Monday and Tuesday, the 22nd and 23rd of March. The meeting was held primarily for the benefit of the ONR contractors receiving support from the Fundamental Limitations portion of the ONR/ARPA Laser Program. However, others interested in this aspect of the ONR/ARPA Laser Program were also invited to contribute to the meeting.

It was intended that the conference primarily be devoted to discussion of certain specific topics without the presentation of formal papers. In order to start off each session, specific contractors were asked to discuss work on their research programs together with comments on the possible future direction of their work. The original agenda for the meeting follows:

Agenda for Laser Physics Conference

Monday
22 March 1965
3:00 P.M. - 6:00 P.M.

Session I Moderator: R. E. Behringer, ONR

Part 1 Energy Exchange in Solids (including crystal field effects)

Discussion
Leaders: D. S. McClure, University of Chicago
W. Holloway, Sperry Rand Corp.
C. Naiman, Mithras Corp.

Part 2 Energy Exchange in Gases

Discussion
Leaders: T. Marshall, Columbia University
M. Muller, Varian Associates

Tuesday
23 March 1965
9:00 A.M. - 12 Noon

Session II Moderator: J. A. Soules, New Mexico State University

Part 1 Nonlinear Effects

Discussion
Leaders: R. Braunstein, UCLA
Y. R. Shen, UC Berkeley
M. Subramanian, Purdue

Luncheon
12 P.
Aligan 's at Concord Inn

Tuesday
23 March 1965
1:00 P.M. - 4:00 P.M.

Session III Moderator: F. T. Byrne, ONR

Part 1 Gas Breakdown

Discussion
Leader: A. Haight, United Aircraft Corp.

Part 2 Refractive Index Variation

Discussion
Leaders: J. Izatt, New Mexico State University
H. Daw, New Mexico State University

In addition to those on the agenda, several participants made contributions which added substantially to the success of the conference. Transcripts were provided to all contributors for editing purposes, with some additional editing done by the organizer. Most editing was held to a minimum, although in some instances a considerable amount was done.

Many thanks are due Lloyd White and Richard Miller of ONR Chicago for the excellent job they did in making local arrangements and providing for both transcribing and recording services. Prof. Jack Soules and Lloyd White contributed many helpful suggestions and constructive criticisms in the planning of the program and thereby assured the overall success of the conference.

Robert E. Behringer
Office of Naval Research
1030 E. Green Street
Pasadena, California

Session I Moderator: R. E. Behringer, ONR

Part I Energy Exchange In Solids (including
crystal field effects)

Monday Afternoon
22 March 1965

McClure	University of Chicago
Lohr	University of Chicago
Holloway	Sperry Rand
Schawlow	Stanford University
Ohlman	Westinghouse
Naiman	Mithras
diBartola	Mithras

MONDAY AFTERNOON SESSION

March 22, 1965

The Monday Afternoon Session of the Laser Physics Conference was called to order at three o'clock p.m., March 22, 1965, at the Lexington Room of the Concord Motel, Des Plaines, Illinois, Dr. Robert E. Behringer, Moderator.

DR. BEHRINGER: I believe we are ready to start now. I think just about everyone is here. I will now turn the meeting over to Prof. Don McClure and he will give us a synopsis of the sort of work he is doing at Chicago.

PROF. D. S. McCLURE: Thank you. The work we are doing is in several parts. The part I will spend most time on is what we call the collective effects on transition intensities. This is not exactly in energy transfer, although the effects we are talking about are those which enhance the intensity of an absorption band as a consequence of the closeness of several ions in the crystal.

The first observation that struck my attention was that the pairs of manganese ions which occur randomly in a manganese-doped zinc sulfide crystal and which we identified and have already published some years ago, were ten times more strongly absorbing than the single ions themselves. This suggested that there were some interesting effects of exchange on this intensity.

The next observation was that in pure chromium oxide the quartet transitions are about five times more intense than they are in ruby, which these transitions resemble; there is one-to-one correspondence between the ruby transitions and those in chromium oxide. The doublet transitions were enhanced many more fold than the quartet transitions.

Then Ferguson has observed some very sharp bands in KMnF_3 which intensify by an order of magnitude or more when the manganese is present as a pure compound compared to the diluted form in KZnF_3 .

We have collected a number of other examples of this nature and Larry Lohr who will follow me, is working with me on these problems, and he will discuss them briefly.

Our interest was to see if this is a general phenomenon, and having found that it is, we want to explain it.

However, we have had to back up a bit and explain the single ion transition moments in more detail, which Larry has largely done.

The next aspect of this work has been the study of the extra bands which appear in antiferromagnetic compounds. We have found in the literature and in our experimental work a number of cases in which a band appears below the Néel temperature and disappears above it.

A band in NiO was the first of these, discovered by Neuman and Chrenko. This band appears in the

infrared and no one as yet has found a suitable explanation for it except that it has something to do with the antiferromagnetism of NiO .

An interesting one which we have been working on is in cobalt fluoride, a rutile type structure. A band at about 23,000 wave numbers appears below the Néel temperature and disappears above it. It is polarized perpendicular to the C axis and is an electric dipole transition.

We think this might be an excitation of some kind in the cobalt fluoride lattice and, if so, it will be very interesting to identify it positively, because this would be a new kind of excitation. Although excitons are observed in molecular crystals and in inorganic crystals such as cadmium sulfide, no one has yet positively seen one in transition metal salts in which the excitations are d to d electron transitions.

In order to find out a little bit about these transitions we have been using our pulsed magnetic field apparatus and have been able to alter the spectrum of this band in fields up to 200 Kilogauss. I can't yet say what this is telling us, but interesting things have happened and we believe that shortly we will be able to give a reasonable interpretation of these data.

Since there are two ions per unit cell in this crystal they may have a collective state which has odd parity. You realize that the states of single ions all have even parity.

Well, this is about all I want to say on the collective effects in transition intensities.

We are also doing some work on the analysis of the divalent rare earth spectra and I will just give a very brief idea of what this is like.

We are working mainly on the divalent rare earths which are uninteresting to laser people, I am sorry to tell you, but it is these particular ones which do not luminesce which I think will tell us important things about the 5d electrons in these compounds.

We put the rare earth into calcium fluoride or strontium chloride and reduce it by various means to +2, while it is in the crystal. We are now doing various chemical reduction techniques which work satisfactorily, although as you well know we can reduce these by radiation methods and by electrolytic methods. We have tried them all.

But our main interest in studying these ions is to find out whether the ground state in the series of rare earths, starting from lanthanum, going to gadolinium, ending at ytterbium, ever becomes a 5d electron state.

You realize the +3 rare earths always have 4f electrons in the ground state and so also do the +2 rare earths. In the latter the low energy transitions are of two kinds, the 4f to 4f and 4f to 5d.

But in the particular cases of lanthanum, gadolinium, cerium and terbium, it seems that the 5d electron intrudes into such a low energy region that the ground state may contain a 5d electron.

We have done a quite complete analysis of the ytterbium spectrum, which shows us something about the parameters of the crystal field and the electrostatic coupling, in this one example, and we think we can be equally successful in cerium. We are getting good spectra and we have a complete crystal field analysis.

There are one hundred forty states in ytterbium in zero symmetry, and something like fifty in the cubic symmetry. In cerium there are fifty states, also, in the fd configuration and about the same number in the

f^2 configuration. We have to find out which configuration produces the ground state in this case.

Well, these are all the remarks I want to make about those two problems in general, and Larry can give us a little bit more detail on the particular problem of the manganese spectra and the collective effects. Perhaps we should have questions first.

DR. BEHRINGER: Questions any time they arise, I would say.

PROF. ARTHUR SCHAWLOW: Have you identified a case where the d level is lowest?

PROF. McCLURE: Well, it seems to be fairly certain for gadolinium and lanthanum, and cerium and terbium are on the borderline.

DR. LARRY LOHR: The sub-title of this afternoon's session is crystal field effects, and that will be the emphasis in my part of this, although we will see that there are certain aspects of experiments that as previously mentioned seem to require some cooperative interactions in order for them to be explained.

As mentioned, we are concerned with the optical spectra of divalent manganese salts. If you ask why divalent manganese, you recall that divalent manganese is the ion with a half filled 3d shell and with that you get more possible arrangements of electrons and, hence, more states than with any other possible number of electrons. That means the possibility of more data with which to test out the ideas.

In addition, some of these transitions are extremely sharp. The sharpest one that I know of is a transition in the blue, which has a width at liquid helium temperature about one and a half wave numbers at an energy of 25,000 wave numbers, which is quite sharp.

The experiments, with very few exceptions, have consisted of visible and ultraviolet absorption spectra, a bare minimum of emission and diffuse reflection work.

Of course, we observe energies and intensities together with vibrational structure and perhaps finer structure, splittings of the order of one to ten wave numbers, as a function of the nature of the salt, the temperature, concentration of manganese in a few cases when it is in a dilute salt, polarization of light, and also, as mentioned, a strong magnetic field up to 200 Kilogauss.

The information which we attempt to extract from all this data, first of all is the assignment of excited states in terms of symmetry and spin, this is actually the least interesting because at the present state of the art it is pretty well understood for any octahedral complex. However, it is the starting point for all the rest of the analysis, so it is important although there are very few surprising results.

The second thing is the question of intensity mechanisms, which is not nearly so well understood. Other information we would like to obtain, of course, are geometry of excited states, information about the nature of the vibrational structures we observe in absorption: are these frequencies different in the excited states than they would be in the ground state; in the case of an ion which has an impurity in a crystal, are we observing localized modes or are they lattice modes?

The spin couplings are of great interest, especially that of an optically excited ion to a neighbor paramagnetic ion in its ground state, or between ions of two different electronic states.

I have been especially interested in the effects of the co-valency or delocalization of electrons on the inter-electronic repulsions.

Lastly, there are questions, as mentioned, concerning the energy transfer to other ions.

Can we see slide number one, which is a list of compounds we have been considering, and I should say here we have not been doing experiments on all of these. These are the compounds we have been considering in our analysis. There are about eight of these or so that we have been doing experiments on ourselves in the last

year or two. These include the manganese chloride dihydrate, sulfate tetrahydrate, the manganese perchlorate hexahydrate, manganese carbonate, cadmium fluoride with manganese, zinc sulfide with manganese. One or two more represent our own experimental work. The rest represent experimental work in literature and unpublished experimental work by other researchers.

The second column just lists the chemical complex, so to speak. The third column is the site symmetry.

Nearly all of these are six coordinated. The only exceptions are cadmium fluoride, which is eight, and four in the two forms of zinc sulfide.

In addition, most of these are centro-symmetric, even though they may not be perfect octahedra, as you can see here. Nearly all of these site symmetries contain the inversion, the exceptions being the chloride tetrahydrate and sulfate tetrahydrate and, obviously the tetrahedral complexes.

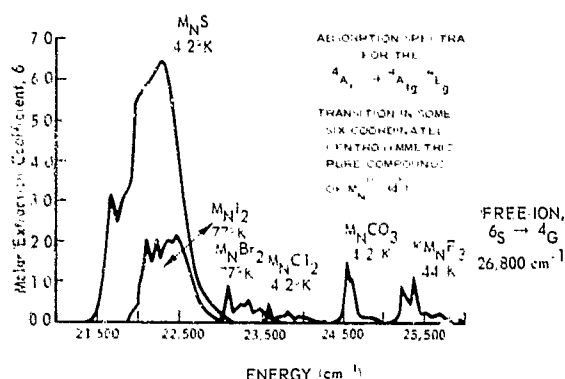
Among the six-coordinated species, the tetrahydrate ones are the only non centro-symmetric ones. Of course, this is important when you recall, as mentioned, these transitions are within the d shell, hence they are even states to even states.

The last column lists the manganese distances in these various compounds in the form of X-ray data. You see in a number of simple compounds, especially the binary compounds, there are manganese-manganese distances of between three and a quarter to four Angstroms. This is of importance for the following reason.

Mn^{+2} SALTS			
COMPOUND	COMPLEX	SITE SYMMETRY	$M_1, M_N(\text{\AA})$ AND NUMBER OF N N N
MnF_2	MnF_6	D_{2h}	3.28 (2), 3.81 (8)
$MnCl_2$	$MnCl_6$	D_{3d}	3.68 (6)
$MnBr_2$	$MnBr_6$	D_{3d}	3.82 (6)
MnI_2	MnI_6	D_{3d}	4.16 (6)
$MnCl_2 \cdot 2H_2O$	$MnCl_4(OH_2)_2$	C_{2h}	3.70 (12)
$MnCl_2 \cdot 4H_2O$	$MnCl_2(OH_2)_4$	C_1	~6, NOT BRIDGED
$MnBr_2 \cdot 4H_2O$	$MnBr_2(OH_2)_4$	C_1	—, NOT BRIDGED
MnO	MnO_6	O_h	3.13 (12), 4.43 (6)
MnS	MnS_6	O_h	3.68 (12), 5.21 (6)
$ZnS:Mn$	MnS_4	T_d	3.84 (12)
$ZnS:Mn$	Mn_4	C_{3v}	3.811 (6), 3.815 (6)
$KMnF_3$	MnF_6	O_h	4.18 (6)
$KZnF_3:Mn$	MnF_6	O_h	4.05 (6)
$CdF_2:Mn$	MnF_8	O_h	3.81 (12)
$MnCO_3$	MnO_6	C_{3i}	3.76 (6)
$MnS_2F_6 \cdot 6H_2O$	$Mn(OH_2)_6$	C_{3i}	—, NOT BRIDGED
$Mn(ClO_4)_2 \cdot 6H_2O$	$Mn(OH_2)_6$	C_3	—, NOT BRIDGED
$MnSO_4 \cdot 4H_2O$	$Mn(OH_2)_4O_2$	C_1	—, NOT BRIDGED

That will be all for that slide, please.

In examining all of this data, one of the most interesting conclusions or observation that has come out of this is that the integrated intensities, that is the oscillator strengths, can be roughly divided into two groups. There are compounds where you have manganese neighbors. In such situations you get oscillator strengths of the order 10^{-7} , say, up to 10^{-8} or possibly up to 10^{-5} . Now, these refer to the pure, simple binary compounds. Several examples are shown in Slide No. 2. It also refers to the cases where you have impurity ions in large enough concentration so that you have pairs or larger clusters, for example manganese in ZnS and $KZnF_3$.



On the other hand, the other group have oscillator strengths that are, say, roughly one-hundredth of that. These include isolated manganese ions in, say, a nearly centro-symmetric or even exactly centro-symmetric complex. This includes all of the higher hydrates, such as tetra or hexahydrates, where even though they are pure compounds you have essentially discreet complexes, so there is a large distance. There is no simple bridging. It includes that group and then, also, of course, the situation where you have an impurity ion of a very low concentration.

It is observed in these concentration studies, of course, that these intensities do not obey Beer's law quite strictly; they do not by one or two orders of magnitude departure.

We don't know as yet just what this intensity mechanism is in this concentrated case, except it must involve some sort of cooperative mechanism.

In the dilute cases it is more or less understood that there are only three possibilities, all of which involve the spin orbit coupling, since these are all spin-forbidden transitions. The first possibility is that the transition is magnetic dipole; these are intrinsically weak.

The second is that it is electric dipole, by the small odd distortion that you have in some of these complexes, like the chloride tetrahydrate, and the third being they are made allowed by a coupling with an odd vibration in the centro-symmetric ones.

All of these mechanisms, since they all involve spin orbit coupling, can only give rise to oscillating strengths, of the order of something like 10^{-7} or 10^{-9} .

DR. ROBERT C. OHLMAN: Are these at room temperature or below the Néel temperature in cases you are describing?

DR. LOHR: A very good point; it really doesn't matter. This is what I was getting to next, is that although the band shapes of these compounds are very sensitive to temperature in some cases, not all, in integrated intensities (the area) is remarkably insensitive to temperature. It doesn't matter whether you are above or below the Néel temperature. This is very surprising. If these things are ascribed to be vibronic, one would anticipate a temperature dependence which goes something like the hyperbolic cotangent of one over the other.

This is observed in divalent cobalt and divalent nickel spectra in some cases, but here we don't see it even in the centro-symmetric systems. To the accuracy you can measure the oscillator strength in $KMnF_3$ or in $MnCO_3$ there does not seem to be any temperature dependence of the areas, which is a puzzling point.

We have made some progress recently in trying to interpret the polarizations of these; all our spectra, by the way, are essentially single crystal spectra. For those few compounds that are non centro-symmetric, we perform simple semi-empirical extended-Hückel molecular orbital calculations, from which one can generate one electron energies and approximate one electron wave functions. These can be combined in such a way to produce five electron states and one can get the five electron, total oscillator strengths.

This, of course, is not applicable in case of the centro-symmetric systems.

Only one compound to my knowledge has been shown to be definitely magnetic dipole in some of its characteristics. It is manganese hexafluorosilicate hexahydrate. If the oscillator strength is greater than 10^{-9} you can just about rule out that mechanism, for diluting systems anyway.

PROF. SCHIAWLOW: You say the oscillator strength greater than 10^{-9} rules out magnetic dipole. Does the polarization also confirm that?

DR. LOHR: Yes, this is it essentially. This is how one knows you are looking at an electric (or magnetic) dipole aside from the question of intensity. In fact, the polarization argument is, of course, really the conclusive one and the other is sort of confirming, but not quite as reliable. But I think it is.

One other thing I would like to briefly mention is the work we have done in connection with the analysis of all the spectra in terms of the energies and wave functions obtained from using a slightly different formalism than the traditional ones. One usually thinks in terms of the Orgel matrix or the Tanabe-Sugano matrix, in which the energies of all states are represented by three parameters; in terms of cubic crystal field $10Dq$ (or Δ) and in terms of Racah parameters of Slater-Condon parameters (F_2 and F_4 or B & C), whichever you prefer.

We have found it convenient to recast all of these expressions in a slightly different formalism, in which instead of taking B and C (or F_2 and F_4 as adjustable parameters for the complex ion, which does not lend

itself very well to interpretation, because in the free ion they are essentially a measure of the shape of the radial function. When you no longer have a spherical system it is not easy to interpret these parameters, although you can fit them fairly well; we have found it convenient to do something like the following:

I will not go into any great detail on this, but just sort of outline the kind of thing one means. Say if you have a given electric repulsion integral, this would be a Coulomb integral,

$$\int \phi_d^*(1) \phi_d(2) \frac{1}{r_{12}} \phi_d(1) \phi_d^*(2) d\tau_1 d\tau_2$$

involving just one d orbital now, we can write it symbolically as $[d^2, d^2]$, just the classical repulsion of this charge distribution d^2 with another electron in the same charge distribution; this integral has a value in terms of the Racah parameters of $A + 4B + 3C$. I will put subscript zeros in here, $A_0 + 4B_0 + 3C_0$, indicating this a free ion. Normally, for a complex one would just take a B and C as readjustable parameters; in other words, I am just taking new values of these.

Well, we have taken the scheme that you go back and think of this d now as having not been a pure d; it is somewhat delocalized, it has some mixing of ligands, in other words, it is representing a general wave function ψ , which is some coefficient of this d orbital plus the coefficient of the ligand;

$$\psi = C_d \phi_d + C_l \phi_l$$

to a very good approximation this integral (when you say what you really mean here, you want the integral $[\psi^2, \psi^2]$ analogous to $[d^2, d^2]$) is equal just to the one center term $[d^2, d^2]$, multiplied by the square of the fraction of d character (f_d) in this molecular orbital, where f_d is defined in accord with Mulliken as C_d^2 , (this integral must be fourth power in the coefficient as the orbital appears four times) plus half of the overlap term between the d orbital and the ligand orbital.

$$f_d = C_d^2 + C_d C_l S_{dl}$$

Such a scheme effectively is including more than the one center term; it is including the one center Coulomb, plus two center exchange integrals, but it does neglect two center Coulomb integrals, which are large, but one can show that providing you are looking at transitions which are crystal field independent that these are largely cancelled out.

Now, we have set up many of our fitting schemes in terms of these, in which these factors (f_d), in general one for each of the five d orbitals, will be your adjustable parameters for fitting, multiplied by the atomic expressions using atomic numerical values for B_0 and C_0 . Additional parameters are the orbital energies, or merely 10Dq for cubic complexes.

Now, the advantages of this scheme are several. I must mention this is not completely new; it is an extension of some ideas that were used some years ago by Koide and Pryce in analysis of manganese spectra. Their scheme is a special case of this.

One thing that it gives directly is the splitting of some of the accidentally degenerate, crystal-field independent

levels, not only in manganese, but also trivalent chromium and many other systems. Sometime you have two spectral terms which accidentally have the same energy if you assume the electron repulsions to have the free ion form. These degeneracies are automatically lifted here.

An even bigger advantage is this extends itself very nicely to consideration of low symmetry. For those transitions which don't depend upon crystal fields, that is they don't depend upon differences in orbital energies, the transitions are essentially atomic in that they depend upon rearrangement of electrons, and the energy is just that for going to an unfavorable electron repulsion situation.

We can do several things as far as the values of these (f_d), either use them in a fitting scheme or we just use them arbitrarily or also we have had some success taking these from some molecular orbital calculations of the type I mentioned previously in connection with oscillating strengths. It means writing out a list of repulsion integrals, one by one.

Another thing that has been applied to, as a sideline in checking this out, is the case of some Stark effects on optical lines, in which the interpretation is that the electronic field (the particular case was ruby) is changing the molecular orbital slightly due to electrostriction. If the transition in question is crystal field independent, it depends only on the electron repulsions, so what you are actually doing by changing the wave functions, is that you are modifying the electronic repulsion integrals and that is essentially the pseudo-Stark effect one observes in ruby.

There are a number of other aspects of our work which I won't have time to go into. One is some of the analyses of some of the fine structure, that is some of the second-order spin orbit splittings you see in excited states, splittings of the order of five to ten wave numbers. We have been able to calculate these in case of a cubic site and a quartet E state which is second-order split, and we believe this has been observed for manganese in zinc sulfide. We hope to extend this to low symmetry to account for some of our recent experimental splittings of this type in low symmetry compounds.

The vibrational analysis is making some progress, but we have a long way to go there. Well, we hope to have more to say about that. We do think that there is evidence from experiments and also from our calculations that the excited states of divalent manganese, and there are quite a number of these, are more or less unstable with respect to various distortions and in some states unstable with respect to many distortions, not just a totally symmetric one. This is the reason you may just get a broad band instead of a lot of discrete lines; in other words, the band you see, even at low temperature, shows no structure, it is just a superposition of many vibrational progressions.

Other states, even the crystal field independent transitions, are occasionally broader than you would anticipate. However, the fact that a transition is independent of 10Dq does not mean that the transition energy is independent of a totally symmetric distortion. These are not quite the same thing, when you consider the energies in terms of a scheme such as this (variable electron-repulsions), and there is some experimental evidence that this is the case in some of the higher states of manganese carbonate.

DR. CHARLES NAIMAN: We have been studying some similar pair effects for a while and have found parallel results which may shed light on what has been presented here.

In these cases we have been looking mostly at chromium, heavily doped ruby in particular. There are bands in the near UV, which display some of the same properties that you have just heard about manganese systems.

We believe that we have at least one possible explanation of the experimental observation (similar to what McClure mentioned earlier) that when you have pair effects you can get violations of symmetry that lead to an enhanced intensity.

Another important experimental fact is the temperature dependence which is quite critical. I think there are some people in this audience that are better aware of this than I, but let me just mention what we have observed briefly.

If you take a look at heavily doped ruby we find on the tail of the blue bands four relatively sharp bands; two in one polarization and two in the other. These absorptions appear to go as the square of the concentration. Furthermore, if you study the temperature dependence of these same bands, you find the same interesting question which came up earlier.

For example, you might look for a $\coth \frac{h}{2kT}$ dependence for the absorption intensity. You don't find this. In other words, it doesn't seem to be made by vibrations even though there is a lot of vibrational structure on top of these bands.

The other thing you might look for, is the type of interaction Professor Schawlow and others have found for the pair lines, such as the N lines near the R lines. Here one has ferromagnetically or anti-ferromagnetically coupled pairs. If that is the case then you have some energy level system which either starts with total S equal to zero antiferromagnetic coupling or if you take the two spin 3/2 coupled ferromagnetically you will end up with a total spin of three. Either way one ends with a Lande interval rule and then you will also get an exponential dependence for the absorption intensity reflecting the population of these states and the selection rules that go with them. These bands again don't show this type of dependence. The latter occupied our first thoughts because there are known to be some doublet energy levels that are spin forbidden from the ground state in this region. They then might have been made allowed by this magnetic pair spin coupling.

We think there is another possible explanation, that runs something like the following:

What happens is that you probably have in the ground state a d^3-d^3 pair complex, but the excited state is a d^2-d^4 state with proper symmetry normalization. In other words, here we have somehow produced a double "charge transfer" or "oxidation-reduction" transition.

For example, you think of this whole complex as two chromiums embedded in nine oxygens, where you have two outside triangles of oxygens sitting on their

bases and another one between them standing on its apex. Each chromium resides along the trigonal axis between the central triangle and an outer one. If you follow this model and maintain trigonal symmetry at least for the ground state, then you find what your ground state has to be by just coupling their orbital angular momenta.

The lowest of such excited states should correspond to a d^2 ion in its ground state and a d^4 ion in its ground state. Take these states and now couple them together and you will find that in total you can get, in a trigonal field, four states, of which two will appear in one polarization and two in the other. This is the main absorption characteristic found.

Interestingly, we found at least one other chromium complex which is very similar to this, where we can also explain some pair spectra that occur in the same region.

That is a rather exotic beast which looks like the following: You've got a chromium ion, with an oxygen bridging the two chromiums and then surrounding each Cr at the other five coordinating positions we have an ammonia. Here we have in tetragonal symmetry the parallel of what we had in the trigonal symmetry of ruby. Schaeffer very interestingly found that this complex also has four bands in the near UV region. Here again these intensities are also high for three of them, (they are almost as strong as the blue and green band), while one of them is weak.

Now, you can postulate the same transition mechanism. Again go to your d^2-d^4 ground states, couple their orbital angular momenta together, and again you end up with four bands. Now you have tetragonal selection rules, and in fact you can go a step further. You can assume, to the first approximation, that the pair splittings will just be due to the single ion splittings in tetragonal symmetry. If one uses the e_g and t_{2g} formalism of McClure for the e_g and t_{2g} tetragonal splitting and just add the single ion energies you can then compare these with the experimental data. Because there are two unknowns (α & β) there is still some ambiguity which however can be resolved because, using D_{4h} symmetry one of the transitions will be electric dipole forbidden. This is the one which we assign to the weak absorption. We get self consistent results with the tetragonal splitting of transition metal ions in porphyrins.

Now, the same mechanism, appears to be applicable to a lot of other systems.

For example, you can ask yourself the following question in ruby. If I have gone ahead and produced an excited d^2-d^4 state where the d^2 and d^4 ions end up in their single ion ground state what will that electron configuration look like? This will be $d^2(t_{2g}^2) - d^4(t_{2g}^3 e_g^2)$. In addition to producing this excited state I can also produce that one which corresponds to $d^2(t_{2g}^2) - d^4(t_{2g}^4)$. In fact in the single ion approximation the difference between these two is approximately the value of $10Dq$ for the d^4 system. For example, Mn^{3+} in Al_2O_3 . In other words, there should be a pair absorption band at a frequency higher than the pair bands which are at $30,000 \text{ cm}^{-1}$ by about $17,000 \text{ cm}^{-1}$.

I understand from Nelson at Bell Labs they have seen such pair effects in the $48,000\text{ cm}^{-1}$ region and so it seems to be quite a general mechanism. Copper acetates, which are the first pair effect complexes, have also shown such transitions that appear in the near UV, so we think this may be a very general mechanism.

The other thing I would like to point out is that I think Balhausen has also seen some unusual intensity effects in nickel systems. He has ascribed them to excitons, in the $d^N \rightarrow d^N$ system. This appeared in a government report around a year and a half or two years ago, providing another possible mechanism to be explored.

DR. HOLLOWAY: I would like to summarize that portion of our work which involves transfer of energy in solids and is pertinent to the present discussion.

This work has been discussed in some detail in the technical summary reports, with which I am sure you are all familiar.

We have studied the transfer of energy between active ions by the examination of the fluorescence properties. The experiments may be divided into two major sub-headings, the effect of the interactions between rare-earth ions on the rare-earth ion fluorescence and the studies of the fluorescences in concentrated manganese systems.

Since the rare-earth ion work is most pertinent to this section and is also the best understood, these studies will be emphasized. There are two types of studies which have been done involving the rare-earth ion, the quenching or the deterioration of the fluorescence of an active ion by a second ion and the transfer of excitation energy from one fluorescent ion to a second ion.

These results are consistent with the resonance transfer of energy theory. That is, a virtual photon may be exchanged between ions with appropriate energy levels. In the particular examples which we have studied, this means there is an overlap of the fluorescence lines of the excited ion and the absorption lines in the second or quenching ion.

For our first example we have studied the radial dependence of the quenching interaction of the tri-valent holmium ion on the tri-valent terbium ion fluorescence in rare-earth trichloride hexahydrates. Experimentally, our technique has been to flash-excite the terbium ion fluorescence and then measure its decay as a function of the concentration of the holmium ions. May I have the first slide which indicates the procedure used in these experiments.

$$\frac{1}{\tau_{Obs}} = \frac{1}{\tau_{Fl}} + \frac{1}{\tau_{Int}}$$

$$P_{Int} \propto \frac{1}{\tau_{Int}}$$

$$\propto \frac{1}{R^6} \quad (\text{dipole-dipole})$$

$$\propto \frac{1}{R^8} \quad (\text{dipole-quadrupole})$$

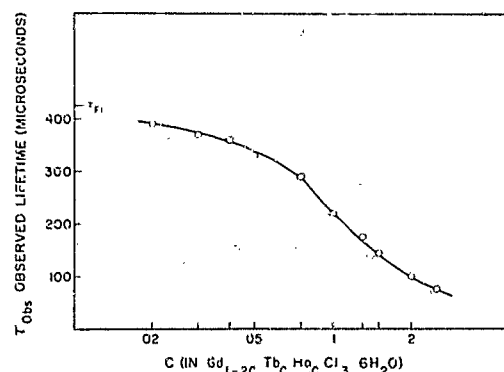
$$\propto \frac{1}{R^{10}} \quad (\text{quadrupole-quadrupole})$$

The quantity which we observe experimentally is τ_{Obs} . The τ_{Obs} is composed of (1) an intrinsic fluorescence lifetime τ_{Fl} , which is determined by the temperature and crystal site symmetry and is just the lifetime without ionic interactions and (2) an artificial lifetime τ_{Int} , which is determined by these ionic interactions. This artificial lifetime is inversely proportional to the

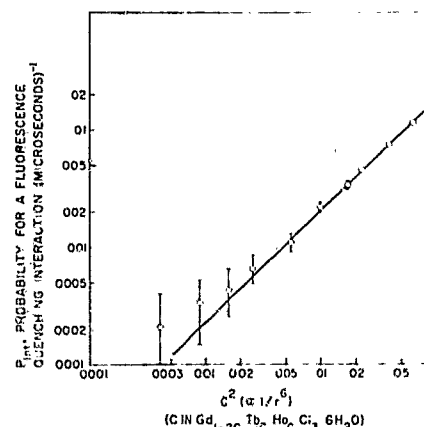
probability for quenching interaction. From the resonance transfer of energy theory, the radial dependences which one expects for various types of interaction are well known and are listed on this slide.

In the data which I will show either P_{Int} or τ_{Int} is given as a function of concentration. Since the concentration is proportional to the inverse cube of the radius, this is equivalent to plotting the radial dependence.

The next slide shows the typical data for τ_{Obs} as a function of concentration. The experiment can be viewed as a dilution of crystals of $Tb_{15}Ho_{15}Cl_3 \cdot 6H_2O$ with $GdCl_3 \cdot 6H_2O$. Only the holmium ions effect the terbium fluorescence. This slide shows a typical curve. The τ_{Fl} may be obtained by extrapolation of the data to the point where no interactions are present due to holmium ions so that $\tau_{Fl} \approx \tau_{Obs}$.

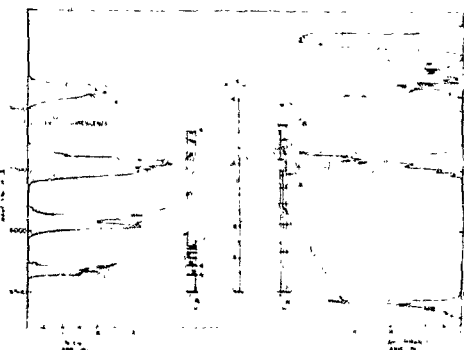


In the next slide, we show this data reduced in the manner described in Slide 1. The probability for a quenching interaction is shown as a function of C^2 . The brackets indicate our errors. Indeed, we see that the probability for quenching interaction is roughly proportional to r^{-6} or C^2 , which we believe indicates a dipole-dipole interaction between the terbium and the holmium ions.



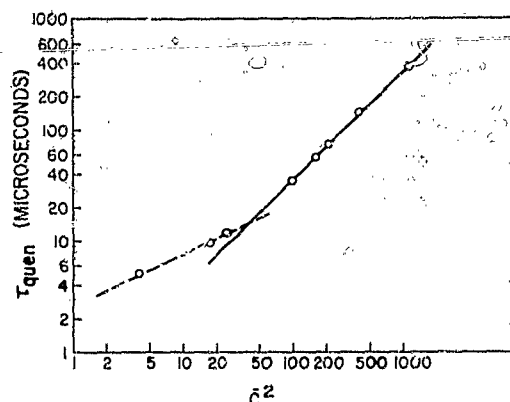
The other fact that is important in the resonance transfer of energy theory is that there be an overlap of the fluorescence bands of the excited ions with the absorption bands of the quenching ions.

In the next slide we show explicitly the terbium fluorescence lines and their designations and the holmium absorption lines and, demonstrate explicitly the overlap in this case.



From the literature one can also find lifetime data for τ_{obs} as a function of concentration. The one case in the literature which we reduced by the method described above was performed for concentration quenching of the neodymium ion in sodium gadolinium tungstate.

May I have the next slide.



DR. FRED McCLUNG, HUGHES: Do you want to look at the overlap of terbium absorption with holmium fluorescence instead of terbium fluorescence and holmium absorptions?

DR. HOLLOWAY: No. The energy goes from terbium to holmium.

This is lifetime data, plotted versus C^{-2} and the graph is just inverted from those previously shown. Instead of the probability for quenching interaction, I have plotted $\tau_{\text{Int}} + 1/P_{\text{Int}}$, which on this slide I call τ_{quen} . We are measuring the lifetime of the neodymium ion as quenched by other neodymium ions. For cases where there are small concentrations of the neodymium ions, again it follows, C^{-2} dependence, and indicates a dipole-dipole interaction. For higher concentrations

this dependence changes and becomes linear in concentration. We believe that this is due to the filling of the nearest neighbor sites. In this case you have the energy drained off; the physical analogy would be parallel resistors on a capacitor; and you'd expect it to be linear with concentration.

PROF. SCHAWLOW: At what concentration does that happen? These are the concentration of percent squared?

DR. HOLLOWAY: Yes, inverse. There should be a minus two here (i.e. in this slide). This data, by the way, is from Peterson and Bridenbaugh, Applied Physics Letters, 4 173(1964).

Now, I would just like to digress briefly and report some work we have done on solutions. Because solutions are so easy to make I usually do my preliminary work on them.

DR. NATHAN T. MELAMED: Are you looking at the neodymium fluorescence all the while?

DR. HOLLOWAY: This is the lifetime of the neodymium fluorescence (i.e. on slide 5).

DR. MELAMED: Shouldn't it reach a stable lifetime at some point where there are no interactions?

Shouldn't the lifetime reach a constant value?

DR. HOLLOWAY: Yes, true. That is why on my original data the curve folded over, it is just a question--

DR. MELAMED: You just didn't show it on the second curve.

DR. HOLLOWAY: I didn't show their original data just the reduced data.

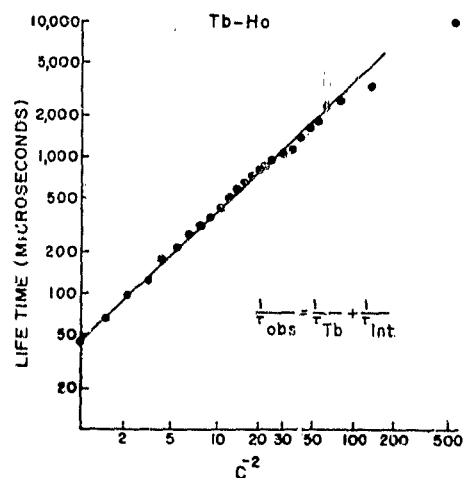
DR. ROBERT C. OHLMAN: Does the holmium fluorescence increase?

DR. HOLLOWAY: There is no holmium fluorescence in this particular system.

DR. OHLMAN: The terbium-holmium--

DR. HOLLOWAY: That is right. It just turns out in these crystals there is no fluorescence observed.

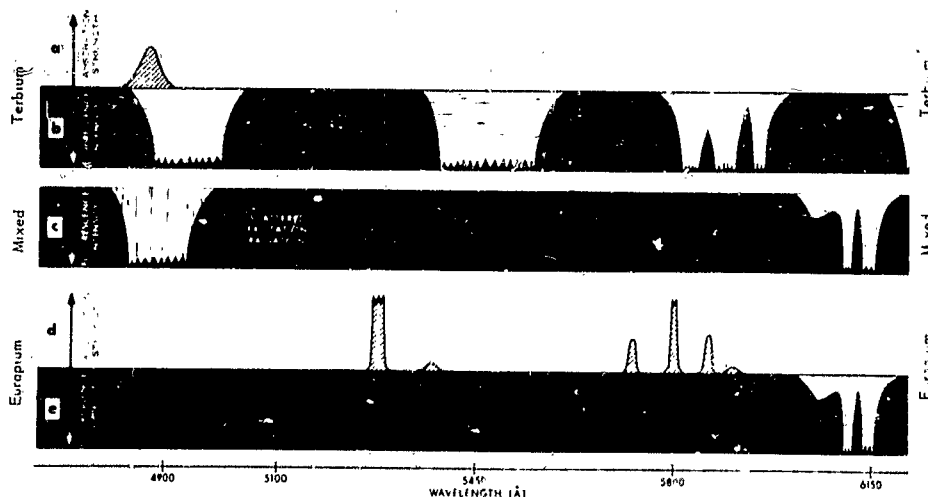
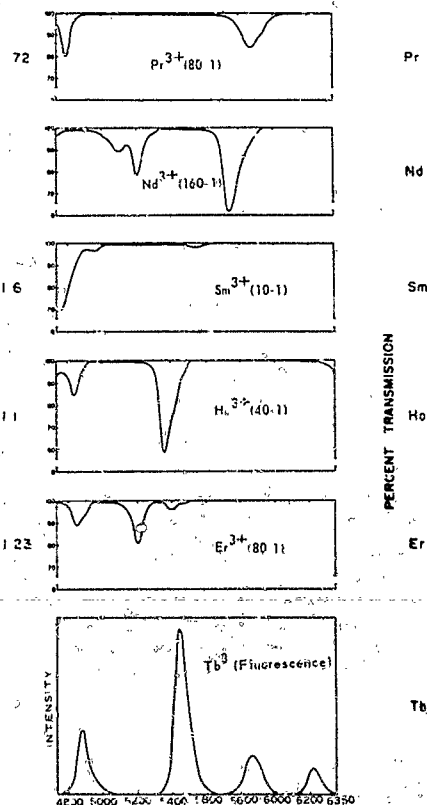
In the next slide, the radial dependence of the quenching of the τ_{b} fluorescence by holmium ions in aqueous chloride solutions, or τ_{quen} , is plotted versus the inverse concentration squared. We see the data is much more consistent, an indication that it is a lot easier experimentally to do these studies in solutions.



In these experiments I have been obtaining an estimate of the probability for quenching interaction from the lifetime measurements.

Now, the actual amount of overlap of the fluorescent lines of the terbium ion and the absorption lines of the holmium ion or some other ion will also determine this quantity, i. e., the probability for quenching interaction. So I have performed the integration of overlap numerically.

The next slide shows the fluorescence of the terbium, and the absorption spectra of several rare ions. The



ratio that I have on the far side here is the ratio of the probability for quenching interaction as determined from the lifetime measurements divided by the quantity, the probability for quenching interaction is determined from the overlap integrals. The reason that I haven't given a value for neodymium is because the agreement is very bad. However, this is almost raw data, and there are several corrections which I haven't used. This method appears promising and we are working on this same sort of thing in solids.

PROF. McCCLURE: What kind of quenching do you think this is, radiative capture?

DR. HOLLOWAY: No, non-radiative. You can tell this by looking at the photographic plates. If it were radiative capture, you would see one line missing.

This concludes what I wanted to say on the quenching experiments. Now I will talk about the energy exchange between rare ions.

Our original experiments were done on the terbium-europium ions' energy exchange. Again this seems just another manifestation of this resonance transfer of energy and, from our previous experience, requires an overlap of the fluorescence lines with the absorption lines.

May I have the next slide.

On the top two lines are the optical characteristics of terbium. Here is the absorption line. These are fluorescence lines. These are taken from densitometer tracings of photographic plates. The fluorescence is over-exposed and therefore appears broader than it is in fact.

I wanted to demonstrate here, that there is an overlap between the absorption lines of europium and terbium fluorescence lines. The bottom line of the slide has the same data for the europium ion. The mixed crystals contain both europium and terbium and are irradiated with monochromatic light. One sees the scattered radiation in a region where there are no absorption levels of europium. The absorption takes place into an absorption level of terbium, but we see fluorescence characteristics of europium fluorescence and not of terbium fluorescence. This is the

demonstration of energy transfer by selective absorption in one ion and observing the fluorescences in the second ion.

Now in the next slide I show energy transfer among a group of ions that have been studied. These four ions have visible fluorescences in this sodium rare-earth tungstate.

Host

$\text{Na}_2\text{Ln}_2\text{WO}_6$ Ln = trivalent rare earth

Expected Transfers

Dy $\rightarrow$ Tb $\rightarrow$ Sm $\rightarrow$ Eu

Observed

Dy $\rightarrow$ Tb

Tb $\rightarrow$ Sm

Tb $\rightarrow$ Eu

Sm $\rightarrow$ Eu

Questionable

Dy $\rightarrow$ Sm

Not Observed

Dy $\rightarrow$ Eu

We assumed that the transfer would proceed in the following manner. The transfer was expected to proceed from a higher excited (i. e. fluorescent) level to the lower excited (and excited) level of second ion. Therefore the transfer was expected to proceed Dy³⁺ $\rightarrow$ Tb³⁺ $\rightarrow$ Sm³⁺ $\rightarrow$ Eu³⁺.

We have actually observed by the method of selective excitation, the energy transfers listed on the slide. The one which I have marked questionable almost certainly involves a transfer of dysprosium to samarium. But in method of selective excitation it appears that the energy goes back to the dysprosium ion from the samarium ions. There is a ladder effect to get rid of the excitation energy. The one case where we do not observe energy transfer is the case of Dy³⁺ $\rightarrow$ Eu³⁺. And again this data is consistent with this resonance for transfer of energy idea.

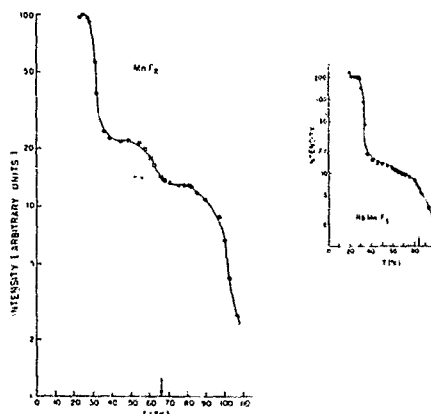
DR. OHLMAN: How do you determine the ladder effect and separate that out from no transfer at all?

DR. HOLLOWAY: That is why I've marked it questionable. I don't know yet that this is true. But I intend to establish this mechanism by just increasing the concentrations and examining the lifetimes of the individual ions. It should show up there, but it is still questionable on this chart.

That is all I would like to say about work on the rare ion fluorescence and the interactions. Again, the energy transfer and the quenchings both seem to be manifestations of this resonance of transfer of energy and all the cases which we have studied, this seems like a consistent mechanism.

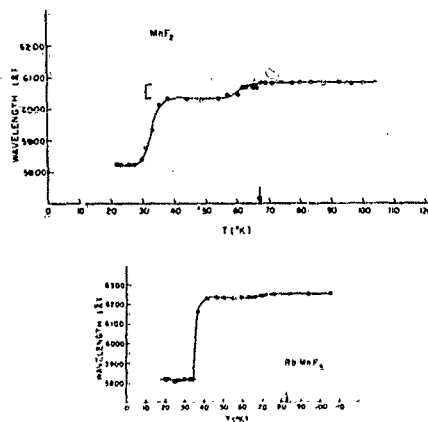
Next I shall comment briefly on the fluorescences in concentrated manganese systems. This ion is an example of transition metal ion which is strongly self-quenched at high concentrations at room temperature and also it has appreciable Stokes shift.

We have observed as shown on the next slide dramatic changes in the manganese fluorescence intensity with temperature. In fact, we are able to distinguish between two regions. There is one very abrupt region, corresponding to roughly one-half the Néel temperature and the smaller region at roughly Néel temperature in MnF₂.



There is also a small change in RbMnF₃ at roughly the Néel temperature. Again at roughly half the Néel temperature a large and abrupt change occurs in RbMnF₃.

The next slide, please. Associated with these changes in intensities are changes in color, which are demonstrated by this slide. We show here the peak value of the fluorescence as a function of temperature. You can actually see this color change and it is quite dramatic. It goes from a red in the high temperature region to an orange color in the low temperature region. It is quite abrupt with temperature.



We attribute the changes near the Néel temperature to the magnetic opening. The much more rapid and dramatic changes at lower temperature, we attribute to an ordering of the excited state of the manganese ion. When the manganese ion is excited, the excited state will have a weaker interaction with surrounding ground state manganese ions than the manganese

ground state-manganese ground state interaction. We believe therefore that the ordering takes place at a lower temperature and is the ordering of excited manganese ion.

We have some other evidence that this might be the case. But this is far afield from the topic I am discussing here.

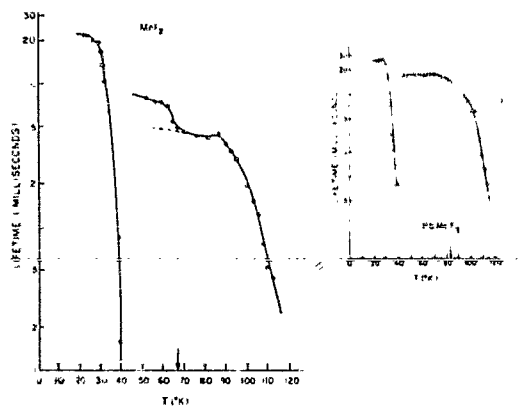
In summary, as far as the rare earth ions are concerned, we have evidence and all of our results are consistent with the resonance for transfer of energy. For the manganese systems the situation is much more complicated. We believe that the larger changes occur because of the coupling to the Stokes shift of the manganese fluorescence, that this Stokes shift serves as an amplification of these other effects, i.e. the excited state ordering of the manganese ion.

Any questions?

DR. B. DiBARTOLO: You found the intensity consistently proportional to the fluorescent lifetime?

DR. HOLLOWAY: Yes. May we go back to the previous slide.

Keep this slide in mind and put this next slide in the projector. This is the intensity and then the lifetime you find here.



Now, if you hold these two slides so they overlap, there is a direct superposition of the lifetime and the intensity in the regions of change. We seem to be seeing a very rapid temperature quenching of this excited state in this region.

DR. DiBARTOLO: I have another comment to make. I think Professor Shawlow has seen changes of the line shape of the europium fluorescent as a function of the concentration of an additional neodymium.

PROF. SCHAWLOW: I can discuss that later.

DR. CHARLES NAIMAN: I think perhaps I would like to add something on this last topic. I don't know if it is outside of the topic of the conference. I think it may be partly a crystal field effect that is going on and this is, if you take a look at the orbital diagrams for manganese systems, there is a very interesting excited state relationship not too far from the region of fluorescence that occurs here.

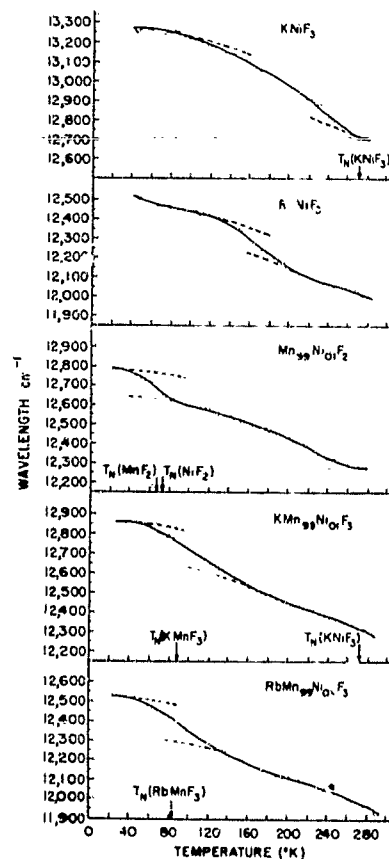
For those of you who are familiar with this, you take a look at the ground state, which is a $6A_1$ and your level which is supposedly giving your fluorescence, your broad fluorescence I think this is a $4T_1$ state, if

you take a look in about a region where your relationships occur, especially if you take into account the Stokes shift in the excited state and any changes in size, then you will find there is another doublet state which evidently becomes the ground state, which is not too far away, and I was wondering if you considered the crystal field effects when you are quite close to these and they will be affected by spin-over interactions and vibrations on top of that, especially some of your depopulation in terms of thermal effect seem to be perhaps due to the fact that these will interact and you will get many levels involved here and then by small changes in size you can end up with localized minimums which are not too different from the minima you postulated with your magnetic interaction. And I just don't know if you have ever considered some of these effects. These are crystal field effects.

DR. HOLLOWAY: Yes, we haven't considered effects such as those mentioned by Dr. Naiman. One thing would bother me about this explanation. We see these effects in the alkali manganese trichlorides and all the alkali manganese trichlorides, except for the Li members of these series, it would be too much to expect that this would always happen.

DR. NAIMAN: I think the major question that comes up is there may be a magnetic interaction between these two states.

DR. HOLLOWAY: There is another thing I didn't want to discuss here. I have a slide for it however.



It is a little complicated, but there are known temperature dependent shifts in this nickel absorption lines that are apparently related to the magnetic ordering, e.g. in potassium nickel fluoride and nickel fluoride. We have put nickel ions in a manganese host and we see a change in the nickel absorption which seems to take place between the Néel temperatures of the manganese host and the pure nickel compound. We think we are seeing some sort of ordering related to the effects seen in the Mn^{2+} ion fluorescence. The nickel ion and the surrounding manganese ions form a local ordered cluster. The ordering occurs above the host ordering temperature because of the stronger Ni-Mn interaction compared to the Mn-Mn interaction. Further, we think we can measure the nickel-manganese exchange constant.

DR. NAIMAN: One thing I think would help determine this is, first of all, there is some question, I think, where the exchange effect is strongest, be cause there is some question as to whether it is expanded in the excited state or contracted, which is definitely something that is not decided yet.

PROF. McCCLURE: Or just distorted or both, in other words?

DR. NAIMAN: Right. And so you may not be able to define some sort of mean exchange integral. But the other thing is if you pump very hard on your system and get a large population in your excited state, you might see effects of excited pairs which would be - which would change. I mean if you are getting such a dramatic effect with one of them surrounded by ground state ions, if you pump still higher and you get enough excited ones you should see still further dramatic changes.

DR. LOHR: I would like to address a question to Dr. Naiman. I think that doublet T₂ you mentioned is a little bit low down in the diagram. Did you find it in this region by numerical calculation?

DR. NAIMAN: No. I might say we have not done any calculation on this system. We have just noticed it is there and it might possibly interact.

DR. LOHR: I see. Our fitting scheme includes all the spin doublets in manganese, as well as the quartets; as I recall it, where we have ligands like oxygen or fluorine -

DR. NAIMAN: If you are to the left --

DR. LOHR: No, the lowest doublet is a doublet T₂, as you say, it comes somewhere between 20,000 wave numbers to 27,000 perhaps. It should not be down around 17,000 wave numbers in MnF_2 .

DR. NAIMAN: Have you considered spin orbit effects between the doublets and quartets and other distortion? I mean they may be quite --

DR. LOHR: I have considered spin orbit effects from doublets to certain quartets, but I think in the case of manganese fluoride since 10Dq is less than 10,000 wave numbers, there would be no doublets in this region.

DR. NAIMAN: Just reverse this system. In other words, don't talk about necessarily energy going from this state to this, you can have it going from this state to this in steps. I don't know, I mean this is just the general phenomenon logically, the topology of the surfaces that have been published on some of these local minima as a function of magnetic ordering I think could easily be invoked in the same sort of arguments associated with distortions of the lattice with spin orbiting interaction. I don't know. I am just wondering whether this has ever been considered. I might say we have not done any exhaustive studies of this at all.

DR. FRED W. QUELLE: I would like to case out some information on a laser that has operated on energy transfer. This is the erbium laser that American Optical has recently operated. I think it is particularly interesting, because you have such very large energy transfer efficiencies. They are using ytterbium as the absorbing material, there is about fifteen weight percent of ytterbium present in the glass and only a quarter of a percent of erbium, but yet they are getting about a hundred percent of the energy absorbed in the ytterbium fluorescing down in the erbium.

Probably from the point of view of this conference the most interesting thing is the fact you get such a large fraction of the energy transferred.

PROF. McCCLURE: Did you say ytterbium?

DR. QUELLE: Ytterbium, very definitely, not terbium. Although ytterbium has only 1 band the heavy doping has spread that band over hundreds of Angstroms and you are absorbing and transferring in the same band.

PROF. McCCLURE: This is the band in the infrared or --

DR. QUELLE: The transfer occurs around 1.06 microns or 1.03 microns, but the band is so broad that you are absorbing all the way from about I think it is six or seven thousand Angstroms on down. This is due, of course, to the fifteen weight percent concentration.

DR. BEHRINGER: If there are no more comments on that, maybe we ought to stop for a coffee break.

(Short recess)

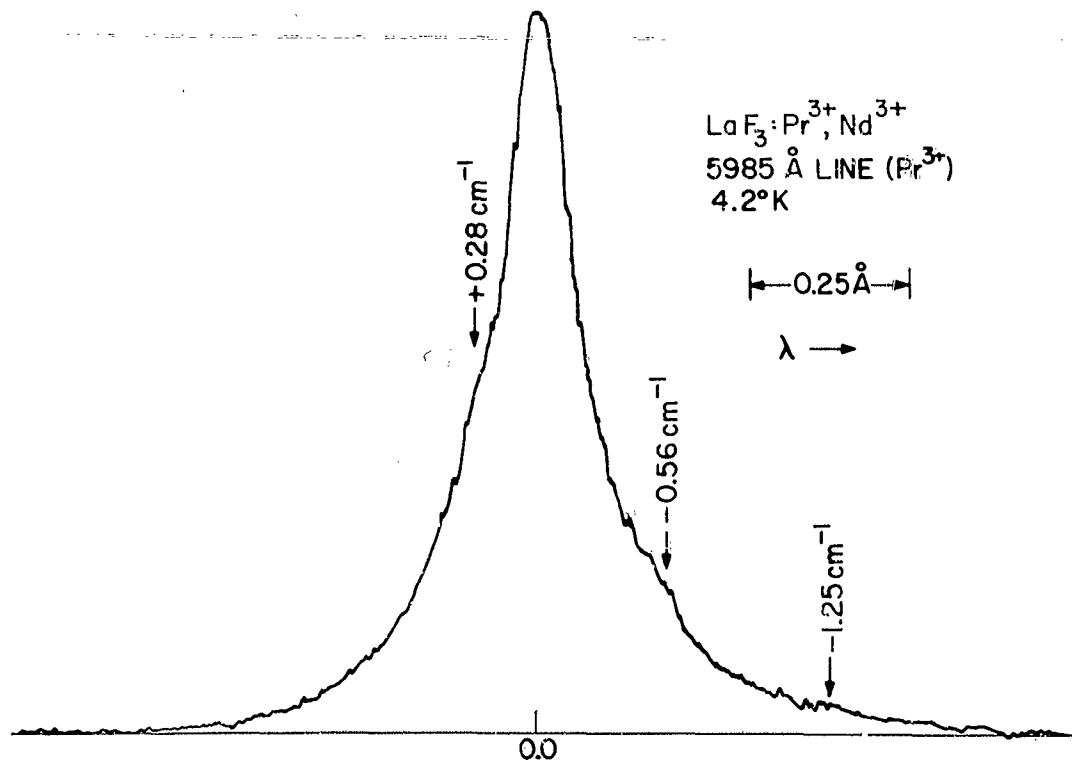
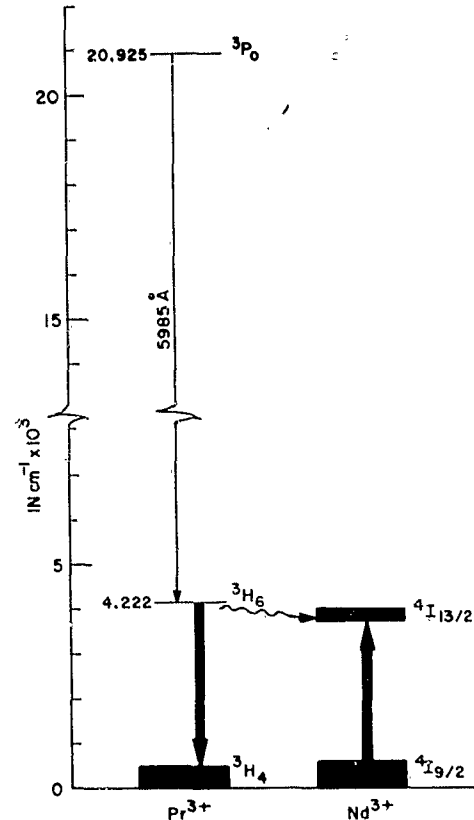
DR. BEHRINGER: Before we go on to the crystal field effects Professor Schawlow will comment on energy exchange.

PROF. ARTHUR SCHAWLOW: I want to say a few words about some work which is being done at Stanford by Dr. W. M. Yen, R. L. Greene and W. C. Scott.

The system shown in the first slide involves rare earth ions in lanthanum fluoride. The samples of lanthanum fluoride come from the Varian Company. We have a case of an energy transfer not in the upper state but rather in the lower state of a fluorescent transition. It does not quench the fluorescence or affect the lifetime as far as we know, but instead it affects the line width. The system which we observe is the praseodymium ion which is present to a fraction of a percent, about 0.1%. Neodymium ions are also present in controlled fractions up to about two percent. Now, there is an approximate resonance between the triplet H_6 lower level of the praseodymium transition and the $^4I_{13/2}$ in neodymium.

However, the neodymium level lies about 100 wave numbers below the praseodymium level. They are not really in resonance. The praseodymium level is sharp, and the transition from the single level up above, the $^3P_0$, has been shown by earlier studies to be very sharp, about a quarter of a wave number at liquid helium, and to have a gaussian shape.

So we start then with a level that is sharp at low concentrations and as more neodymium is added the line assumes a peculiar shape, which is shown in the next slide.



It has still a center which may be gaussian but it develops wings which seem to have a more Lorentzian shape. There is also some fine structure indicated by the bumps marked.

It can be thought of, I think, as mostly - as a combination of Gaussian and a Lorentzian. Praseodymium ions are quenched so rapidly - their lower state is quenched so rapidly -- that the line is broadened.

Now, how to separate these Gaussian and Lorentzian contributions to the line width. This is done by taking a Fourier transform of the line shape about the center and plotting it against $1/\omega^2$ for the Gaussian part, you get a straight line on semilog paper. A Lorentzian line gives a straight line on plotting against $1/\omega$. For a complex line you can get good straight line part on one plot for the center of it for the Gaussian part and a good straight line on the other plot for the Lorentzian wing and so you derive a width and from that a lifetime for the transfer process. The results obtained this way are shown on the next slide.

The Lorentzian line width obtained in this way is pretty much linear with concentration up to about two percent. From that on up, actually they went to five percent, the line width levels off.

Now, this is in contrast to some other energy transfer experiments where the rate of transfer was a higher power than the first power of the concentration.

Now, what this means is at this moment obscure. It would seem that the wings of the line are perhaps most sensitive to the nearest neodymium ion and perhaps may be a measure of the probability that a near site is occupied and no more than one is occupied. When

you get more than one near neighbor site occupied you would get the leveling off.

It would seem to me that you probably cannot in this case assume that there is an average distance for all the neodymium ions and use this as an indication of the power law for the interaction.

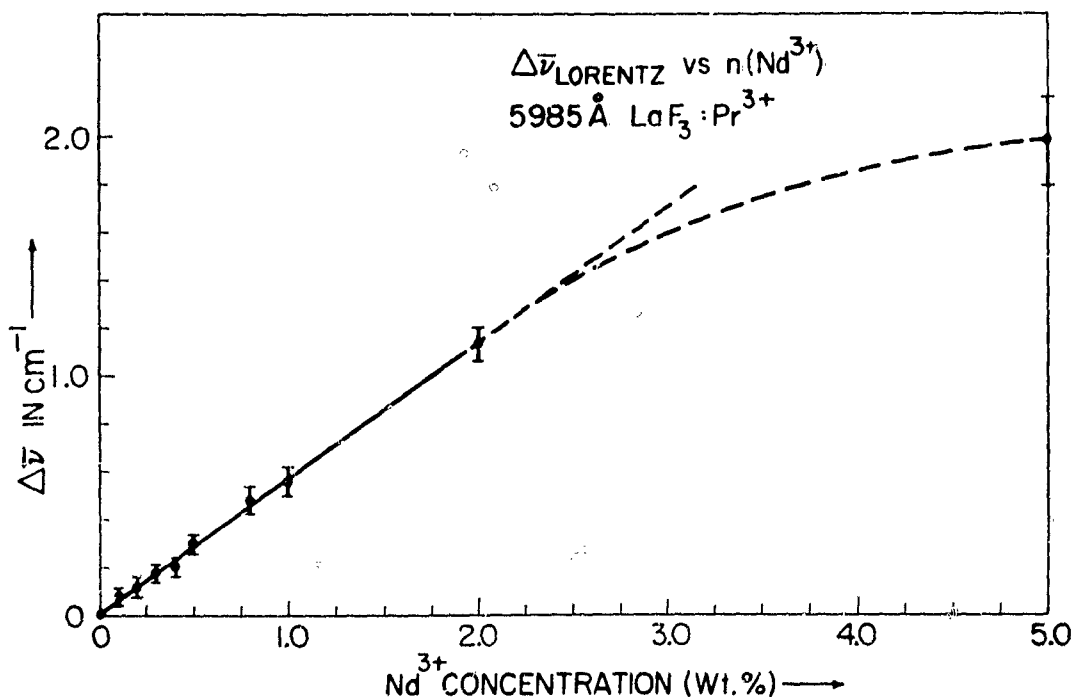
Now, one more thing ought to be said about this interaction. It is not a resonant transfer. It is a non-resonant transfer, because there is several hundred wave numbers difference between the Nd and Pr levels. It must involve the phonon frequency and several processes are being considered.

One of these is simply that the dipole-dipole interaction between the two ions is modulated by the lattice vibrations and you get side bands of the praseodymium transition at the neodymium frequency.

There are other theories in which the crystal field produces the ordinary sort of side bands on the transitions in the praseodymium and these are resonant with the neodymium. But that is not fully understood at the moment.

DR. BHAUMIC: Where is the possibility of a dipole-dipole transition between the vibronic states and the donor state, you could have allowed some part of the--

PROF. SCHAWLOW: I think that is really what I meant by that second type. It is not certain whether that is the common one or whether it is the direct dipole-dipole interaction as modified by the phonon field. I am afraid our thinking is not very clear at this point yet.



(Question Inaudible)

The exchange is probably small. It is thought that perhaps some of these bumps which also show up in the Fourier transfer may be exchanged-coupled pairs but there is no thorough analysis.

I might add one more quick comment, and that is that the word on the exchange coupled ion pairs, in fact I'd like to mention two points, the work on the exchanged couple ion pairs in ruby has come quite a long way even since we talked about it at the Berkeley meeting at Christmas and we now, Mr. Mollenauer now has pretty positive identification of the first, second and third and fourth nearest neighbors. We now believe that the first, second and third are anti-ferromagnetically coupled and the fourth are ferromagnetically coupled.

One other point, Mr. Johnson and Dr. Scott have been making measurements on the absorption line, the sharp absorption line of Cr^{3+} in MgO .

The sharper line cubic site there is known to give a magnetic dipole absorption.

The question was raised whether it could also be a two phonon absorption. It was either zero phonon or two phonons. They find that there is very little temperature dependence in the integrated absorption, so it seems to be a magnetic dipole even though the oscillator strength is somewhat greater than those mentioned earlier for magnetic dipole transitions in manganese.

DR. ROBERT OHLMAN*: I would like to say a few words about some experiments we have been doing.

We have been studying the energy transfer in gadolinium aluminum oxide, and this is an interesting host for a number of reasons. First of all, in very concentrated gadolinium material you would find an absorption in the gadolinium lines, of course. We have put chromium in this material and neodymium in this material separately and together. First of all, let's consider the chromium spectrum. We find that there is excitation of chromium fluorescence by pumping into the gadolinium lines, those that occur at 2750 Angstroms and 3140 Angstroms, and quite effective transfer occurs from gadolinium to chromium. There is also the normal excitation of chromium in the two bands in the blue and green.

If you look at the fluorescent spectrum at 77° K, which is as low in temperature as we have gone at present, you find the chromium R line is split into five lines, which is somewhat unusual. One must consider the exchange effects of the concentrated gadolinium around each chromium ion. It seems reasonable that if you couple the gadolinium ground-state spin with the spins of the chromium ground state and excited state you can conceivably come up with the proper number of states, considering selection rules, to explain five lines. These lines are somewhat broad and overlapping and there may be sub-lines hidden within them.

We have also put in neodymium in this crystal and energy transfer also occurs from gadolinium to neodymium. When we put chromium and neodymium together into this system there is energy transfer from chromium to neodymium. That is, if we pump into chromium absorption bands, the neodymium fluoresces. This is particularly evident in the blue excitation band around 4100 Angstroms where neodymium has very poor absorption characteristics.

To consider the rates of these transfer processes we have studied the decay times of these ions. The chromium decay time without neodymium present is about 18 milliseconds at 77° K. In the mixed crystal the chromium decay speeds up a little bit, about 30% at two percent neodymium concentration. The neodymium lifetime stays about the same, at 130 microseconds, regardless of the amount of chromium present, at least up to a half percent.

Let me describe very briefly the character of the fluorescence decay you get from neodymium in this double-doped system. We have studied the decay for about five decades of intensity change. First of all, there is a very fast neodymium decay of 130 μ sec decay time. After a few milliseconds the decay character changes and a long decay time tail is observed which appears to have a decay time of 10 to 20 milliseconds. The shape of this decay curve does not change, i.e., it has both fast and slow components, even if we pump just into the chromium band at 4100 Angstroms.

Now if one pumps just into the chromium absorption band and the only energy transfer is a slow transfer via the ^2E level, one would expect to observe only the slow component of the neodymium fluorescence decay. However, when we do this we find that a large portion of the neodymium fluorescence decay is a fast decay. This leads us to assume that the fast rate of energy

transfer must be from a higher excited state of the chromium, that is not from the ^2E level.

The neodymium fluorescence decay curve cannot be fitted by the sum of just two exponentials. One needs three or more exponentials to fit its curvature. We believe that the intermediate decay rate is due to transfer via either the pairs of chromiums or by the vibronic system. In terms of the spectral overlap of the neodymium and chromium system, the neodymium excitation line falls right between the chromium single-ion and pair emission lines.

DR. NAIMAN: Your first data was on gadolinium?

DR. OHLMANN: I am talking about gadolinium aluminum oxide.

DR. NAIMAN: And you put in some chromium?

DR. OHLMANN: We put in chromium and neodymium.

DR. NAIMAN: Just the chromium for the moment. What is the transfer from the gadolinium to chromium, what frequency does that occur? Is that a resonant transfer or non-resonant one?

DR. OHLMANN: It is not clear in this crystal. Let's put it this way, the excitation of the chromium is occurring at 3150 Angstroms and at higher energies. The chromium has charge transfer bands possibly up that high.

DR. NAIMAN: I think that is exactly the question, because there is evidence for doublets in this region and the question is whether this transfer would go directly via the doublets to the ^2E state or it would go via the quartet and down.

DR. OHLMANN: I think it is easily said that it is an awful big gap to jump directly from the 30,000 wave numbers to the ^2E energy at 14,000 wave number. Much more likely it is going via some intermediate states from the doublet state up in that region of chromium.

DR. NAIMAN: I mean to say doublets up in that region or up to the quartet, blue band and then down.

DR. OHLMANN: It is not clear. However, I can say that in a similar crystal, lanthanum aluminate, where we looked at the chromium excitation spectra, there are no excitation bands around 3150 Å.

DR. HOLLOWAY: I tried similar things on powder samples of aluminum oxide. I was worried about the different sites here and again I didn't see any change in the lifetime of the chromium due to the presence of neodymium so I concluded it wasn't resonant from this state.

My question is do you think or have you tried transfer from a non-fluorescent chromium into the neodymium?

DR. OHLMANN: What do you mean by non-fluorescent?

DR. HOLLOWAY: Well, chromium doesn't fluoresce in everything you put it in, it requires special symmetry. If you put it in a host in which it didn't fluoresce could you try and pump into the chromium and see if you get transfer that way?

DR. ÖHLMANN: But if the chromium is not fluorescent and transfer does occur, that doesn't necessarily tell us from which state the transfer is occurring.

DR. HOLLYWAY: Yes, sure.

DR. ÖHLMANN: Experimentally we haven't tried any samples in which chromium was not also fluorescent.

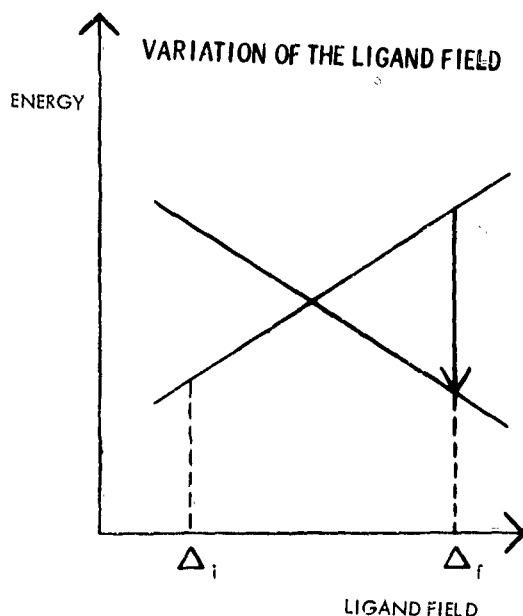
DR. HOLLOWAY: It just struck me as something that might be interesting.

DR. NAIMAN: The subject of our investigations surrounds a particular concept called the Ligand Field Maser Principle*. In presenting this material, I would like to skim through a number of topics that we have investigated based on this same central idea, and finally localize on a particular one which involves magnetic susceptibility data on lanthanum cobaltate. After that, Dr. Di Bartolo will take over and go into some specific heat calculations of the same system and also discuss some of the maser properties of this type of device.

Our main object is to study a new method of producing population inversion. The method utilizes internal electric fields in crystals and molecules due to the nearest neighboring ligands and therefore we call it variation of ligand field. It is based on the fact that the order of energy levels of an electronic system depends upon the symmetry and/or intensity of the surrounding ligand field. For ions near a changeover or crossover of energy levels, if one can vary this field within the relaxation time of the system then one can produce a population inversion between the levels.

Now, this means that one aspect of our investigation has been on the dynamic properties of energy levels near the crossover region. However, another basic objective was to utilize the fact that small changes of the ligand field at the ground state crossover give large changes in the properties of this electronic system. Therefore, even statically, you can deduce experimentally information that can shed light on the basic crystal field theory itself; on approximations such as the various types of crystal field calculations, use of parameters, etc.

We can visualize the general idea here by a simple diagram. May I have the first slide.



*Patent Pending

Here we simply have the two-level system. We have some initial ligand field or crystal field Δ_i and we go rapidly from this condition to the final condition Δ_f . If we can produce this within the relative relaxation time of the system we can produce a population inversion.

Now, a simple equation that could illustrate these energy levels is tetragonal variation due to distortion of a cube along the z-axis.

Assume that we have a level that is triply degenerate in cubic fields due to the equivalence of the three axial directions x, y, z. We now consider what happens to the energy levels as one distorts along the z-axis. It is not too hard to see that if an axial elongation (that lengthens z with respect to x and y) produces a splitting of the energy levels corresponding to Δ_i , then an axial contraction of this same z direction with respect to x and y, will produce an inversion of these energies, corresponding to Δ_f .

LIGAND FIELD VARIATION	RELEVANT FREQUENCIES	PUMP METHOD
1. Trigonal, Tetragonal, etc.	Microwave and down	Electrostrictive, etc.
2. Intensity	Far IR and down	Electrostrictive, etc.
3. Symmetry ($O_h \rightarrow T_d, T_h$)	Optical	Chemical Separation, Crystallographic, etc.

You can classify the various types of ligand field variation conveniently as outlined in the next slide. For example, we can talk about exactly the method we have just mentioned, small variations of symmetry such as trigonal and tetragonal distortions. We next look at how large a frequency change do you get when you produce such change. For metal ions in crystals, these fall typically in the microwave and down.

As an aside, it is interesting to mention that a student of Professor Bloembergen's many years ago, in studying the paramagnetic resonance of nickel fluosilicate applied hydrostatic pressure to this crystal which has trigonal symmetry. However the crystal didn't squeeze hydrostatically, and in fact he thus changed the orders of the ground state energy levels and produced an inversion of these energy levels. For many reasons this is not the most interesting system to actually study.

Then we can take a look at the method that is much more important, namely, variation of the ligand field intensity or the strength of the crystal field, called $10Dq$ or Δ (depending on the notation you happen to use). Based on the simple point charge model, for Δ , and looking at the magnitudes of distortions and crystals in which you can produce variation of the nearest neighbor distance with piezoelectric effects, you find that the far IR and high microwave region appears to be a reasonable region for the maser output.

Then we can go to a system which is entirely different in design though similar in concept, namely where one changes the symmetry of the nearest neighbors drastically. There are a number of molecules that go through such as a function of temperature and pressure. Here we envisage the physical system essentially a chemical laser. One can show

that in certain systems you expect the conversion to produce more products in excited electronic states than in the ground state. This is particularly true for cases such as the d^5 ion, where you have certain spin selection rules that help guarantee this.

Based on this general approach, we have surveyed the literature and we have found what appear to be about forty odd promising cases. With limited funds you have to make a decision and we have chosen for our first efforts a combination of 2 and 1. More specifically we are studying the crossover $\text{Co}^{+3}(d^6)$, which is expected to occur in perovskite oxides.

In order to give you an appreciation for the types of things on which we have concentrated in this investigation, I will just briefly list some of them, and I will be happy to go into detail in any of them if there are any questions. For example, we have looked at the octahedral ground state energy levels in the crossover region and taking into account spin orbit interactions to the second order.

Then we have also looked at the magnetic susceptibility of the ions, d^4 , d^5 , d^6 , and d^7 , which are known to have at least two different ground states. The reason is that we obviously wanted to cover as many materials as we could and we had to find rapid experimental techniques to find a way of knowing how close we were to the crossover. One of these is by the change in magnetic properties of our ions.

Then we have looked at the optical absorption properties of these same systems. As it turns out, one often will find an absorption of one ground state overlapping with the absorption of the other ground state. This can bring to mind to many of you, I am sure, many interesting applications of such a material where a small change of external electric field changes the absorption properties dramatically. We have looked into such overlapping effects as these occur in these d^4 , d^5 , d^6 , and d^7 systems.

In addition to the optical $d^n \rightarrow d^n$ transitions, a much more dramatic change occurs in the higher near UV and UV region due to so-called "charge transfer" transitions. If one studies the two different ground states it is possible to show that there will be large changes in the optical absorption of the charge transfer region. Here, by electron or charge transfer I mean taking an electron from one of the central metal ions, and moving it on to the ligands or from the ligands or from the ligands on to the central metal ion. The two different ground states are very different in their electronic configuration and in their chemical stability. Therefore, in some cases it is easier to remove an electron while in the other ground state, it is much harder to remove an electron. Consequently the optical absorption moves way out toward the UV region.

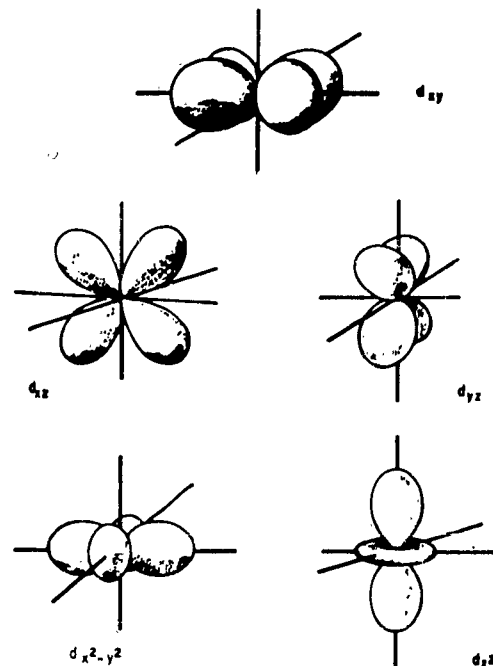
Experimentally, the high point of our most recent work has been the growth of a single crystal lanthanum cobaltate where we have been able to find and measure a very characteristic temperature dependence from 4.2°K to 300°K of the magnetic susceptibility. We have also looked at other crystals, such as Co^{+3} in KTaO_3 and in these cases, for example, no temperature dependence was found. This is due to the fact, as verified by optical data, that the Co^{+3} is in a strong field and therefore you wouldn't expect it to be temperature dependent.

To get a better evaluation of our ability to vary the ligand field we have performed a Stark experiment on the spectra of Co^{+3} in KTaO_3 . Unfortunately, because of the semi-conducting properties of the host crystal, this was not too successful. It is now being repeated with other crystals.

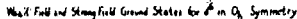
We have measured the properties of cobalt doped strontium titanate, and again found our cobalt +3 in a strong field, diamagnetic state. Also, we didn't find any paramagnetic resonance.

We also performed this experiment with barium titanate utilizing some very excellent barium titanate grown by Dr. Arthur Linz of MIT's Crystal Physics Lab and there we found a considerable amount of cobalt +2. In recent work which we have done in lanthanum aluminate (to be discussed at the Kansas City meeting) we have also found a considerable amount of cobalt +2 in addition to the +3, not noticed before by other workers.

To outline some aspects of the theory, in the next slide, we show the five different d orbitals. I think you can appreciate that these three orbitals xy , yz , and zx , will feel the effects of the six ligands at the $\pm x$, $\pm y$, and $\pm z$ axes much less than the two $x^2 - y^2$ and z^2 , which point directly at the neighbors. Therefore in the next slide you see the actual energy level splitting which does come about in simple crystal field theory in the cubic field. We will consider two different cases based on the relative magnitude of the ligand field, Δ , and the so-called spin-pairing energy, R . Two different sorts of ground states can occur, depending upon the value of Δ with respect to R . They are shown here for the case of d^6 , which is the configuration that we will discuss further in detail.



The angular distribution of the d orbitals.



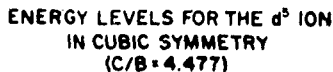
For the strong field case, our energy separation here is so large that it costs us less energy to put our fourth and fifth spins down in the lower energy level or "spin pair" it. Here we now have three spin up and three spin down, and so we have a diamagnetic state. Looking at the spin change alone, you can see that the optical absorption is going to be dramatically different for the two ground states. One is a quintet and one is a singlet. Likewise the magnetic properties are going to be drastically different.

May I have the next slide.

Next slide.

ENERGY LEVELS OF $\text{Co}^{+3}(\text{d}^6)$ IN Al_2O_3
($A = 17,818 \text{ cm}^{-1}$, $B = 558 \text{ cm}^{-1}$, and $C = 48$)

<u>LEVEL</u>	<u>COMPUTED (cm⁻¹)</u>	<u>OBSERVED^a (cm⁻¹)</u>	<u>COMMENT</u>
$^1A_1(1^6)$	0	-----	ground state
$^3T_1(1^6a)$	11 210	(g)	forbidden
$^5T_2(1^6a^2)$	15 180	-----	highly forbidden
$^3T_2(1^6a)$	14 960	see text	see text
$^1T_1(1^6a)$	15 700	15 500	used for fitting
$^1T_2(1^6a)$	23 300	22 920	used for fitting
$^3T_2(1^6a^2)$	29 400	30 000 (g)	shoulder
$^3T_1(1^6a^2)$	29 190	30 000 (g)	shoulder
$^1T_2(1^6a^2)$	36 680	-----	charge transfer region
$^1A_1(1^6a^2)$	39 610	-----	charge transfer region
$^1T_1(1^6\hat{a}^2_r)$	38 700	-----	charge transfer region

⁶ from D. S. McClure, *J. Chem. Phys.* **36**, 2157 (1962).

In the next couple of slides, without going into detail, we will show similar fits of Co^{+3} optical data in other crystals. The next one discusses Co^{+3} - KTAO_3 . Next slide. This is just a comparison of the so-called spin pairing energy which we take as $2.5B$ plus $4C$ in these various crystals that you have just seen through the spectra.

23

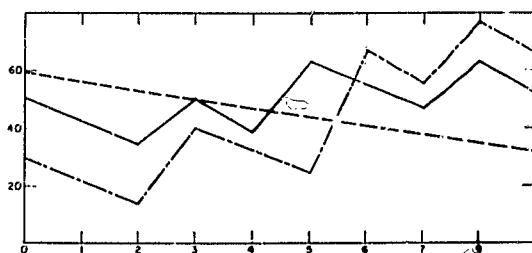
ENERGY LEVELS OF $\text{Co}^{+3}(\text{d}^6)$ IN KTaO_3
($\Delta = 17,120 \text{ cm}^{-1}$, $B = 583 \text{ cm}^{-1}$, $\zeta = 4B$)

LEVEL	COMPUTED (cm^{-1})	OBSERVED (cm^{-1})	COMMENTS
$^1\text{A}_1(\text{t}^6_{\text{g}})$	0	-----	ground state
$^3\text{T}_1(\text{t}^5_{\text{g}}\text{e})$	10 230	9 350	very weak
$^5\text{T}_2(\text{t}^4_{\text{g}}\text{e}^2)$	12 900	-----	highly forbidden
$^3\text{T}_2(\text{t}^5_{\text{g}}\text{e})$	14 050	-----	see text
$^1\text{T}_1(\text{t}^5_{\text{g}}\text{e})$	14 900	14 680	used for fitting
$^1\text{T}_2(\text{t}^5_{\text{g}}\text{e})$	22 700	22 200	used for fitting
$^3\text{T}_2(\text{t}^4_{\text{g}}\text{e}^2)$	27 830	27 000	shoulder
$^3\text{T}_1(\text{t}^4_{\text{g}}\text{e}^2)$	28 150	27 030	shoulder
$^1\text{T}_2(\text{t}^4_{\text{g}}\text{e}^2)$	35 420	-----	host absorption region
$^1\text{A}_1(\text{t}^4_{\text{g}}\text{e}^2)$	37 400	-----	host absorption region
$^1\text{T}_1(\text{t}^4_{\text{g}}\text{e}^2)$	38 500	-----	host absorption region

COMPARISON OF THE SPIN-PAIRING ENERGY FOR
 $\text{Co}^{+3}(\text{d}^6)$

HOST CRYSTAL	$B(\text{cm}^{-1})$	SPIN-PAIRING ENERGY* (cm^{-1})
SrTiO_3	500	9 250
Al_2O_3	558	10 323
KTaO_3	583	10 786

*taken as $2.5B + C \approx 18.5B$



Predicted charge transfer energy (in units of B_0) for high spin (—) and low spin (---) octahedral fields for d^6

crystals for strong field and weak field configurations in the optical region. Another interesting area was the charge transfer spectra that I mentioned earlier. I think that with the help of this slide and a little "chemical" intuition, based on the fact that closed and half-closed shells are particularly stable, we can appreciate how this occurs.

Let us center our attention on an electron or charge transfer, where we are removing an electron from the central metal ion and having it end up on the ligands. Let us take two dramatic examples. Let us take the d^5 ion in the weak field configuration, where, because we have a half filled d shell, we'd expect it would be chemically stable. This is shown in such a curve by the fact that in the d^5 line (which refers to the high spin ground state, the

energy associated with this transition is quite high. By contrast, six d-electrons in a weak field, where if you remove just one electron you will end up with a half-filled d shell, is much less stable to removal of an electron. Such a transition is energetically much lower than the previous one.

However in the strong field d^6 case, which is denoted by the dotted line in the figure, we have a fully closed $\text{t}_{2\text{g}}$ sub-shell. It therefore "costs" us quite a bit of energy to remove an electron. This absorption will be at a higher value than the one for the other weak field ground state and so you get this shift due to a strong, fully-allowed transition which will occur in the near UV region. These conclusions are based on calculations following an extension of the crystal field-model using molecular orbital approximations.

A specific crystal that has brought us close to the crossover region is lanthanum cobaltate. Our approach, associated with interpreting our data, may be discussed with the help of the next slide.

EXPECTED BEHAVIOR OF $\chi(\text{d}^6)$ WITH GROUND
STATE "CHANGE-OVER" at T_0

$$T < T_0$$

- diamagnetic

+ Temperature Independent
Paramagnetism

$$T > T_0$$

- paramagnetic $\sim 1/T$

$$T \approx T_0$$

- go thru at least one maximum

A number of groups have studied this crystal and they have shown that the magnetic moment is considerably smaller than the spin only value. Others have interpreted some of the properties, especially a plateau in susceptibility between 400 degrees and 600 degrees, as due to a ligand field crossover generated by the thermal expansion of the lattice. So of course this led us to investigating the system.

Now, what is of great importance here, is that small amounts of Co^{+4} are known to be central in the interpretation of the properties of the powdered materials. Because of this we have made a careful analysis of our single crystals of lanthanum cobaltate and find that they are less than a half percent off stoichiometry. By studying this susceptibility we find an interesting role played by other than cubic distortions in this crystal. Now you might ask yourself what would we expect as a function of temperature of the susceptibility, where we have a strong field, diamagnetic state and a weak field paramagnetic state, and where the thermal expansion of the lattice causes a ground state crossover?

First of all, at very low temperatures where the crystal is contracted and you are in the strong field state you'd expect that eventually the crystal becomes diamagnetic. (That is, except for temperature and paramagnetic which is known to be considerable for cobalt complexes.) At very high temperatures we

know that it must drop even if it becomes paramagnetic, because the susceptibility is proportional to $1/T$. At some temperature, near T_0 , the temperature where the crossover occurs, the susceptibility would produce a maximum.

Let's take a look at the next slide where we have a simple, order of magnitude, calculation of what you could expect from variations of the nearest neighbor distance and their effect on the ligand field. In the most elementary calculation, one can assume the point charge model. Let R denote the nearest neighbor distance and the exponent n will be anywhere between five and seven. This is known to be a good approximation from some high pressure measurements of Drickamer and co-workers. Define a parameter, δ , which measures the variation from the crossover point and you can then get a temperature dependence for the energy difference of such a crossover. This is quite straight-forward and is the basis of our calculations of estimates for optical absorptions and susceptibility, etc.

TEMPERATURE VARIATION OF Δ

Let $\Delta = \frac{C}{R^n} \quad 5 < n < 7$

and $R = R_0 (1 + \alpha T) \quad \alpha \approx 10^{-5} \text{ cm}/^\circ\text{K}$

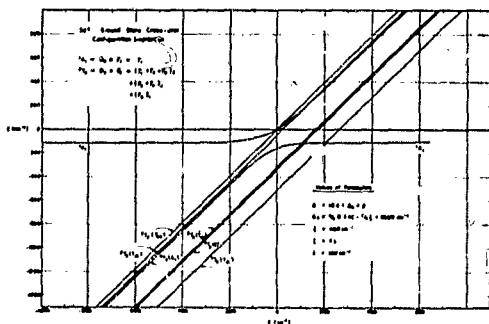
Then $\Delta \approx \frac{C}{R_0^n} (1 - n\alpha T)$

$\Delta_0 = \frac{C}{R_0^n} (1 - n\alpha T_0)$

Let $\delta = \Delta - \Delta_0$

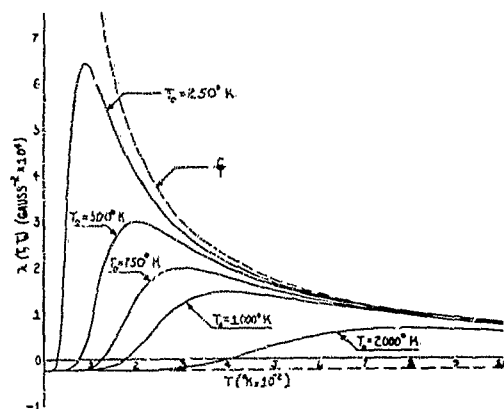
Then $\delta = -n\alpha \Delta_0 (1 + n\alpha T_0) (T - T_0)$

Next slide. Here you have an example of the spin orbit interaction between the two ground states for d^6 . It turns out, as was mentioned earlier, these two states are two away from each other in spin so they will not affect each other directly. But there are higher states by which they can interact and so there is an A_1 state, for example, that will arise from the $1A_1$ state and also from the $5T_2$ which will interact with each other.



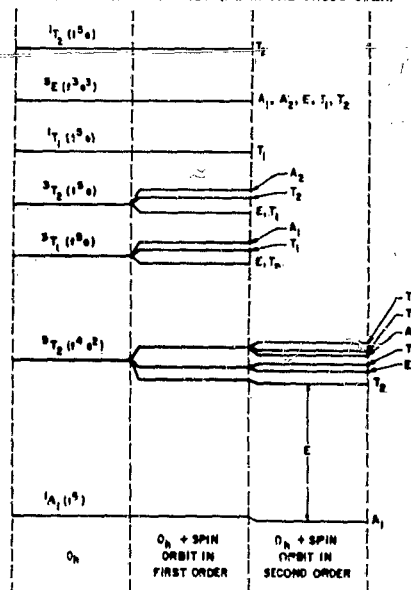
Next slide. Here is an example of the type of susceptibility one might get from such system for

different values of T_0 , the crossover temperature, as defined previously.



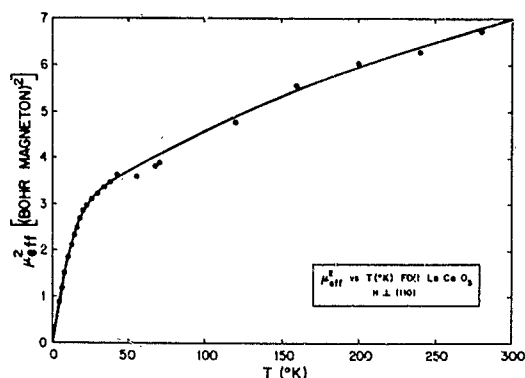
Next slide. These are the d^6 energy levels on which we should focus our attention. We begin at low temperatures with the $1A_1$ state, assuming we are now in the strong field case. We then have the $5T_2$ state, which is the next excited state, the paramagnetic, weak field state. Here we have introduced first order spin orbit splitting. We define our parameter E as energy between the ground state and the first of these spin-orbit excited states in an octahedral field. At least for now we will define it like that, and we will redefine it when we look at our data more carefully.

ENERGY LEVELS OF A d^6 ION IN A STRONG CRYSTAL FIELD (NEAR THE CROSS-OVER)



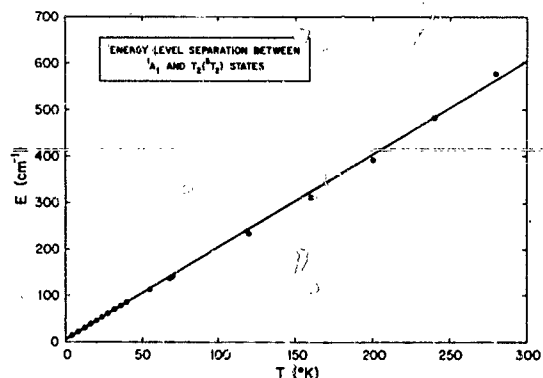
Next slide. Here we have the actual measurement of the susceptibility of our single crystal between 4.2 degrees and room temperature. This is given in terms of $\mu^2_{\text{effective}}$ - for plotting purposes.

Now we can go back and take our expression for susceptibility given in terms of the parameter E , and derive from our data the variation of E as a function



of temperature this is shown in the next slide. From the slide one can see that E is nicely linear as a function of temperature, but it goes exactly the wrong way! One would expect that as we went to higher temperatures the ${}^5T_2$ state would become lowest and at lower temperature the ${}^1A_1$ would become lowest and this data represents just the opposite! So we have to look at our results more carefully.

We have assumed cubic symmetry and we derive this formula for the energy level splitting as a function of temperature in terms of the susceptibility with only spin orbit splitting of the ${}^5T_2$ and ${}^1A_1$ states to first order.



Now, the latter is a pretty good approximation, something like two to five percent. But since this does contradict our results considerably we believe that what it really implies, is that the former approximation is not valid. Specifically, we believe that there is a low symmetry distortion from the cubic structure which is probably trigonal. Then, the T_2 (${}^5T_2$) state, which is the lowest of the excited states, will be split further in such lower trigonal symmetry. What happens is that this trigonal splitting is temperature dependent and increases as you go down in temperature so you actually bring the lowest of the excited states and the ground state closer together opposite to what the center of gravity would actually do. This is very interesting, because it is almost exactly what is found for chromium in lanthanum aluminate of the same structure. Here too the trigonal splitting increases, as you go down in temperature, almost linearly and so this seems to corroborate this data quite nicely.

This work has led to a slight controversy which serves to introduce some of Dr. DiBartolo's talk. What happened is that the research was presented at the Magnetism and Magnetic Materials Conference last fall. Coincidentally two other groups presented papers on the same material, but, on the powders, not single crystals. Their powder susceptibility implied an anti-ferromagnetic ordering at around nitrogen temperature, something which our samples definitely do not show. We have been able to rule this out, well within experimental results. The question arises how can one distinguish between an excited state effect and a magnetic ordering effect. One way, of course, is with neutron diffraction and the Lincoln Lab group has informed me that they are carrying this out on their powders. Other properties such as electron paramagnetic resonance, NMR, etc., according to Dr. Goodenough would never show up because of a delocalizing effect that is the basis of their new theory. We believe that another method of studying this would be with the specific heat properties of the system. Dr. DiBartolo will discuss the specific heat of such a system, which is also of general interest in magnetically coupled pairs.

May I just conclude with mentioning that we have performed optical Stark experiments on the $Co^{+3} \cdot KTaO_3$. These are now being expanded to other crystals such as $Co^{+3} \cdot SrTiO_3$ whose energy levels are shown on the next slide. Our next approach in the theory is to look at some of the Jahn-Teller effects near these crossovers to see what might happen in terms of possible distortions. We are also studying the maser properties of the various energy level systems. For example, we have been concentrating on a system that might work on a natural Q-switch principle. On the other hand, experimentally, the major problem will be to extend our quest for materials at or close to the crossover. Thank you.

ENERGY LEVELS OF $Co^{+3}(d^4)$ in $SrTiO_3$
($a = 15.077 \text{ cm}^{-1}$, $B = 500 \text{ cm}^{-1}$, $C = 48$)

LEVEL	COMPUTED (cm^{-1})	OBSERVED (cm^{-1})	COMMENTS
${}^1A_1(d^4)$	0	-----	ground state
${}^3T_1(d^4)$	9160	2100*	very broad
${}^5E_g(d^4)$	11940	-----	highly forbidden
${}^3T_2(d^4)$	12470	see (cm)	see text
${}^1E_g(d^4)$	13190	13000*	used for fitting
${}^1T_2(d^4)$	19400	19500**	used for fit. ig.
${}^3T_1(d^4)$	24430	-----	host absorption region
${}^3T_2(d^4)$	24930	-----	host absorption region
${}^1T_2(d^4)$	31200	-----	host absorption region
${}^1A_1(d^4)$	33020	---	host absorption region
${}^1T_1(d^4)$	32910	---	host absorption region

*This work

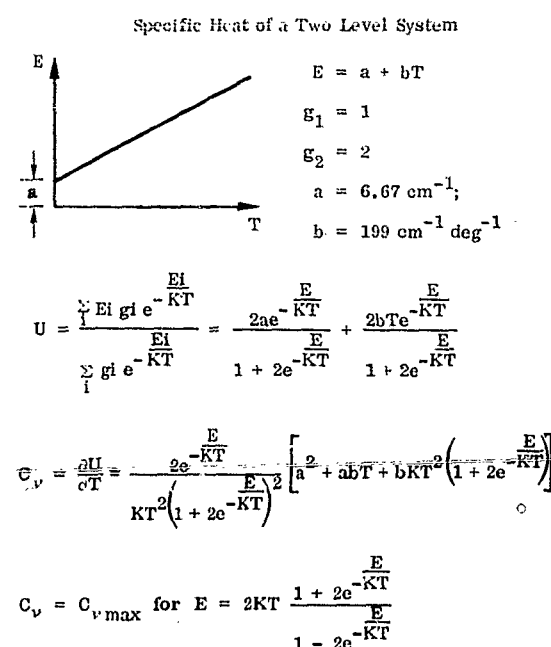
**from R. A. Miller, Paramagnetic Resonance, ed. W. Low, p 17 (Academic Press, N. Y., 1963)

DR. DI BARTOLO: As Dr. Naiman has said our approach has been to consider systems near the crossover, statically. In other words, we have examined the adiabatic changes of certain characteristics when the magnetic ion is close to the crossover.

A system that we have examined is LaCoO_3 ; we have done measurements of magnetic susceptibility on it, and we have interpreted them by assuming a linear dependence with temperature of the energy separation between the two levels which are of interest in the phenomenon.

We thought that perhaps this system could show some characteristic properties if we considered also its specific heat.

May I have the first slide, please.



We have here a two level system, whose difference in energy varies linearly with temperature. The ground state is a diamagnetic state and the excited state is two-fold degenerate.

Now, if we go through the simple calculation of specific heat described above we see from relation (3) that C_v may present a maximum.

PROF. McCLURE: This will be the V^{3+} type of ground state; is that what you have in mind?

DR. NAIMAN: It turns out in effect you'd have a singlet in the trigonal field similar to what one has for V^{3+} in Al_2O_3 , for which the doublet is around a thousand cm^{-1} above the ground state according to Professor Low.

PROF. McCLURE: This is now Co^{3+} ?

DR. NAIMAN: Yes, this case is Co^{3+} .

PROF. McCLURE: Then spin orbit splitting is giving you this level structure?

DR. NAIMAN: Both spin-orbit and trigonal perturbation are causing the splitting of the $5T_2$ level. I might say that electron paramagnetic resonance was tried with this system. The absence of detectable signal implies either a diamagnetic Co^{3+} or a highly concentrated paramagnetic Co^{3+} .

DR. DI BARTOLO: The second slide shows the temperature dependence of the specific heat of a two level system with an energy difference independent from temperature. This type of temperature dependence of C_v has actually been seen in paramagnetic salts.

Values of $a < 0$ correspond to systems in which the ground state is diamagnetic and the first excited state is two-fold degenerate. Values of $a > 0$ correspond to systems in which the ground state is two-fold degenerate and the first excited state is non-degenerate.

In the next slide the case $b = 0$ corresponds to a two level system with an energy difference independent of T , and the characteristic peak in C_v . We have also here the T dependence of C_v for systems with energy difference varying linearly with T . For $b = 0.5$ we see that the peak in C_v shifts to higher temperatures. Finally for higher values of b the peak disappears. The value of $b = 1.99$ is the one which fits our susceptibility measurements for LaCoO_3 . Then for this system we expect a contribution to the specific heat of about 0.5 cal/mole deg in the $200-300^\circ$ range.

Evidently this type of measurements could be correlated with magnetic susceptibility measurements and the presence or not of a peak could give some indication about the temperature dependence of the difference between the two levels which are involved in both thermal and magnetic effects.

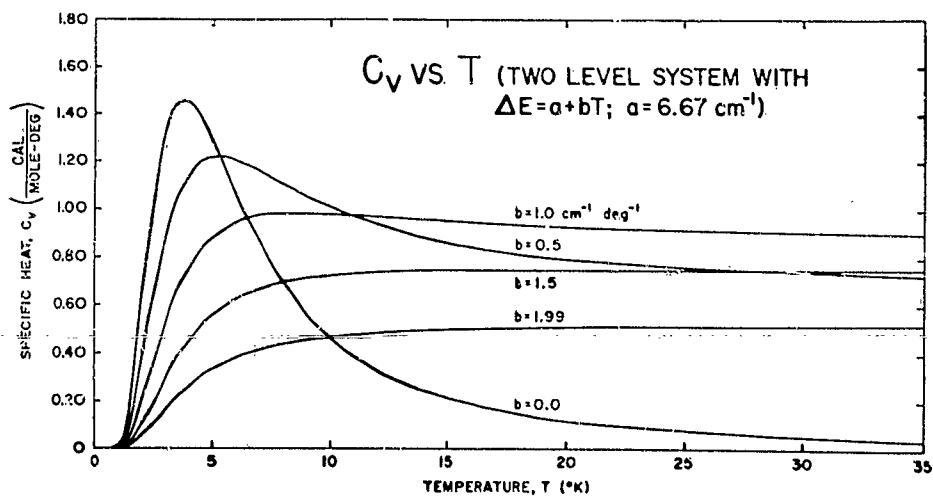
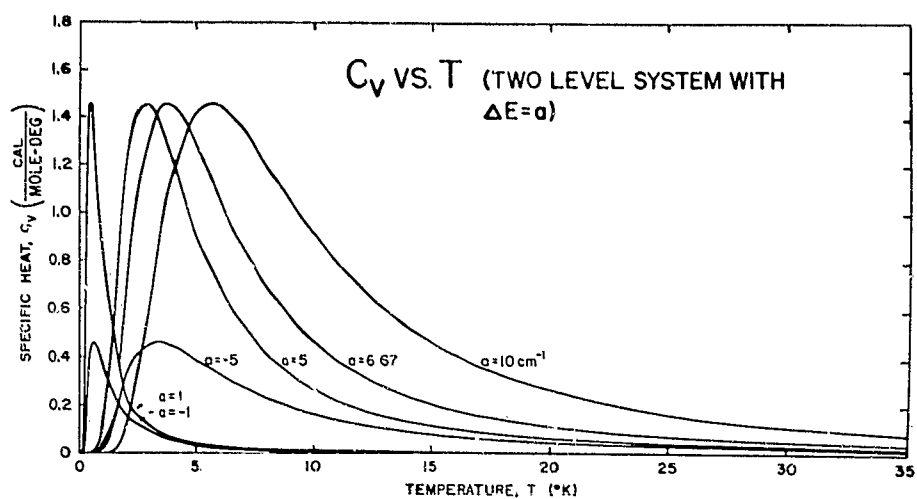
The next thing I would like to talk about is the ligand field maser. I would like to make some observations on the conditions we have to establish to achieve a negative temperature in the presence of the relaxation processes.

We may consider in the following slide the simple example of a two level system which is close to the crossover. ΔE is the energy difference of the two levels. We may call p the parameter that we change to produce a variation in ΔE . We may, for example squeeze the crystal; in this case p is the pressure.

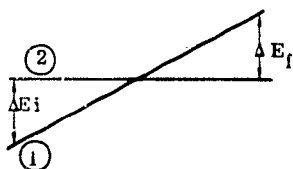
Now we ask ourselves: what are the dynamical conditions of the system as we go through the crossover? The initial conditions are the conditions of thermal equilibrium, determined by the energy difference ΔE_i .

As we go through the crossover, the very simple equation (1) tells us how the difference in population between level 1 and level 2 changes. In this equation τ is the relaxation time relative to the relaxation processes which try at any time to re-establish thermal equilibrium.

Now in order to solve this equation exactly we need to know how the energy gap depends on time t through the parameter p and how τ depends on t through p . Also we need to know how p changes with time: if we have an impulse of pressure, how exactly pressure changes with time.



DYNAMIC EQUATIONS OF A TWO LEVEL SYSTEM



$$\frac{d}{dt} (N_1 - N_2) = -2 \frac{dN_2}{dt} = -2 \left[-\frac{N_2}{\tau} + \frac{N}{\tau \left(1 + e^{\frac{\Delta E}{KT}} \right)} \right] \quad (1)$$

Initial Condition

$$N_2(0) = \frac{N}{1 + e^{\frac{\Delta E_i}{KT}}}$$

and where

$$\tau = \tau [p(t)]$$

$$\Delta E = \Delta E [p(t)]$$

Let us now go to the next slide

CONDITIONS FOR MASER ACTION

$$P_{\text{cryst}} = P_{\text{lost}} \quad (1)$$

$$P_{\text{cryst}} = (N_1 - N_2) t_f V_{\text{cryst}} h \nu_f W; \quad (2)$$

$$W = \frac{1}{t^2} |M|^2 H_s^2 T_2 \quad (3)$$

$$P_{\text{lost}} = \frac{\omega_f E}{Q} = \frac{\omega_f}{Q} \frac{1}{8\pi} H_s^2 V_{\text{cav}} \quad (4)$$

where we consider the conditions for maser action of a two level system. Equation (1) tells us that for a maser action the power given by the crystal to the cavity should be equal to the power lost in the cavity. The power lost in the cavity is given by the product of the frequency of oscillation by the energy in the cavity divided by the Q of the cavity, and the power given by the crystal is expressed by the product of whatever inversion of population we have achieved by the energy of the photon by the transition probability by the volume of the crystal. We assume a magnetic dipole type of transition, as in Equation (3).

By using the relation (1) and replacing P_{lost} and P_{cryst} with the expressions we have found we have in the next slide an expression for the density of population inversion we have to achieve with a cavity of a certain Q in order to achieve maser action. ϵ is a shape factor; it depends on the type of mode we are exciting in the cavity. If we plug some numbers for the relaxation time and for Q in Equation (2) we come out with a value for the population inversion which is about one and 1/2, two orders of magnitude less than what we have before going through the crossover, at the beginning of the pressure pulse, for an initial energy gap of 15 kilomegacycles.

OSCILLATION CONDITION

$$(N_1 - N_2) t_f V_{\text{cryst}} h \nu_f W = \frac{\omega_f E}{Q} \quad (1)$$

$$(N_1 - N_2) t_f = \left(\frac{V_{\text{cav}}}{V_{\text{cryst}}} \right) \frac{\hbar \epsilon}{T_2 |M|^2 8\pi Q} \quad (2)$$

where

$$\epsilon = \frac{H_s^2}{H^2} \quad (3)$$

In other words, for a difference in energy of 15 kilomegacycles, we have, in static conditions, a difference in population $N_1 - N_2$ which is about a hundred times the inversion of population which is needed for maser action. So we have about two orders of magnitudes that we can lose when we go through the crossover.

The problem is now: will the relaxation process allow us to have just this loss as we go through the crossover? Far from the crossover the spin-lattice relaxation time is the relevant time. It is at the crossover that the things get mixed up.

A similar problem was faced by Rimai and coworkers in the Research Division of Raytheon. They achieved practically an inversion of population in the Zeeman ground levels of Ruby by suddenly reversing the magnetic field. They went through a kind of crossover; that was a magnetic field crossover. We want to do the same thing by going through a ligand field crossover. As they pointed out, the important thing is that the two levels involved should get the least possible amount of mixing.

Now, what mixes these two levels? Possibly it is the spin-spin interaction. So if we choose properly two levels which differ in their effective spin number, possibly this spin-spin interaction is not going to be very effective. As a matter of fact, they achieved interaction between levels, in which the spin-spin interaction was not very effective.

I want to point out that the same broadening mechanism which affects the two crossing levels may mix the two crossing levels. If spin-spin is the broadening mechanism (it could also be cross-relaxation) we may want to choose crossing levels with the least possible spin-spin mixing.

DR. OHLMAN: You made a statement that your population inversion was two orders of magnitude greater than some number.

DR. DI BARTOLO: I talked of a system in which the difference in energy levels at the beginning was 15 kilomegacycles. This energy gap at 4°K gives you a certain $N_1 - N_2$. If you can transfer this difference in populations through the crossover you have two orders of magnitude more than what you need to achieve maser action. This is the point.

DR. OHLMAN: In that equation, you had what lost time or what relaxation time? You have to assume some time.

DR. DI BARTOLO: Yes. That T_2 in Equation (2) of last slide has nothing to do with the crossover, that time is T_2 at the end.

DR. OHLMAN: What T_2 at the end did you assume to get this number for $N_1 - N_2$?

DR. DI BARTOLO: I assumed 10^{-7} sec. This is the point; what happens during the crossover, I mean all the history from the beginning to the end affects $N_1 - N_2$ at the end. So does the shape of the pulse, namely the way we go, in time, through the varying energy gap.

PROF. McCLURE: You have another problem: once you do get through with a spin difference helping you get through, you still have the problem, once you've gotten there, that the spin difference is going to inhibit the radiative process that you want to happen afterwards.

DR. NAIMAN: May I show you an example that we have considered—exactly because of that; namely a three-level system. This is why much of what we are talking about now is in practice being explored more directly with three level or multi-level systems. It turns out that if you take the Co^{3+} case in tetragonal symmetry, such as the symmetry you get with the piezoelectric crystals we have been investigating, that your lowest states at the crossover will give you an A_1 state and then two other states, I think an E and B state.

In these systems you find that you can produce a ground state, A_1 to cross over, not one but at least two levels B and C. Between the upper of these two levels, C, and the crossing level, A_1 , there may be a fairly large interaction while A is fairly forbidden with the lower of the two levels, B. However, the transition between B and C is somewhat allowed, so one can get energy out of it. Thus the transition which one has to sweep through rapidly where A crosses B, is the one which is fairly long-lived, and here the upper levels C to B become the operating maser transition rather than A to B which is the one that is doing the pumping for you. This is essentially a three-level maser based on the original Ligand Field two-level maser. Actually, if you look at the original two-level Ligand Field Maser it really could be considered in time as a three-level laser. This is because the level which is used for a pump as a function of time can be considered two levels, a level below and above. The three level Ligand Field Maser then becomes equivalent to a four-level laser and it has many of the same conditions and advantages as a four-level laser does over the ordinary three-level type.

You can also appreciate that in the three level Ligand Field Maser process, where A and C interact but A and B do not, often when the splitting is caused by the spin-orbit interaction B and C are relatively independent of the crystal field involved, thus you may just get the sharpening effect you need for Q switch operation as you move away from the A-C interaction region.

As you can see from these characteristics, the spin-orbit multilevel structures are very useful and so these are the energy levels we have actually calculated. It is just that our first calculations on the maser device properties have started out with two-level systems because the others are that much more complicated.

DR. OHLMAN: Do you have to sweep through this transition in the 10^{-7} second time or faster?

DR. NAIMAN: This depends exactly on the question, of what are the relative relaxation times? Another point is that you don't have to sweep through the whole range in that time. This is because the spin lattice relaxation time, away from the actual crossover region, is quite ridiculously low. It is the crossover part you have to sweep through rapidly. Also keep in mind the fact that when you are at these crossovers that are due to the variation of the intensity of the ligand field, your variation of energy with respect to nearest neighbor distance is very rapid. So that is exactly why we are bothering with it. By contrast, tetragonal splittings or trigonal splittings just don't vary that fast.

It is at just such an intensity crossover that you could hopefully sweep through this portion here fast enough. Frankly, we are just learning about this right now. To our knowledge no one has ever seen such a system so it is hard to do anything but estimate. In fact, that in itself is really one of the most worthwhile aspects of the research, just studying such an effect.

DR. QUELLE: What amount of population inversion in ruby might you get?

DR. DI BARTOLO: There is no data on that in the Raytheon paper.

DR. QUELLE: Because I think that might give one some clue of the extent to which this relaxation takes place when those levels cross.

DR. NAIMAN: Except for the simple fact that you don't have the same type of states for the two cases at all.

DR. OHLMAN: I could answer the question. With this fast passage you are talking about, 100% inversions are quite possible and seen quite often.

Session I Moderator: R. E. Behringer, ONR

Part 2 Energy Exchange in Gases

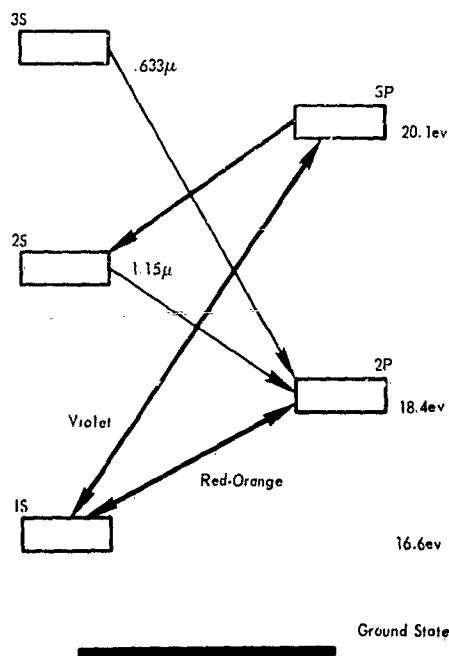
Monday Afternoon
22 March 1965

Marshall	Columbia University
Muller	Varian Associates

DR. BEHRINGER: We are ready to go to the gases, starting out with Prof. Marshall.

PROF. THOMAS C. MARSHALL: As you know in gas lasers and similar device the role of the metastables is very important. This is topic for considerable discussion and investigation, because the measurement and control of metastable populations in gaseous discharges or afterglows is a difficult matter. I wish to discuss one particular aspect of the metastables - the control, not the generation of them and then show how it may be applied to studying the generation of energy in a laser cavity as a function of time.

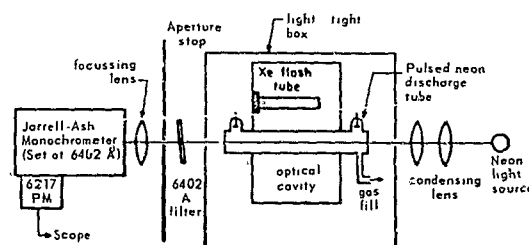
The situation I would like to describe is that in the helium-neon laser, or even a gas containing helium metastables by themselves or neon metastables by themselves. If I could have the first slide we will look at the very simplified energy structure of neon.



The metastable state is the lowest one of interest. One can observe that by flooding the system with visible radiation you could establish something of an optical equilibrium between the states by an optical pumping process, which take metastable levels up to 2P, 3P, and higher levels.

This process interests us because it is a way of controlling the population of metastables and also - in the particular case of neon - removing them. It is interesting to do this with light rather than with hot electrons, since the electronic energies cannot be controlled to the extent that the photon energies can. One must accept excitations from the ground states as well when you are considering electron bombardment.

The experimental situation is defined in the next slide. There is a simplified schematic of many experiments we are doing. The metastables are generated in the afterglow of the gaseous discharge in reasonably pure neon. The afterglow, for those of you who are not familiar with this term, is a region following an active DC current pulse in the gas. In the afterglow the electron density is moderate, and it decays exponentially with time; the electron energies are as a rule fairly low, so the electrons will not excite neutral neons to metastable or higher states.



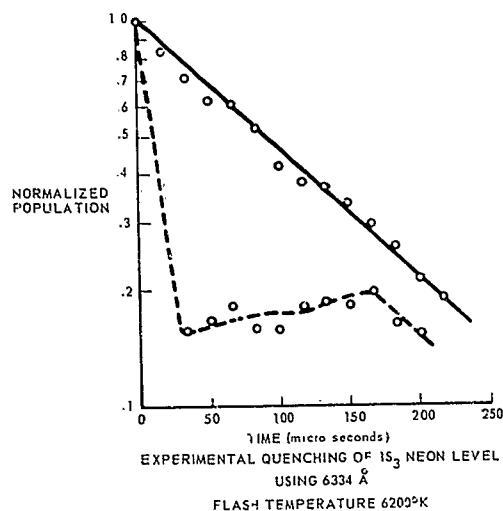
The metastables may be measured by propagating through this afterglow at any time a beam of probing radiation from a neon lamp. By measuring the absorption one can deduce the relative value of the metastable concentration and if oscillator strengths are available, also the absolute value.

In the course of the afterglow we have illuminated the ensemble of metastables by broad-band radiation provided by a xenon flash tube. The amount of radiation we use is not very much; we run something like 7 or 50 Joules per pulse, so the experiment can be pulsed repetitively, and one can take advantage of signal averaging techniques.

The radiation is enclosed in an optical cavity and one can calibrate the radiation field there photometrically; we get roughly 6000° Kelvin equivalent black body temperatures from the flash tube pulse.

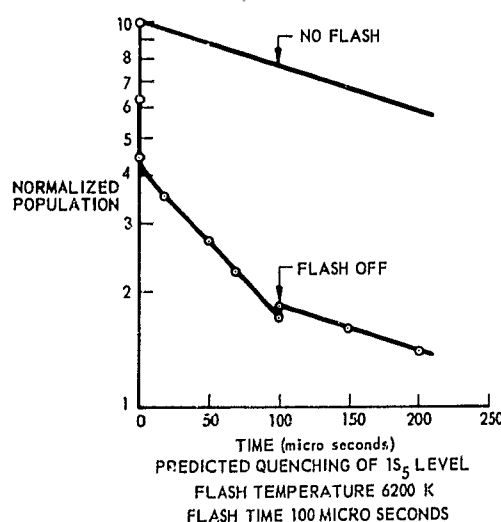
The question is: what happens to the metastable density when such broad band radiation is cast upon the metastables, causing the metastables in the neon afterglow to absorb whatever they please from this energy flux?

If we start the pulse of light several hundred microseconds into the afterglow, one observes the graph slide 3. In the absence of light the decay of metastable concentration follows an exponential decay with a time constant governed by the gas pressure and other considerations in the system. Upon illuminating this with optical radiation one observes a sizable decrease of the population, say on the order of 50% of its initial value. The pulse is about a hundred microseconds long and is not too good geometrically, but notice after the pulse is over you again have a decay parallel to the initial curve, but now metastables have been removed.



This is due to the fact that in neon there is a mixture of decays from the P states to either the triplet or singlets series. In other words, neon is not a good Russel-Saunders atom and when you pump the triplet series from the S states to the P states these can also decay back to the singlet levels. However, the singlet levels are connected radiatively to the ground state by photons (which can be resonance-trapped) so the lifetime of the singlets states is rather short. As a result the metastables cycle through the upper states of neon and drain out via the singlet transitions; if you let this run long enough the metastables are removed from the afterglow. The interesting thing about this technique is that you are able to do this without really perturbing the electrons.

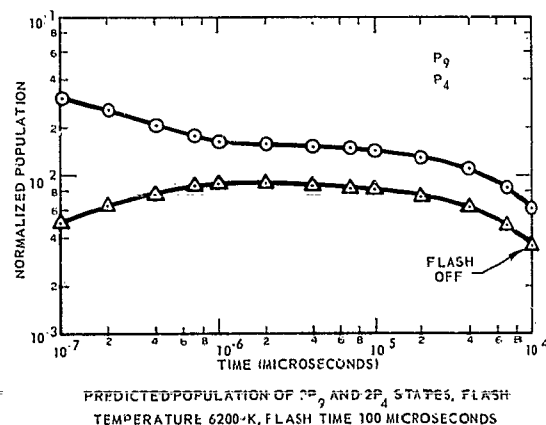
Could I have the next slide, please.



To check some of these ideas on paper, we set up a very idealized theoretical model which connected the

four lowest S states of neon to the $10\ 2P$ levels, and applied a square pulse of radiation with black body temperature of about 6000°K. We used the oscillator strengths one gets from the literature and asked for a comparison between the metastable population without a flash (which decays with a diffusion time constant we can adjust on a computer) with the population dependence with the flash. As the pulse is switched on you initially store the particles in the metastable level in the upper states and since these are of the order of 10 or 20 of these, the metastable population drops rapidly within a few spontaneous emission time constants. Following that, the population of the metastables will be removed via the singlet transitions, as well as by ordinary diffusion. Upon shutting off the flash there is some recovery of population, but metastable particles have been lost. How many have been lost depends on the shape of the pulse and its radiation temperatures.

Could I have the next slide.

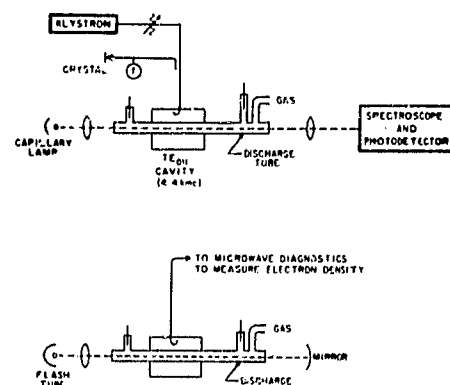


It is informative to examine the populations of the P states, where one sees in the particular case of the P_4 state (the lower level in the conventional gaseous helium-neon laser) that after a few spontaneous emission time constants one achieved a population of the order of one percent of the metastable population.

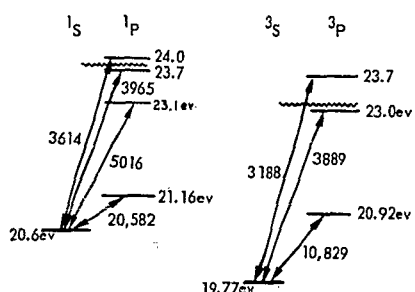
Now, typically, one would obtain in a neon afterglow or a laser about 10^{10} or 10^{11} metastables per cc; this implies one should obtain about 10^8 or 10^9 in the P_4 level.

It should therefore be possible to turn a He-Ne laser off with the light flash.

Could I have the next slide, please.



At this time I wish to add parenthetically an application of the above which is of some importance to the people who deal exclusively with gaseous electronics. If you have a way of removing the metastables of neon, then at sufficiently low electron concentrations you can also quench the process which generates ions of neon and electrons by the collision of two metastables. The optical flash will decrease the metastable density. The metastables will collide less frequently with each other and generate fewer electrons, the density of which you can measure with a microwave cavity technique. This can be used to check the idea that metastable-metastable collisions do ionize and contribute significantly to the electron population, and also determine whether these hot electrons would play an important role in the afterglow physics.



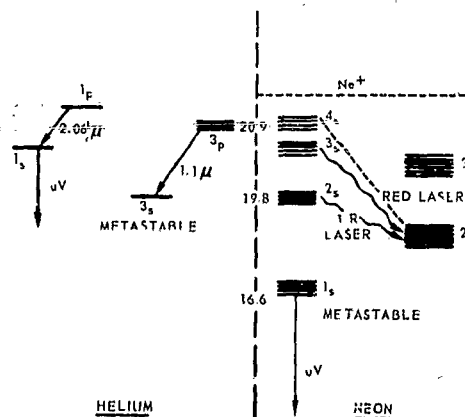
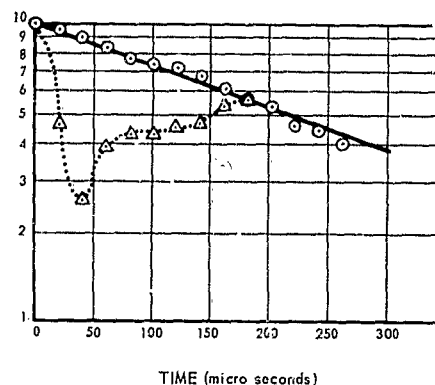
— GROUND STATE
SIMPLIFIED ENERGY LEVEL DIAGRAM OF HELIUM

One can construct a parallel argument for helium briefly. However, in helium one has good Russell-Saunders coupling and if the energy level is not too high one does not cross decays between the triplet and the singlet series as in neon. It is also of interest to note that in helium the number of levels available for pumping is much less than neon. However, there is an order of magnitude more pumping in the infrared transitions as well as a considerable infrared output of the flash tube; hence there is a way of separating metastable pumping in the neon gas which occurs primarily in the visible region from pumping of helium metastables which will occur primarily in the infrared region.

Some tentative results on the pumping of triplet helium levels are shown in slide 8 and one sees again ~50% decrease of the triplet metastable population of helium followed by a relaxation (as the pumping intensity decreases) up to its original value. This shows no particles have been pumped out of the system; namely one has as many excited states at all times as would be present if the system were unpumped. Very little pumping contribution has been found from the visible.

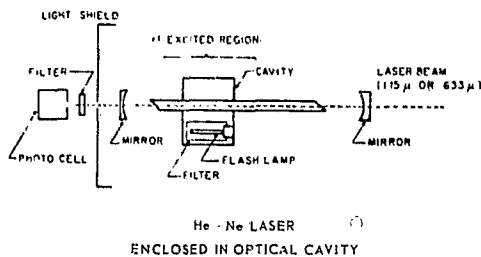
Suppose one has an infrared He-Ne laser oscillating on the 2S-2P transition. The laser is exposed to a flash of infrared radiation. We have found that about 30% of the 3S density was transferred to the 3P level immediately above, hence it might be possible to

effect an energy transfer from the Helium 3P level to the neon 4S level. One might then be able to establish simultaneously a parasitic oscillation which can be switched on and off with a flash tube.

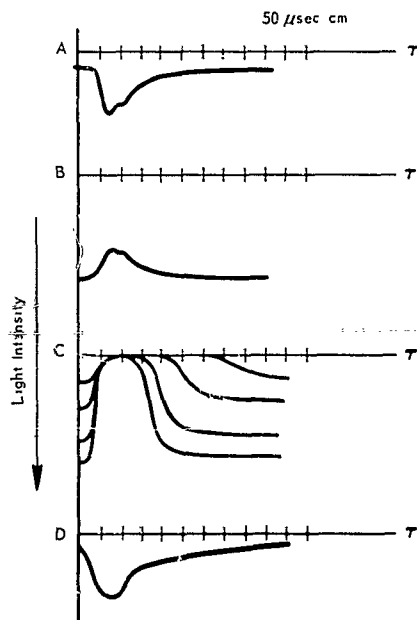


SIMPLIFIED ENERGY LEVELS OF He AND Ne

Suppose we take the measurements that we made in afterglow physics where life was simple, where there were no exciting electrons, and try to apply them to the much less understood situation that occurs in helium-neon laser of a conventional variety. Let us excite a small fraction of the tube with rf, causing it to oscillate in a single mode, and introduce a filter over the flash tube that passes visible radiation and thereby pump only neon metastables. The output laser radiation is monitored by a well filtered photocell. We emphasize that we are not changing the electron density or temperature, we are not changing the optical properties, and we are not changing any of the operating conditions of the laser except the metastable concentration.



On the top graph of slide 11 we plot the pumping light flash intensity; this can be isolated completely from the detector if necessary. Now, if the laser is running at fairly high level and the pumping flash is not too high (something ~20 Joules) then one observes a cross-modulation of the flash on the laser output. Intensity increases downward. This is caused by the blocking up of the lower (2p4) level of the laser.



However, something rather more interesting occurs if you reduce either the laser level quite a bit or increase the pumping excitation from flash. In the third trace one sees the laser signal is completely quenched, but requires a very substantial time (~50 - 100 μsec) to recover its full intensity. Once the laser is turned off, the pumping light decreases rapidly, and after the pump has been off about 10^{-6} sec the states of the neon atom return to their previous population distribution. The laser will require a certain time to oscillate once more, as the cavity energy increases. Professor Lamb has derived an equation (slide 12) which governs the time rate of change of the electric field in a single mode of laser cavity:

To integrate this, we assume α and β are constants, and obtain an equation which starts from amplitude

zero, builds up initially in an exponential fashion and then saturates to a value of α/β .

$$\frac{dE(n)}{d\tau} = \alpha(n)E(n) - \beta(n)E(n)^3$$

$$\alpha(n) = -\frac{1}{2}\left(\frac{\nu}{\omega_n}\right) + \frac{1}{2}N\left[\frac{\epsilon^2}{\epsilon_0 n^3 \gamma_a \gamma_b K u}\right] Z_1(\nu_n - \omega)$$

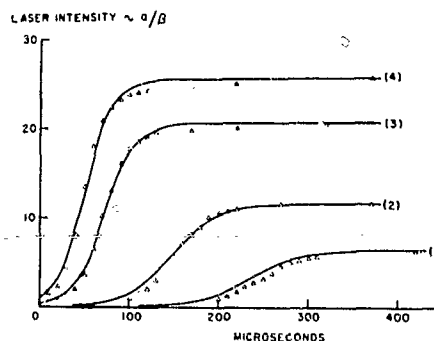
$$\beta(n) = \left(\frac{\nu}{\omega_n}\right) \pi^{\frac{1}{2}} N \left[\frac{\epsilon^4}{\epsilon_0 n^3 \gamma_a \gamma_b K u}\right] [1 + \gamma_{ab}^2 (\nu_n - \omega)]$$

$$\text{Let } I \sim E^2$$

$$I(\tau) = \frac{I_0 \omega / \nu}{I_0 (1 - e^{-\alpha \tau}) + \beta / \alpha e^{-\alpha \tau}}$$

$$I(\tau=0) = I_0$$

On the next slide we have taken some refined data and tried to fit the integrated form of Lamb's equation to our laser signals. The solid lines are theoretical fits of Lamb's integrated equation to the triangles which are our experimental data.



He Ne LASER OUTPUT AS A FUNCTION OF TIME AFTER QUENCHING FOR FOUR DIFFERENT INTENSITIES

I would like to point out a few interesting things about this data. First of all, the most intense laser signal here starts essentially from a coherent level. Any deflection on this graph is due to coherent laser light. The "noise light", the discharge light, is very much attenuated here and would not show on this level. However, those transitions which occur at much lower excitation start from noise level, so the concept of assigning them an initial intensity $I_0 = 0$ will not do as the growth of the laser signal may commence at a random time when there has been a very large noise pulse. It would be informative to study the growth of the coherent light with an image converter camera equipped to take rapid photographs. Again I emphasize that the interesting point behind this is that we are not turning the laser discharge off and starting it again, changing the optical cavity parameters and watching the equilibrium to be set up, but are rather changing the gain of the system by tampering with the state populations. This process has the advantage of changing the other variables of the system very little for example we have never been able to see any change of the gas discharge impedance when we have illuminated a system with the light flash presently being used.

DR. MARCEL MULLER: I will report on an attempt to make a molecular vibration gaseous laser and I have no slides, but I will draw one big diagram to remind you what I am talking about.

A molecular vibration laser is a laser based on an anharmonic oscillator. It has to be clearly an anharmonic oscillator because no amount of population inversion in a harmonic oscillator can lead to amplification.

The way we propose in the anharmonic oscillator to bring about a population inversion, I will illustrate by means of a potential diagram for the ground state and excited state of a diatomic molecule; similar arguments can be made for polyatomic molecules, but we will stick to vibrational energy levels shown for a diatomic molecule.

The statement of the Franck-Condon principle is that in an optical or electronic impact excitation of this state, an excited vibrational state, namely the one lying vertically above the ground vibrational state of the ground electronic state will be preferentially excited, and when this happens, with the picture as I have drawn, if I draw a population versus energy level diagram in this upper state, it will have an envelope something like this and there will be inversions on the left-hand side in energy of the maximally excited state.

The desirable features of a molecule to be used in such a scheme are: one, you would like to have a large vibrational transition dipole moment, and a large in this sense means if you are going to do this in a gas discharge and do it at reasonable pressures and current densities, something in excess of roughly a tenth of a debye. You would like at least one of the atoms of the molecule to be light, preferably hydrogen, because of course there is additional structure, each of these vibrational levels comprises a number of rotational levels, you would like few rotational levels to be populated, this is to say the rotation constant is to be large. Consequently, hydrogenic molecules are desirable.

It is, of course, essential that the excited electronic state have an inter-nuclear distance different from that of the ground state in order that the Franck-Condon vertical transition provide a population inversion; also it is desirable, and this will always accompany the previous condition, that the vibrational frequency in the excited state be substantially different, by more than several KT , from the vibrational energy difference (vibrational frequency) in the ground state, so that collisions with ground state molecules are not capable of giving vibrational relaxation.

Another thing that is essential for practical reasons is that this electronic state be metastable. Otherwise the radiative relaxation back to the ground state, being at a very high frequency, will be fast and you will never be able to get any large population in this excited electronic state.

This means that the excited state has to be either a metastable state, or it can be an ionized state. The advantage of an ionized state in addition to this is that typically ionized states have larger vibrational dipole movements, particularly when they are not ionic molecules. If they are asymmetrical covalently bound molecules then if they have a net charge

in the excited state, the vibrational dipole for obvious reasons will be rather larger than that of a neutral molecule.

On the basis of all these considerations and on the basis of some published data on ionization probabilities, we chose as a molecule to concentrate on heavy hydrogen, HD . The transition that is to be inverted, and it would have been the $2-1$ transition of vibrational states, is in the vicinity of five microns. It has not been seen in emission spectroscopy. This choice turned out to be unfortunate and after investing some considerable time in this project we have now been forced to abandon it.

The reason for this is that the reported data on ionization efficiencies which indicated that the Franck-Condon principle was obeyed in the impact ionization process, (this was done with energy selected electrons) contained apparently a fair amount of wishful thinking. Very recent results reported in an issue a couple of weeks ago of *Phys Rev Letters* by Briglia and Rapp indicate that in hydrogen the ionization process is not a direct process, but takes place largely by auto-ionization of excited states of the molecule which coincide roughly in energy with the ground state of the ion that we want to work with. As a result of this complicated process, it is primarily the ground vibrational state of the ion that becomes populated; so I think perhaps another criterion for a future experiment in this area ought to be a careful examination of the molecules and perhaps a selection of molecules which tend not to have Rydberg series or a large accumulation of excited states near the ionization continuum. This may be somewhat difficult to find.

DR. A. V. PHELPS: Just one remark. I don't think the whole story is in on that yet. I think this depends at least at the present on how one does the experiment and so it may very well be that one can get around this. In other words, selection of the molecule.

DR. MULLER: Oh yes, I am not saying that all molecules --

DR. PHELPS: I am talking about hydrogen. I think there is evidence that some types of experiments do satisfy Franck-Condon principle, at least so far as the measurements are a measure of the vibrational state, and they are not a direct measure.

DR. MULLER: Well, the data that were reported were those of Marmet, Kerwin and some others.

DR. PHELPS: I think there are two sets of experiments on each side of the fence right now.

DR. MULLER: Which showed a very nice curve with breaks actually in it, as you would expect from the Franck-Condon principle. Briglia and Rapp have a curve which extrapolates, which does not bend and it is quite convincing. I have seen a lot of detail on their work. It has only a very tiny bend over here corresponding to what you expect of the energy spread and it seems fairly convincing here.

Also there are some data on photon ionization which I can find the reference somewhere among the papers here--

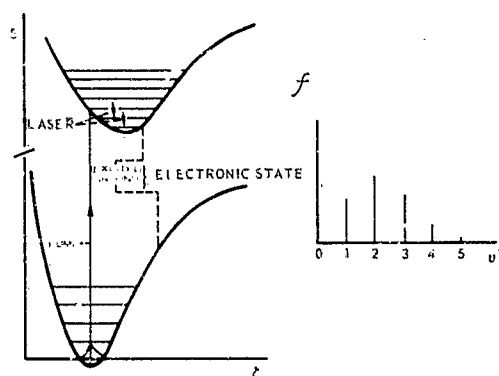
DR. PHELPS: That is all right, I have it.

DR. MULLER: Which also indicate that in the photoionization experiments, the Franck-Condon principle of course is satisfied, but there are many other states involved and this means that the net effect on

exciting the ionic ground state is to excite the vibrational ground state, too.

DR. BEHRINGER: If there is no further discussion we will adjourn.

FRANCK-CONDON PUMPING OF VIBRATIONAL ENERGY LEVELS



Session II Moderator: J. A. Soules, NMSU

Part 1 Nonlinear Effects

Tuesday Morning
23 March 1965

Braunstein UCLA

Shen UC Berkeley

Glass IDA

Subramanian Purdue University

Wang Philco

MODERATOR - PROF. SOULES: The first speaker this morning will be Rubin Braunstein of UCLA, formerly of RCA Laboratories. Rubin has been getting started on campus so I don't know whether he is going to describe the work he has already done there, or the work he did at RCA, or a little of both.

PROF. BRAUNSTEIN: The work I shall discuss this morning represents primarily, the results that were executed at the RCA laboratories, but shall also contain some work in progress at UCLA.

The major aim of this program was a study of the interactions of intense coherent optical radiation with solids. Specifically, the interest was a study of experimental cross-sections for double-photon absorption, harmonic generation, and frequency-mixing in semiconductors and to compare experimental results with theory. The semiconductors of the groups III-V and II-VI compounds were selected for this study since reasonable predictions can be made regarding the strengths of these interactions utilizing the known band structure of these solids. The linear, or single-photon interactions are reasonably well understood in these materials so as to provide the major band structure parameters which can be used to estimate the high order intensity dependent processes involving multiple-photon transitions via virtual states.

We shall discuss the accomplishments to date of this program and indicate the future directions this work can take as a consequence of these accomplishments. The results of a study of double-photon absorption, harmonic generation, and frequency-mixing in semiconductors, and the frequency tuning of injection lasers by uniaxial stress will be reported.

We shall first discuss the work on optical double-photon absorption in semiconductors. An intrinsic semiconductor normally does not exhibit any optical absorption capable of producing electron-hole pairs for incident photon energies less than the energy gap. However, for sufficiently high incident intensities of photons whose energy is less than the band gap, the multiple-photon excitation of a valence electron to the conduction band can take place and consequently, in principle, a perfectly transparent semiconductor does not exist.

CdS was chosen for experimental study of the double-photon absorption. This selection was made primarily because the single-photon absorption process has been extensively studied in this substance and it was therefore possible to compare double- and single-photon absorption on the same crystal. One can utilize the band structure parameters determined from the single-photon absorption measurements to estimate the double-photon absorption coefficients. The theory developed for this process in CdS can also be readily applied to other III-V and II-VI compounds. In addition, similar perturbation theory calculations for the three- and four-photon processes, that is, second-harmonic generation and tripling can also readily be cast in a form that takes account of the band structure parameters of these substances.

Observations were made of the two-photon excitation of an electron from the valence band to the conduction band in CdS ($E_g = 2.5\text{ eV}$) using a pulsed ruby laser

($\hbar\omega = 1.76\text{ eV}$). The radiative recombination emission from exciton and impurity levels subsequent to the simultaneous absorption of two-quanta of $\hbar\omega = 1.78\text{ eV}$ was observed as a function of laser intensity and compared to the emission excited by single-quanta absorption for photon energies of $\hbar\omega \approx E_g$. It was found that the intensity of the recombination radiation is proportional to I_0^n for single quanta excitation and I_0^{2n} for double-quanta excitation. Where I_0 is the excitation intensity and n is a constant which differs for different groups of emission lines. The observed cross-section of double quanta excitation compared favorably with theory utilizing the band parameters of CdS. These results were published as an article in the Physical Review.

Because of our success in observing the double-photon absorption in CdS and obtaining reasonable agreement with theory, it was decided to consider this process in the III-V semiconductors as well. The theory developed for the double-photon process in CdS utilized a three-band model for the band structure of this substance. However, the double-photon absorption cross-section can easily be obtained, using a two-band model, employing a single valence and conduction band. This double-photon calculation utilizing the simpler band structure model, reveals simple generalizations regarding the underlying parameters which determine the double-quanta absorption cross-section which applied to all the III-V compounds. This calculation enables one to set a lower bound to the absorption cross-section while requiring a knowledge of very few band structure parameters. The theoretical development is essentially similar to that previously given for CdS except that it utilizes an allowed intra-band optical matrix element for one of the virtual transitions.

The results of this calculation applied to the III-V compounds is shown in Slide 1. The double-photon absorption cross-section σ_2 is given in terms of α_c, α_v, E_g , where α_c and α_v are the inverse effective mass ratios for electrons and holes respectively and E_g is the energy gap. The numerical term in this equation contains all the constant terms as well as the inter-band momentum matrix element $|P_{vc}|^2 = 11.5\text{ eV}$ which has been shown to be the same for all the III-V compounds. In addition, the intra-band matrix element of zeroth order in k has been expressed in terms of the group velocity times the free electron mass. We have also assumed that the energy bands are spherical and parabolic.

In order to evaluate σ_2 for a particular substance, a knowledge of α_c, α_v, E_g is required. It can be shown using $k \cdot p$ perturbation theory to calculate the band structure of these semiconductors, that the valence and conduction band effective masses at $k = 0$ can be adequately accounted for by assuming that the inter-band momentum matrix element $|P_{vc}|^2$ is constant for all the III-V compounds and is given by $|P_{vc}|^2 = 11.5\text{ eV}$. The conduction band inverse effective masses α_c expressed in terms of the momentum matrix element is also given in Slide 1 (on the top right). The explicit values for the double-photon absorption cross-sections for some representative compounds are also given in Slide 1, in the table of values, where we have assumed that the heavy-hole inverse effective mass ratio α_v is equal to one and have used the values of α_c calculated from theoretical expression on the slide. The spin-orbit splittings Δ have been inserted using experimental values for this parameter.

2 - Photon Absorption in Semiconductors

$$\sigma_2 = 3.6 \times 10^{-48} \frac{\alpha_c^2}{(\alpha_c + \alpha_v)^{3/2}} \frac{1}{E_g} \frac{1}{\hbar} \quad \alpha_c = 1 + \frac{20}{3} \left[\frac{2}{E_g} + \frac{1}{E_g + \hbar} \right]$$

	GaAs	InP	InAs	InSb
σ_2 -cm ⁴ sec	2.8×10^{-49}	3.7×10^{-49}	4.0×10^{-48}	1.4×10^{-47}
E_g -ev	1.53	1.34	0.45	0.25
α_c	13.3	15.2	38.5	65.5
∇	0.33	0.24	0.43	0.84

2 - Photon Discrete Trans.

$$\sigma_2 = \frac{5.1 \times 10^{-48} f^2}{n^2 E_g^2 (\Delta E_g)} \quad f = f\hbar \quad E_g, \Delta E_g - \text{ev}$$

$n = \text{index}$

It can be seen in this table that the double-photon absorption cross-sections increase as the band gap of the solid decreases. The characteristic feature that the optical double-photon absorption cross-section increases as the band gap of the solid decreases, is not limited to the case of a band-to-band transition in a semiconductor but comes from the frequency factors in the optical matrix elements. This result is also obtained in the case of double-photon absorption between discrete levels and non-linear absorption cross-section for such a process is also given in the bottom of Slide 1. In this equation n is a refracted index, ΔE_g is the width of the real excited state at $2E_g$ and f is the l -number for the transition. In the derivations of the above double-quanta absorption cross-section, it was explicitly assumed the absorption occurs by a single intermediate state which allows coupling between the initial and final states. In fact, it is necessary to sum over all possible intermediate states. Consequently, these calculations represent a lower bound for the double-photon absorption cross-sections.

Let us now turn our attention to the transmission laws obeyed by medium within which a linear and a quadratic loss process can simultaneously take place. In the steady state, the transmitted flux through such a medium is given by the continuity equation shown on top of Slide 2. Where σ_1 is the linear absorption cross-section in units of cm², σ_2 is the absorption cross-section for quadratic loss process in units of cm⁴ sec, and N_1 and N_2 are the densities of centers responsible for the linear and quadratic loss processes, respectively and F is the flux per unit area in photons/cm² sec. We have assumed that N_1 and N_2 are independent of

incident flux. That is, the lifetime for recombination to the ground state is extremely fast. For a plain parallel slab of thickness r and neglecting reflection losses, the transmission is obtained by integrating this equation, the results are shown in Slide 2. Also are shown similar results for spherical and cylindrical geometries, considering in these cases only quadratic losses taking place. We see that for high incident intensities the transmission ultimately saturates for all geometries.

Transmission with Quadratic Loss

$$\nabla \cdot F = -\sigma_1 N_1 F - \sigma_2 N_2 F^2$$

Plane: $F/F_0 = \frac{\sigma_1 N_1 r}{\exp(\sigma_1 N_1 r) [\sigma_1 N_1 r + \sigma_2 N_2 r F_0] - \sigma_2 N_2 r F_0}$

$$\nabla \cdot F = -\sigma_2 N_2 F^2$$

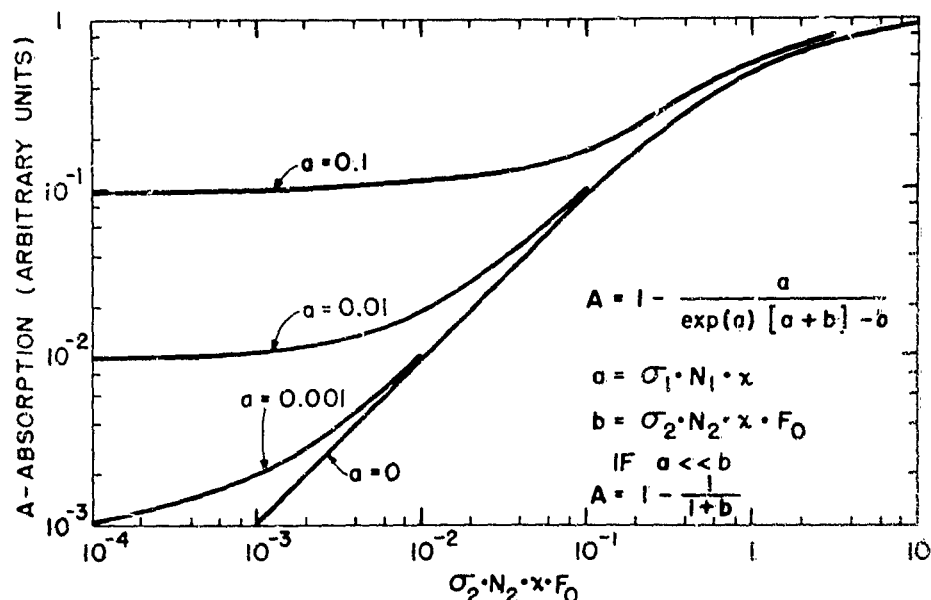
Spherical: $F/F_0 = \frac{1}{\sigma_2 N_2 \frac{r^2}{2} F_0 + \frac{r^2}{2} - \sigma_2 N_2 r F_0}$

Cylindrical: $F/F_0 = \frac{1}{\sigma_2 N_2 r F_0 \ln r + \frac{r}{r_0} - \sigma_2 N_2 r F_0 \ln r_0}$

$$\sigma_1 - \text{cm}^2$$

$$\sigma_2 - \text{cm}^4 \text{ sec}$$

$$F = \text{Photons/cm}^2 \text{ sec}$$



Transmission law for a medium with linear and quadratic losses simultaneously present.

Slide 3 shows a plot of the absorption $A = 1 - T$ for plain geometry for a medium having linear and quadratic loss processes simultaneously present. When the parameter $\sigma_2 N_2 \lambda F_0 > 1$, the quadratic loss process becomes the dominant absorption process, and in fact the medium ultimately becomes opaque. These results show that there is an intrinsic upper limit to the flux density which can be transmitted through a medium that has a nonlinear absorption process taking place. It should be further noted that it is only the linear absorption process that yields an exponential fall-off of intensity with distance and is independent of intensity while the quadratic and higher order processes will fall-off inversely proportional to the distance and intensity.

Although the double-photon absorption cross-sections appear to be relatively small, since the absorption cross-section for this process depends upon the incident intensity, at high flux densities this process can constitute a major dissipative mechanism when operative.

It is of interest to consider the possible effects of double-quanta transitions on the power output of injection lasers, in particular, that of gallium arsenide. Although the power output presently available from such devices is relatively small compared with that of optically pumped lasers, injection lasers are relatively small area devices so the flux per area is still quite high at the emitting junctions. Furthermore, the emitted frequencies lie slightly below the band-gap, satisfying the threshold conditions for double-quanta absorption. Power densities of the order of 10^{17} watts/cm² can be realized for conventional diodes. If one considers a diode of 0.1 cm length with the above power densities and one employs the lower-bound double-photon absorption cross-sections previously given for gallium arsenide, one obtains for the parameter $\sigma_2 N_2 \lambda F_0 \sim 3 \cdot 10^{-2}$. These results are shown in the bottom of Slide 4, together with values

for the parameter $\sigma_2 N_2 \lambda F_0$ for a number of other cases such as glass, impurities in calcium fluoride, and the case of transmission through an oxygen atmosphere. From the equation shown in Slide 3, we see that under these conditions, in gallium arsenide where double-photon absorption can take place, they can make a reasonable contribution to the loss processes within the gallium arsenide laser. Even if an electron-hole pair created by double-photon absorption subsequently recombines and is re-emitted as a photon, the double photon absorption process will still set an intrinsic upper limit to the output power since two quanta will be annihilated to produce one subsequently re-emitted quantum.

If a focused high-power laser is incident upon an ostensibly transparent substance such as optical quality calcium fluoride or any other optical quality material, it is usually found that most substances tend to be punctured at power levels of approximately 10^9 watts/cm². When one normally examines these materials by measuring absorption at low power levels very little absorption is found. Despite the fact that the band gap of these materials may be far greater than twice the incident photon energies so that a double quanta absorption process is not allowed between bands, it may be possible to have multiple-quanta processes taking place between impurity levels. If one considers a typical example of a case of calcium fluoride, one finds that one can have a distribution of impurity levels at concentrations of 10^{18} /cm³ due to various rare earth impurities. A reasonable estimate of the double-photon absorption cross section for the ruby line can be made by superimposing the energy levels of the various impurities and using appropriate averages of the oscillator strengths and the half-widths of the excited states at twice the laser frequency. The resulting cross-sections σ_2 yield values of 10^{-49} cm⁴ sec. For incident power of 10^{19} watts/cm² and a 1-cm-thick slab, the parameter $\sigma_2 N_2 \lambda F_0 \sim 10^{-3}$. This result is shown on the bottom of Slide 4.

Nonlinear Absorption

$$A = 1 - \frac{F}{F_0} \approx 1 - \frac{\sigma_1 N_1 x}{\exp(\sigma_1 N_1 x) (\sigma_1 N_1 x + \sigma_2 N_2 F_0) - \sigma_2 N_2 x F_0}$$

$$\text{If } \sigma_1 N_1 x \ll \sigma_2 N_2 x F_0 \quad \sigma_1 = \text{cm}^2$$

$$A = 1 - \frac{1}{1 + \sigma_2 N_2 x F_0} \quad \sigma_2 = \text{cm}^4 \text{ sec} \quad N = \#/\text{cm}^3$$

$$F = \text{photons}/\text{cm}^2 \text{ sec}$$

$$\text{GaAs} \quad - \quad \sigma_2 N_2 x F_0 = (3 \times 10^{-49}) \cdot (10^{22}) \cdot (10^{-1}) \cdot (10^{26}) \sim 3 \times 10^{-2}$$

$$\text{Glass} \quad - \quad " = (10^{-50}) \cdot (10^{22}) \cdot (1) \cdot (10^{28}) \sim 1$$

$$\text{Imp. in CaF}_2 \quad - \quad " = (10^{-49}) \cdot (10^{18}) \cdot (1) \cdot (10^{28}) \sim 10^{-3}$$

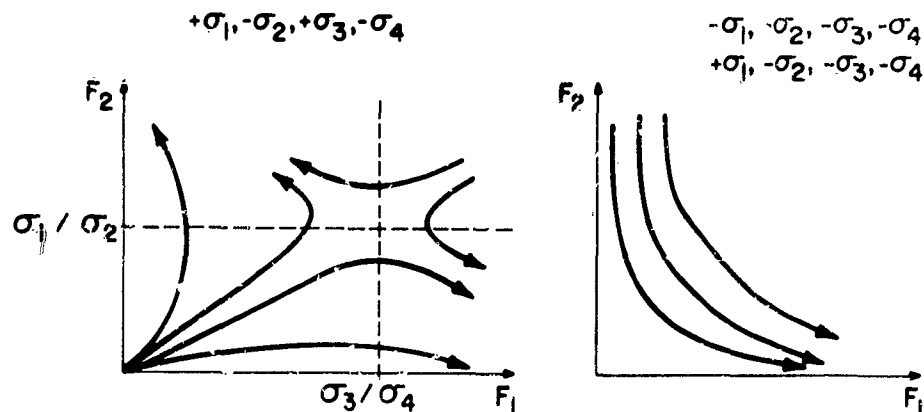
$$\text{O}_2 \quad - \quad " = (10^{-50}) \cdot (10^{18}) \cdot (10^5) \cdot (10^{28}) \sim 10$$

Linear absorption due to scattering from optical imperfections or residual impurities normally yield values of $\sigma_1 \cdot N_1 \cdot x < 10^{-3}$ for optical quality calcium fluoride. Consequently, the normal linear scattering processes cannot account for the dissipation, while the double-quanta absorption due to impurities can be responsible for a reasonable amount of power absorbed from an incident laser beam.

In calculating the propagation of a laser beam through a gaseous atmosphere one normally utilizes the linear absorption coefficient of the appropriate optical window to determine the optical losses. However, if care is not taken so that no states exist at twice the laser frequency to which double-quanta absorption can take place, there is an intrinsic limit to the power that can be transmitted through such an atmosphere. Let us consider the case of a laser beam of photon energy $\hbar\omega \sim 3.1 \text{ eV}$ and a flux density of the $10^{19} \text{ watts/cm}^2$ propagated through a kilometer path length of O_2 at standard pressure and temperature. For such a beam, double-photon

absorption can take place via the Schumann-Runge bands. From the observed half-widths and the oscillator strengths of these bands the cross section σ_2 can be estimated to be of the order of $10^{-50} \text{ cm}^4 \text{ sec}$; consequently as we see in this Slide 4 $\sigma_2 \cdot N_2 \cdot x \cdot F_0 \sim 10$. We see from the curve in Slide 3 that the transmission of such a beam will saturate. Similar considerations will apply whenever one uses any optical window in an atmosphere where there is a state available at twice the frequency of the window so that the double photon absorption can take place.

Uptill now, we have considered the propagation law for a medium in which both linear and quadratic loss processes can take place which involve a single frequency. If we extend the treatment to the case where we have two different frequencies which can undergo singularly linear loss, or together, undergo double photon absorption, we arrive at a coupled pair of nonlinear differential equations of the Volterra type which are shown at the bottom of Slide 5. Although it is necessary to



$$dF_1 / dx = \sigma_1 N F_1 + \sigma_2 N F_1 F_2$$

$$dF_2 / dx = \sigma_3 N F_2 + \sigma_4 N F_1 F_2$$

solve these equations numerically for any particular condition, we can obtain the general features of the solutions by plotting some of the phase trajectories. For the signs of the coefficients σ_1 , σ_2 , σ_3 and σ_4 indicated in Figure 5, regardless of what the initial intensities of either of the two photon beams are, one will ultimately prevail at the expense of the other, as can be seen from the two indicated graphs. However, if one of the quadratic coefficients σ_2 or σ_3 is positive, that is, if we have a double-quanta stimulated emission process taking place, there are a series of stable periodic solutions possible for these equations such that at a given distance one beam has a maximum of intensity while the other has a minimum. At a further distance through the medium the intensities reverse; the results repeat as a function of distance. It should be noted, although the double photon absorption cross-sections might be considered small, the absorption coefficient for this process is proportional to the length of path and the intensity. Although we have considered these processes in cases where we have had high intensity lasers present, there are a number of astronomical cases where exceedingly long paths are involved such as in the case of planetary nebula or propagation through inter-stellar hydrogen where some of these nonlinearities might manifest themselves.

We shall next consider some work on harmonic generation in the III-V compounds.

The III-V compounds comprise a group of materials whose band structure and related parameters are well known. Consequently, they are amenable to calculation of the cross-section for various nonlinear processes. We have previously considered the two-photon absorption cross sections of these materials. Since these materials, in addition, lack a center of inversion in principle, one should be able to generate the

second harmonic of given incident frequency. By comparing the measured harmonic cross sections $\sigma_{2\omega}$ or, as we have done in this work, the nonlinear susceptibilities χ_{14} of several III-V compounds having different band structure parameters, we sought to identify the pertinent parameters responsible for these coefficients.

In this study, we observed the second harmonic of an incident Nd^{3+} laser generated at $5300 \text{ \AA}$ (2.34 eV) in single crystals of indium phosphide, gallium arsenide, aluminum antimonide and gallium phosphide. Our work on indium phosphide and aluminum antimonide is the first reported on these materials. Since the band gaps of these compounds range from 1.24 eV to 2.24 eV while the energy of the exciting photons was 1.17 eV, we were dealing with a case where the second harmonic was completely absorbed within a fraction of a wavelength after generation, while the exciting radiation suffered negligible attenuation. The emitted harmonic could be observed either in reflection or transmission. In the former, the harmonic is generated at the incident surface and is emitted as a reflected beam. In the latter, the only harmonic radiation leaving the material is generated at the exit surface since that produced in the bulk is completely absorbed; we employed the transmission method.

Substantial second harmonic generation was observed in the above compounds. This radiation was generated at the exit bases of the single crystal specimens by excitation using a Q-switched Nd^{3+} glass laser. The dependence of the harmonic intensity on both the polarization of exciting and harmonic radiation as well as the crystal orientations was studied and found to agree with the predicted behavior within experimental errors. The results of these studies yielding the intensities of the coefficients is shown in Slide 6.

MEASURED INTENSITIES AND CALCULATED SUSCEPTIBILITIES

	InP	GeAs	AlSb	GeP
$W_{2\omega}$	$2.2 \pm .4$ volts	22 ± 2 volts	1.1 ± 0.7 volts	3.8 ± 1 volts
$W_{2\omega}^{\text{KDP}}$	22 ± 4 "	22 ± 4 "	21 ± 3 "	20 ± 2 "
I_{ω}	12 ± 1 mv	23 ± 3 mv	12 ± 6 mv	9 ± 2 mv
I_{ω}^{KDP}	40 ± 4 "	40 ± 4 "	28 ± 6 "	36 ± 2 "
χ_{14}	1.06×10^{-6} esu ($\pm 30\%$)	1.21×10^{-6} esu ($\pm 30\%$)	0.31×10^{-6} esu ($\pm 75\%$)	0.26×10^{-6} esu ($\pm 3.3\%$)
χ_{14}^c	0.76 "	1.07 "	0.25 "	0.8 "
χ_{14}^B	—	1.20 " ($\pm 50\%$)	—	—
χ_{14}^G	—	0.87 "	—	—
χ_{14}^S	—	1.53 " ($\pm 50\%$)	—	0.25 " ($\pm 50\%$)

+ Peak intensities as measured on oscilloscope with $10 \text{ k}\Omega$ load.

* Ref. N. Bloembergen, R. K. Chang, J. Ducuing, P. Lallemand (presented at Semiconductor Physics Confer., Paris, 1964).

** Ref. M. Garfinkel, W. E. Engeler, App. Phys. Lett. 3, 178 (1963)
(Note: Authors erroneously give value of 2.6×10^{-6} esu; using their data and formula, we obtained 0.87×10^{-6} esu).

*** Ref. R. A. Soref, H. W. Moos, J. App. Phys. 35, 2152 (1964).

An examination of the nonlinear susceptibilities of seven of the III-V compounds studied so far shows the absolute value of χ_{14} for Nd^{3+} excitation lies between 0.2×10^{-6} esu and 1.2×10^{-6} esu. This compares with the value 3×10^{-9} esu for KDP which is about the strongest harmonic generator among ionic crystals. This 150-400-fold increase in χ has been shown to be due mainly to the resonance between the harmonic and the conduction bands. In the case of ionic crystals this does not occur for excitation by frequencies as low as those produced by the Nd^{3+} and ruby lasers.

Since the harmonics are generated within a fraction of a wavelength of the exit base one might expect that their intensities are very sensitive to chemical treatment of the surfaces. In addition, one might expect mechanical operations, like polishing, would produce lattice distortions at the surface which would result in several crystallographic planes contributing simultaneously to the harmonic intensity. This would show up as a non-vanishing minimum in the orientational dependence of the harmonics. In our experiments, we encountered both of these effects. We investigated the effects of various polishings and etchings of the harmonic intensity. For the incident intensity measurements used in determining χ_{14} , we chose the surface treatments which gave both the maximum emission and a zero, or almost zero, at the sample orientations where it should vanish. Both faces of all crystals were polished with fine carborundum prior to etching. These results indicate that in principle one might utilize second harmonic generation as a means of crystallographically orienting single crystal specimens of substances where harmonic generation can take place.

Extensive measurements of optical second harmonic generation and the linear electro-optic effect have been performed to-date on ionic and inorganic crystals. We have, in turn, now observed similar results on an organic molecular crystal, hexamine which has crystal symmetry (I43m). The nonlinear susceptibility was determined: $\chi_{14} = 30 \times 10^{-9}$ esu for hexamine as compared to 3×10^{-9} for KDP. Electro-optic coefficient of hexamine is 12.6×10^{-3} esu. From the theoretical relationship relating the electro-optic coefficient and the second harmonic coefficient, it was possible to conclude that the electro-optic effect in the cubic crystal, hexamine, is predominantly electronic.

Aside from the semiconductors and insulators whose crystal structure lack a center of inversion and consequently have the necessary condition for second harmonic generation, there are a number of metals with point groups which would indicate that they should also be piezoelectric. However, it would be extremely difficult to try to measure their dc piezoelectric coefficients. If, however, one could generate a second harmonic from these metals, a measurement of the nonlinear susceptibility would enable one to infer the dc piezoelectric coefficients. An example of a potential piezoelectric metal is the α -phase of manganese which has symmetry 43m and consequently, only one piezoelectric coefficient. It was difficult to obtain large, single crystals of α -manganese to obtain good measurements of the angular dependence of the second harmonic generation and hence, a good measurement of the nonlinear susceptibility. Attempts are being made to obtain large enough crystals for these measurements.

PROF. SCHAWLOW: Were these measurements done in reflection?

PROF. BRAUNSTEIN: Yes.

We shall next consider some work on frequency mixing in semiconductors. Magneto- and electro-optic effects have usually been studied where the E- and H-fields are statically applied and an incident radiation field merely causes electronic transitions between levels. In semiconductors and insulators, the intrinsic absorption edges are observed to be displaced by the application of static E-fields of approximately 10^{15} v/cm. The electronic nature of these effects would indicate that if high optical E-fields were incident upon a semiconductor, the radiation field could cause a mixing of levels as well as electronic transitions between levels with the consequence that the real and imaginary parts of the absorption could respond to the different frequencies due to the presence of two optical frequencies incident in the neighborhood of the absorption edge of the semiconductor. The possibility of observing such nonlinearities was discussed by us in a previous publication.

While instrumentation was being assembled to study this type of nonlinear interaction, observations of optical frequency mixing in bulk CdSe was reported by Pantel and co-workers at Stanford. In these experiments, the axial modes of a ruby laser were mixed to obtain microwave power in the 1 to 5 Gc/sec region. The observed frequency-mixing could possibly be interpreted as a manifestation of the previously proposed nonlinear inter-band effect. However, since the axial modes overlapped the band gap, the resultant carrier generation rate could be modulated at the difference frequency and the application of a constant electric field, could cause microwave power to be radiated. Consequently, the observed effect could be interpreted in terms of a photo-conductive mechanism rather than in terms of a nonlinear inter-band effect as we had previously predicted.

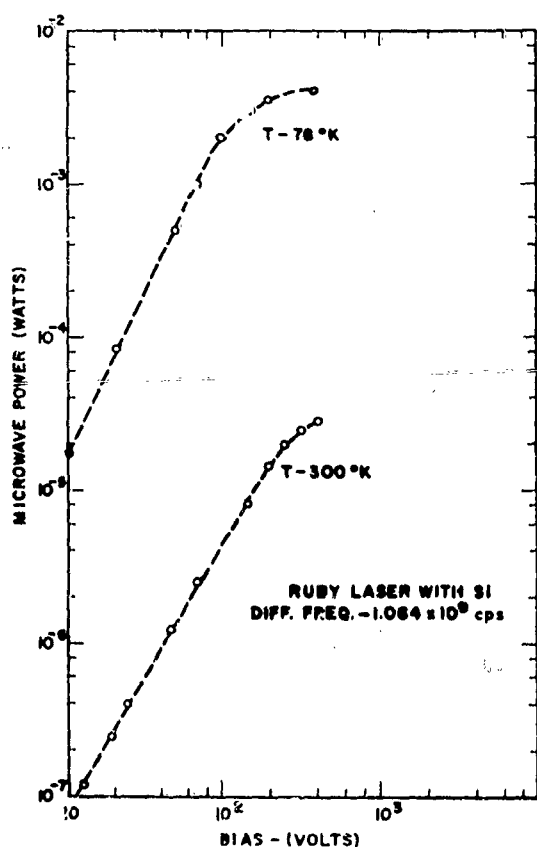
Both the photo-mixing and the inter-band-mixing effects would have some features in common, such as it would be necessary to apply an external bias field to observe the difference frequencies. However, the power produced by the photo-conductive interaction would be sensitive to the mobilities and the lifetimes of the generated carriers, while the nonlinear inter-band effect would be insensitive to these parameters. In addition, the latter interaction is expected to be relatively independent of the frequency difference between the two incident monochromatic beams while the photo-mixing process would be markedly frequency dependent. To understand the mechanism responsible for the frequency-mixing in CdSe, these observations were repeated and extended to Ge, GaAs, and Si, using a ruby and a Nd laser with each of these substances. Since these different laser sources overlapped appreciably different regions of the band edge, a nonlinear band effect would yield differences in microwave output for each source while a photo-conductor mechanism would yield little difference.

The results obtained from these measurements substantiates the interpretation that the observed effects were due to photo-conductive mixing and not to any nonlinear effects associated with the shift of the absorption edges of these substances.

The experimental results of the mixing of the axial modes of a ruby or a Nd laser in CdSe, Si, Ge, and GaAs have the common feature that the microwave output power is proportional to the square of the

incident optical intensity and the square of the bias field and the mobility squared and is inversely proportional to the square of the difference frequency. However, the absolute yields of the microwave power for a given optical power, bias and frequency vary from substance to substance. These observations are in qualitative agreement with the theory for photo-mixing.

Slide 7 shows the results obtained for the mixing of the axial modes of a ruby laser on silicon. The increasing signal by a factor of 400 for silicon in going from 300°K to 78°K can be understood on the basis that the mobilities increase by a factor of 10 for this temperature difference. The influence of minority carrier mobility in determining the absolute values or signals seems further substantiated by the saturation effects observed for silicon in Slide 7. At high fields, one notices the output power appears to saturate at bias fields of 1,000 v/cm, where it is known that the drift velocities tend to saturate. Similar results were obtained for Ge.



Microwave power from Si with ruby laser vs. bias at 300°K and 78°K.

This dependence of the microwave difference frequency on the mobility can be used to determine the mobilities in extremely low mobility materials such as phalacyanide where it has been extremely difficult to measure mobilities by conventional transport means. The advantage of the frequency mixing technique is mainly

due to the great sensitivity of microwave measuring techniques.

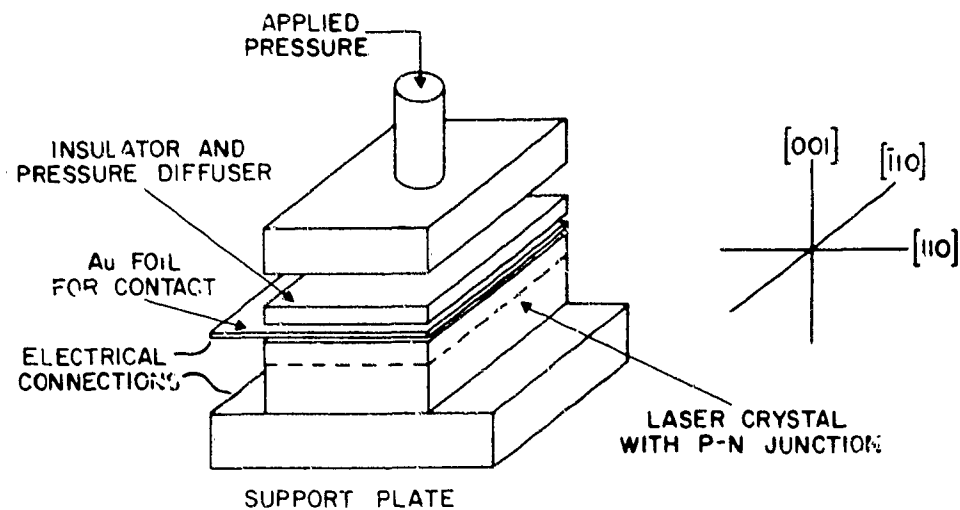
We shall now consider some of the results we have obtained in the frequency tuning of injection lasers by uniaxial stress, specifically, the work we have done on gallium arsenide. In many applications of injection lasers, it becomes desirable to have a means of varying the frequency. Such control will be necessary if diodes are to be used in such applications requiring frequency tuning, stabilization, or modulation. The energy levels and consequently the emission frequencies of a solid can be changed by uniaxial stress. The use of uniaxial stress has advantages over other methods of changing the frequency or the band gap such as hydrostatic pressure, magnetic fields in that the auxiliary equipment can be made simple and small. In addition, the application of uniaxial stress to semiconductors generally splits energy levels which are degenerate in the absence of stress and so can be used as a means of identifying recombination mechanisms.

We have studied the effect of uniaxial stress on the frequency spectrum of spontaneous and stimulated light emitted from gallium arsenide laser diodes, and have obtained preliminary information of the nature of the electronic transitions responsible for the emission in such diodes. In particular, different emission processes seems to be taking place in diodes made from different materials.

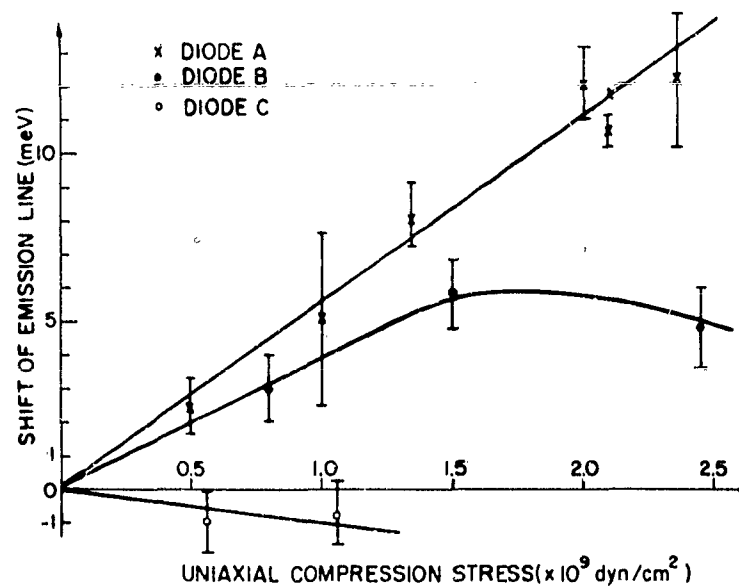
The experiment arrangement used in these studies is shown in Slide 8, as well as is shown the crystallographic orientations of the diodes used. The compression was applied perpendicular to the plane of the junction which is a (100) plane. Other orientations would give additional information but suitable diodes were not available. The diodes were in the form of parallelepipeds with dimensions of 0.6 x 0.16 x 0.10 mm and had cleaved sides.

The results for coherent emission varied from diode to diode since they depend on both the changes in the emitting transitions as well as on changes of the resonant cavity. The interpretation of the data is therefore more complicated since it requires the knowledge of individual cavity modes. We, therefore, also studied the incoherent light emission which should only depend on the electronic transitions involved and not upon the cavity modes. The results are shown on Slide 9 where we see a shift of the frequency as a function of uniaxial compression for three different diodes. It is clear that the three diodes which were made in different ways show very different behavior. The frequency of A increases linearly with stress. B and C show saturation and even negative changes. Other diodes made the same way as A, B or C do reproduce respective curves.

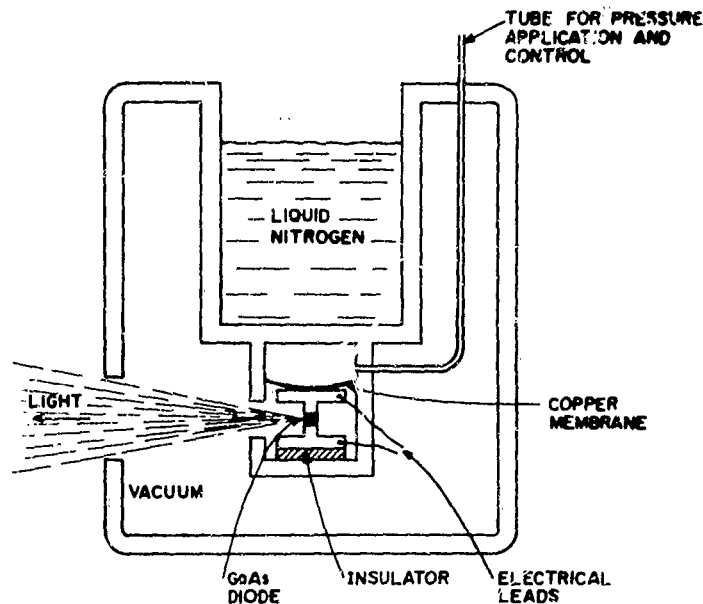
The above measurements were made by employing a mechanical structure whereby a compressional force through a rod and piston arrangement was applied to the diodes which were immersed in the bottom of a liquid nitrogen dewar. Because of a certain amount of unavoidable friction between the piston and the retaining cylinder there is uncertainty of approximately 20% in the stress values, which led to a scatter in the data and consequently an uncertainty in frequency. In order to obtain more detailed measurements to elucidate the nature of the optical transition as well as to give a finer frequency control, more refined stress equipment was designed and tested.



Experimental arrangement for the compression measurements; the crystallographic orientation of the GaAs diodes used is indicated at the right.



Shift of the incoherent emission line from three typical GaAs diodes with uniaxial compression stress at 78°K. The indicated spread of the individual data points represents the variation of the results of all the measurements made at a given stress.



Schematic diagram of uniaxial stress apparatus

One structure comprised a piezoelectric crystal in a laser diode clamped together enabling the force to be applied by electrical means. This structure allowed a fine control of the frequency of the laser diode by remote control. In order to measure the resulting stress, another piezoelectric element was included between anvils containing the diode and stressing crystal. Although the above structure performed satisfactorily at low stress values, it could not be used at high stresses.

A structure employing helium exchange gas as the stress transfer medium was finally designed and tested which yielded satisfactory results. In this arrangement, which is shown on Slide 10, the stress is applied to the diode by a piston-like arrangement which comprises a thin copper membrane under hydrostatic pressure. Extremely fine control of the stress is possible by control of the gas pressure from a tank external to the laser dewar.

To summarize the results of this program: We have shown that in the III-V semiconducting compounds the general features of double photon absorption, harmonic generation, photo-conductive frequency-mixing and frequency tuning of injection lasers by uniaxial stress can be understood in terms of the band structure of these materials.

The fact that a double photon absorption can set intrinsic upper limit to the power density that can be transmitted through media where the mechanism is operative warrants further measurements to obtain accurate cross-sections for this process. Measurements of double-photon absorption in the III-V compounds as well as other semiconductors would be of importance since they would have a bearing on the upper limit to the power obtainable from injection lasers made from these materials. In the case of gaseous atmospheres, such measurements also would be of importance whenever one uses an optical window for transmission where there is a state available at twice the frequency of the window so that double-photon absorption can take place.

In general, the measurements of double-photon absorption would be of value in that they also yield the stimulated emission cross-sections in possible double-photon laser systems.

The further exploration of the use of photo-conductive frequency mixing as a means of determining mobilities where it is difficult to measure small mobilities by conventional transport techniques, seems also worthy of further activity.

Since we have shown that the uniaxial stress will shift the frequency of a gallium arsenide laser by a substantial amount, we expect other injection lasers to show similar shifts since the deformation potentials of most materials are of the same order of magnitude.

PROF. SOULES: How fast does the convergence occur when you sum over the virtual processes in a solid material? Do you have problems with electrodynamic divergencies?

PROF. BRAUNSTEIN: No. The sums converge quite rapidly when properly done. The dominant contribution to the transition probability results from intermediate states which lie closest to the final conduction band.

MR. WHITE: In the case of a structure using a piezoelectric crystal and laser diode clamped together, what limits how high a frequency you can modulate or shift frequency?

PROF. BRAUNSTEIN: In such a structure, the loading of the transducer by the laser diode and the misalignment of the clamping anvil with the diode surface limits the magnitude of the frequency shift as well as the upper limit of the frequency response. It should be possible to frequency modulate at rates of up to 1 mc/sec with practical structures. However, a logical extension of the idea of piezoelectric tuning would be to prepare epitaxially a laser junction on the base of intrinsic gallium arsenide or other piezoelectric material which would serve as the transducer. In this manner, it should be possible to appreciably extend the frequency response of such tuning means.

PROF. SOULES: Our next speaker is Dr. Y. R. Shen of the University of California at Berkeley, who was associated with Professor Bloembergen at Harvard, and I understand that now it's the other way around, at least temporarily.

PROF. Y. R. SHEN: I would like to introduce the (multimode effect in the stimulated Raman scattering). First I think I should review briefly on the coupled wave theory. The stimulated Raman and Brillouin scattering, parametric amplification, and some other problems can be described in a united point of view by the coupled wave theory.

Let us consider first, three electromagnetic waves at different frequencies.

Could I have the first slide?

COUPLING OF THREE WAVES

$$\nabla^2 E_L - \frac{\epsilon_L}{C^2} \frac{\partial^2}{\partial t^2} E_L = - \frac{4\pi\omega_L^2}{C^2} \chi^{NL} E_S E_i$$

$$\nabla^2 E_S - \frac{\epsilon_S}{C^2} \frac{\partial^2}{\partial t^2} E_S = - \frac{4\pi\omega_S^2}{C^2} \chi^{NL} E_L E_i^*$$

$$\nabla^2 E_i - \frac{\epsilon_i}{C^2} \frac{\partial^2}{\partial t^2} E_i = - \frac{4\pi\omega_i^2}{C^2} \chi^{NL} E_L E_S^*$$

$$\vec{k}_L = \vec{k}_S + \vec{k}_i$$

$$\omega_L = \omega_S + \omega_i$$

In linear media, the coupling terms vanish and the three waves propagate independently. In nonlinear media however, because of these nonlinear coupling terms, they propagate in the coupled modes. The coupling is the strongest when momentum and energy matching conditions are satisfied. The coupling constants can be calculated in the usual way from the interaction Hamiltonian, and are proportional to the scattering matrix element with one photon coming in and two photons coming out.

For those who believe only quantum-mechanics, I should say that this kind of description can be justified completely by quantum-mechanics. The total Hamiltonian is $H = H_{atom} + H_{rad} + H_{int}$. If we take the matrix elements over the atomic coordinates, then we are left with a reduced Hamiltonian, which can be described in terms of annihilation and creation photon operators. When the number of photons is large or we are dealing with Glauber's coherence states, we are essentially back to the classical wave description.

To solve this set of nonlinear coupled equations, the simplest way is to linearize it. We'll assume that one wave is the pumping field that remains essentially constant. Then we are left with a set of two linear coupled wave equations for the remaining two waves, and the solution shows that the waves propagate in coupled modes. This is the case of parametric amplification or frequency conversion. I understand that

Dr. Wang has recently achieved optical parametric amplification and he is going to talk about this. Here, in a slightly modified sense, we do have only an optical frequency converter, if we replace one of the EM waves here by the optical phonon waves. This is the case of stimulated Raman scattering.

The next slide gives me a set of coupled wave equations with a vibrational wave replacing an EM wave. Again the solution indicates that the Stokes wave and the vibrational wave will go together in coupled modes. In the particular case when the vibrational wave is highly damped, the solution reduces to the results given by the isolated molecular model, since then the phonon wave is essentially localized.

$$\nabla^2 E_S - \frac{\epsilon_S}{C^2} \frac{\partial^2}{\partial t^2} E_S = \frac{4\pi\omega_S^2}{C^2} \lambda E_L Q_V^*$$

$$\beta \nabla^2 Q_V^* + (\omega_0^2 - \omega_V^2 + i\omega_V 2\Gamma) Q_V^* = \lambda E_L^* E_S$$

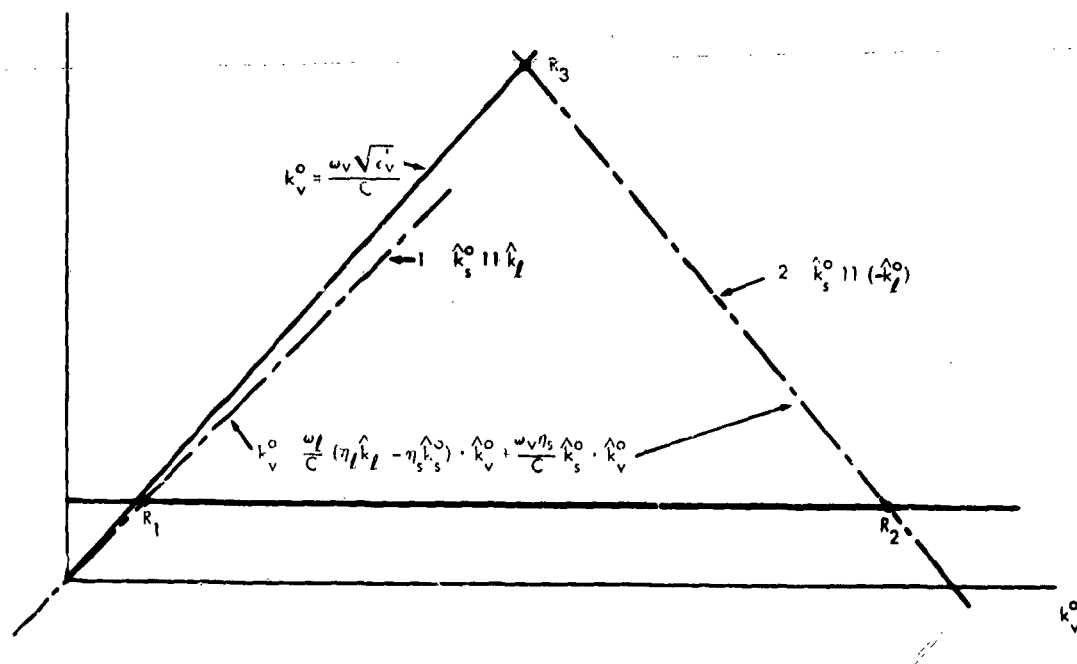
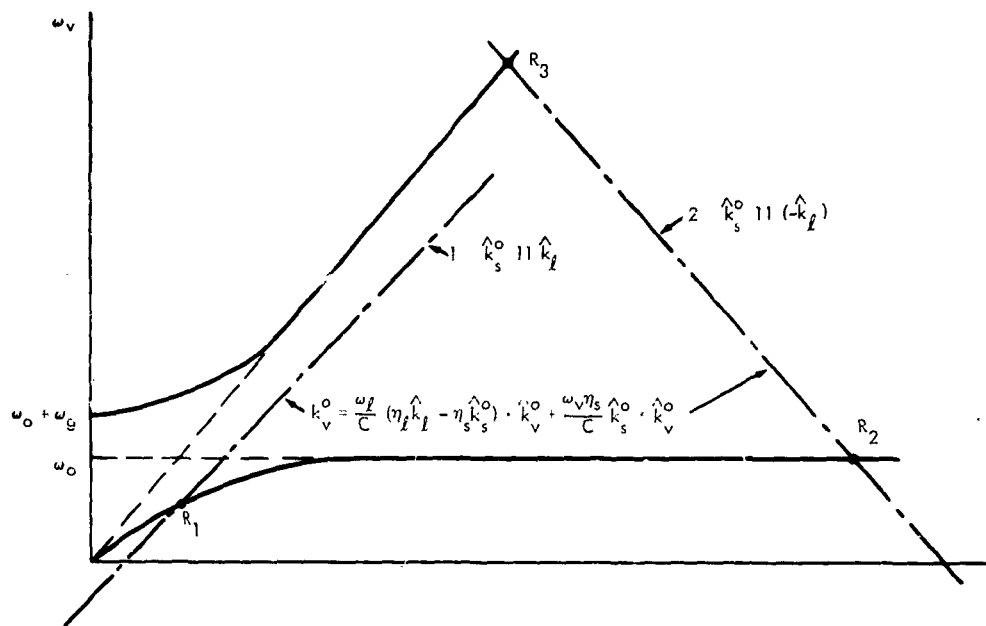
$$E_S = \sum_S \exp i(k_S \cdot r - \omega_S t)$$

$$Q_V = \alpha_V \exp i(k_V \cdot r - \omega_V t)$$

$$\text{Gain} = -\text{Im } k_S = -\text{Im } k_V$$

The next slide shows the energy and momentum matching conditions, $\omega_L = \omega_S + \omega_V$ and $k_L = k_S + k_V$. The horizontal line is the optical phonon dispersion curve. The dotted lines are given by the linear momentum matching combinations for the forward scattering and the backward scattering. The cross points R1 and R2 correspond to linear energy and momentum matching, where the coupling is close to maximum. In principle, Raman and Brillouin effects can be described exactly in the same way except that the dispersion curves of optical phonons and acoustic phonons are different. In the Brillouin case, it is a straight line passing through the origin. However, in the Brillouin scattering, transient effects may set in, if the laser pulse is short and the phonons are not highly damped. We have figured out ways to find whether the transient effect is important. The experiment will be done at Harvard. Also in the same language, we can talk about light coupling with spin waves. We just replace the optical phonon wave by the spin waves. The dispersion curve of the spin waves is $\omega = a + bk^2$. Again in this case many interesting problems appear. Also we can talk about light coupling with plasmon waves. Here, the optical phonon wave is replaced by the plasmon waves. This just shows that all these problems can be described in a general way by the coupled wave approach.

Now we want to show how coupling between laser and Stokes modes may give some interesting effects in the stimulated Raman scattering. Consider two laser modes at the same frequency but propagating in slightly different directions. Momentum matching condition shows that the Stokes radiations in two special directions are coupled together and therefore have different gain coefficients than the Stokes radiations in other directions.

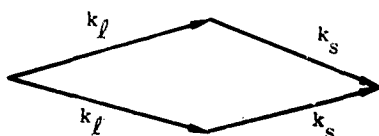


The next slide please.

$$\frac{dE_s}{dz} = C \{ |E_L|^2 + |E_L'|^2 \} E_s + C E_L'^* E_L E_s'$$

$$\frac{dE_s'}{dz} = C E_L' E_L^* E_s + C \{ |E_L|^2 + |E_L'|^2 \} E_s'$$

$$C = (2\pi\omega_s^2 / C^2 k_{sz}) | \chi_s''(0) |$$



Exponential Gain Coefficient

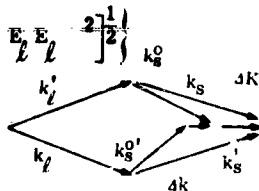
$$g_s = C \{ |E_L|^2 + |E_L'|^2 \pm |E_L E_L'| \}$$

$g_s +$ gives enhanced Stokes gain in the phase-matched direction.

In that case, we have two coupled wave equations for the two Stokes beams. Because of the coupling terms, we now have two gain coefficients, one larger and one smaller than the average gain. It is the larger gain coefficient that dominates the gain of the Stokes waves generated from noise. If the waves are linearly mismatched by Δk , the solution becomes

$$\Delta k = \frac{1}{2} \left\{ - \left[\Delta k - i2\alpha_s = \frac{C}{k_{sz}^0} (E_L'^2 + E_L^2) \right] \right\}$$

$$C = \frac{4\pi\omega_s^2}{C^2} \chi_s''$$



This linear mismatch apparently will give a decrease in the gain. If the mismatch is large, then the two beams are essentially de-coupled, so that the gain again reduces to the ordinary gain for uncoupled Stokes modes. But if $\Delta k < (\pi\omega_s^2 / C^2 k_{sz}^0) \chi_s'' E_L E_L'$, then we have a strong coupling between the two modes and the apparent Stokes gain is enhanced. Now, suppose that we have a laser beam with a narrow cone of wave vectors. Then, only the Stokes radiations in a narrow cone would be effectively coupled together to the laser radiation, and have enhanced gain. This gives rise to the observed strong increase in the Stokes gain in the forward direction, which cannot be explained by geometric consideration alone. In the space-time analogue, this enhancement of gain in the forward direction is analogous to the spectral narrowing in the stimulated process. As the spectral lines in the stimulated emission are usually narrowed, so is the spacial distribution. Also, the multi-mode effect can be explained in terms of hot filaments in the laser beam. In that sense, the laser beam can be divided into N elements, where $N = \frac{A}{2 d\Omega}$. A is the area of the laser cross-section, and $d\Omega$ is the angular spread of the laser radiation in

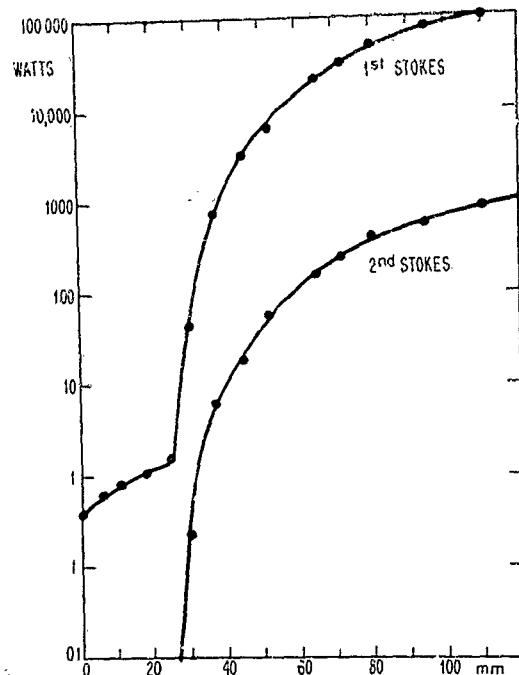
the wave vector space. The intensity distribution of the laser radiation in this cross-section can be calculated from the two dimensional random-walk problem. It is given by $W(I_L) = \frac{1}{\langle I_L \rangle} \exp(-I_L / \langle I_L \rangle)$.

Therefore, some filaments may have higher intensities than other filaments. The Stokes gain will have the same distribution as the laser intensity. If saturation is neglected, the Stokes generation in the i th filament is given by $E_{si} = E_{si}(0) \exp(g_{si} z)$ (where $g_{si} = (2\pi\omega_s^2 / C^2 k_{sz}) \chi_s'' I_{Li}$ is the gain in the i th element. In reality, saturation effect always comes in, so that while some of the intense filaments already start to generate high order radiation, other elements are still below or just above threshold in generating the first-order Stokes radiation. At the output of the Raman cell, one sees Raman radiation of many orders simultaneously present. If the same type of consideration is applied to the temporal modes, we can explain qualitatively many other effects observed experimentally, such as Raman spectral broadening, the dark absorption line in the broadened anti-Stokes spectrum, the broadening of the anti-Stokes ring, and the shifted angular position of the anti-Stokes ring. I shall not spend time here in going into detail. Explanations have been published in the Physical Review Letters. Instead, I would like to show some experimental proof on the multi-mode effects. These experiments were performed at Harvard by Pierre Lallemand in Professor Bloembergen's group. They were designed to show explicitly the multi-mode effects in the stimulated Raman radiation.

The first experiment was to measure the output Stokes radiation from a Raman cell. A polarizer is used to vary the laser intensity without changing the mode structure of the laser beam. The slide shows the Stokes intensity versus cell length. Curves for Stokes intensity versus laser intensity at constant cell length have essentially the same variation. At very low laser intensity, only spontaneous Raman emission is observed, which is proportional to the laser intensity I_L . The sharp bending indicates the onset of the stimulated effect. It is noticed that no section on the curve can be represented by a straight line corresponding to exponential growth. This is because regenerative action for Raman oscillation has set in at a very early stage. The second-order Stokes builds up in a similar manner as the first-order Stokes. This is a confirmation of what we said earlier about the higher-order Stokes radiation.

If, however, we measure the output from a Raman amplifier, by adding another cell in the light path, we find that for a fixed cell length the gain decreases rapidly as the distance between the two cells increases. This cannot be explained merely by the divergence of the beam. It can however be explained by the multi-mode effect. We can illustrate it by the example of two laser beams coming into a Raman cell at a small angle. The Stokes mode which has higher gain consists of two Stokes waves $E_s(k_s)$ and $E_s(k_s')$ coupled together, with the ratio $E_s/E_s' = \exp(i(\phi_L - \phi_L'))$, where $(\phi_L - \phi_L')$ is the relative phase difference of the two laser beams. This is also the ratio of the two Stokes waves coming out from the first cell. Even if we have exact momentum matching among waves in the first cell, they will become mismatched in the air due to change of indices of refraction. Therefore, the ratio E_s/E_s' changes relative to the laser beams as the waves traverse the air between the two cells. When

they arrive at the second cell, the Stokes beam is no longer in the mode which has the higher gain. The deviation is of course larger for layer distance between cells. This explains why the Stokes gain in the second cell decreases with the distance between cells.



The next slide shows the Stokes gain versus cell length of the second cell. For a short cell, the gain is low, such that the exponential growth can be approximated by the linear growth. The initial slope then corresponds to the average gain of all modes. This average gain should be used to determine the Raman susceptibility. For larger cell lengths, the mode with the highest gain becomes dominating, as is represented by the straight-line portion of the curve. Eventually, saturation effects set in as the laser power in that mode is depleted.

The mode effect is also demonstrated in another experiment. The laser beam is split by a beam splitter into beams of equal intensity, which then excites two identical Raman cells. For ideal beam splitters, the mode structures of the two beams should be identical. The Stokes generation should also be identical, so that the points on the slide should fall on the diagonal line. For a non-ideal beam splitter, the mode structures of the two beams would not be identical, and there appears a spread of points about the diagonal line. The spread is narrower for better beam splitters.

PROF. DAW: Was that experimental data you were showing, or is that --

PROF. SHEN: That's experimental data.

MODERATOR SOULES: Are there any other questions?

DR. CULVER: Did you put any material with different dispersion between your amplifiers in addition to just changing the geometry?

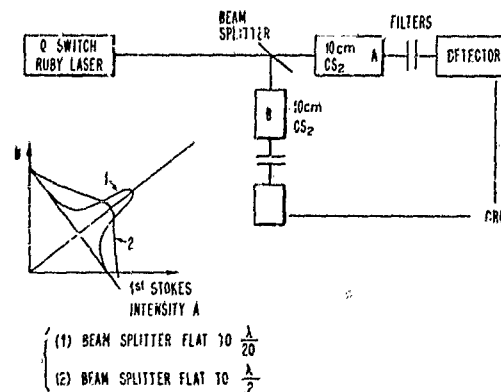
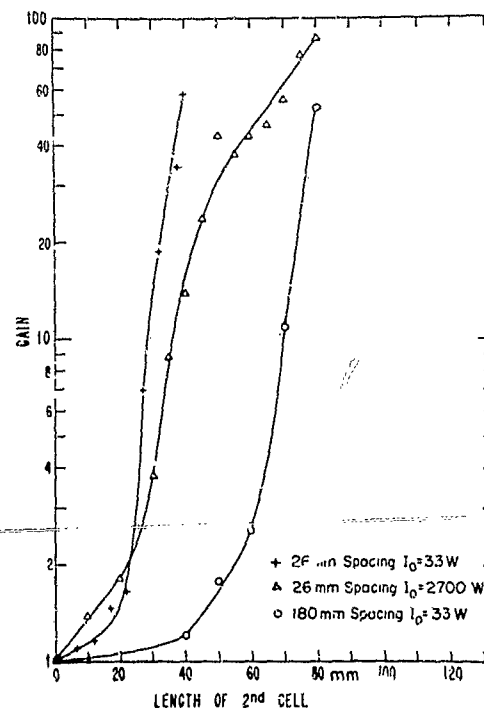
PROF. SHEN: Yes, you can do that, too.

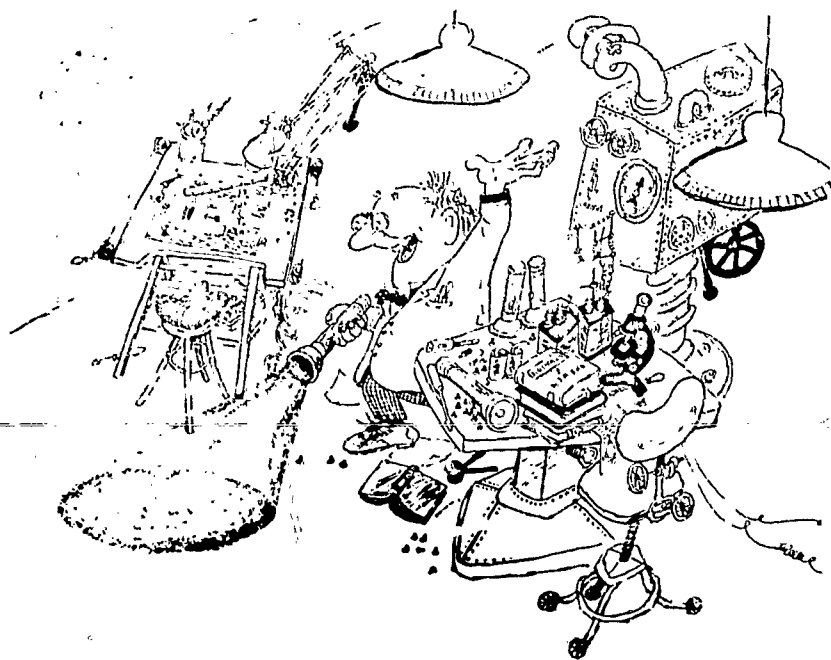
We are planning to put in glass plates, and if you put the glass plates at different places, you will see different results.

MODERATOR SOULES: Before we go to the next scheduled speaker, we have comments by two members of the audience. The first is Professor Schawlow, of Stanford.

PROF. SCHAWLOW: I would just like to ask Dr. Braunstein, in view of the calculations he has made on the nonlinear effects in nonlinear absorption in oxygen, would he have any comment on the feasibility of the device shown in the first slide?

Could you show the slide?





MODERATOR SOULES: The next speaker is Alex Glass, of IDA.

DR. GLASS: We have heard some comments this morning about nonlinear effects and some implications thereof with regard to limitations imposed by the atmosphere on the kind of beams you can transmit. I would like to comment very briefly on some implications of recent measurements of stimulated Raman scattering in atmospheric gases.

The inference is addressed to the same point, what are the limitations imposed by the atmosphere on the transmission of high intensity beams.

The geometry that I am envisioning is something like the following: We have an aperture of a certain area A and we are pushing a high intensity, well-collimated beam through this aperture into a certain solid angle $d\Omega$. What we want to know is, as a function of the distance, how much of the light we originally put in is going to be converted to the Raman-shifted frequency, that is, to the first Stokes line.

The following equation describes the way the Stokes intensity builds up.

$$(dI_1/dX) = \gamma I_0 I_1 + (d\sigma/d\Omega) I_0 d\Omega \quad (1)$$

The first term describes the buildup by stimulated Raman scattering; characterized by a gain coefficient γ . The process is initiated by ordinary Raman scattering, characterized by a solid angle, the cross-section, and dependent on the intensity of incident light. There is a relation between the gain coefficient and the cross-section much the same as that between the Einstein A and B coefficients, which we can insert to get, for the geometry envisioned, the intensity at the Stokes frequency as a function of the distance down the beam, X .

$$I_1(X) = (\hbar\omega_1\Delta/4) (d\Omega/\lambda_1^2) \left[\exp(\gamma I_0 X) - 1 \right] \quad (2)$$

Here Δ is the width of the Raman transition, $d\Omega$ the solid angle, and ω_1 and λ_1 the radian frequency and wavelength of the Stokes line.

Gamma is the gain coefficient and it's very much the same sort of creature as the σ_2 that Dr. Braunstein was talking about, except in this case it's not absorption, it's a scattering process. Gamma has actually been measured in a variety of atmospheric gases for a variety of transitions by Dr. Robert Terhune at the Dearborn Research Laboratory of the Ford Motor Company. His work has been published on vibrational transitions in hydrogen and deuterium, and he has some preliminary results for nitrogen.

A calculation of gamma for nitrogen has also been made there at the laboratory giving a value of gamma something like 1.85×10^{-11} cm/watt. The other quantity which is involved is the linewidth. Now, the width of the Raman transition has been measured, and appears to be something like .04 wave numbers.

We had a quantity introduced by Dr. Shen, which, I believe, I've heard Professor Bloembergen call the étendu. It is the product of the aperture area A times the solid angle $d\Omega$, divided by the square of the wavelength. This ratio is essentially the ratio of the solid angle the beam is spreading into to the diffraction limit.

We can now recast the buildup equation in terms of the simple fundamental quantities, the Raman gain γ and linewidth Δ , which are characteristic of the material, and the incident power P_0 and étendu η , characteristic of the incident beam.

If we call β the Raman conversion ratio, which is the ratio of the intensity at the Raman-shifted frequency to the incident intensity, we can write the following equation

$$\beta = (\hbar\omega_1\Delta/4P_0)\eta \left[\exp(\gamma P_0/2\lambda_1\eta) - 1 \right] \quad (3)$$

If you look at the exponential factor, which was previously $\gamma I_0 X$, you see that it no longer involves the path length X . This was eliminated by assuming that if the phenomenon was going to happen, it would happen in a distance from the end of laser in which the area of the beam increases by a factor of two.

In other words, the beam is diverging and the nature of such an effect is that if it doesn't happen in a distance in which the diameter increases by a factor of two, then it isn't going to happen at all. So that's the sort of argument that was used to eliminate the X , and cast it all in terms of these few simple parameters, which appear to be the fundamental quantities involved.

So, then we can put some numbers in and see what we get.

I should mention first of all that the measurement of γ that has been made has not been made in the open air, but instead has been made in the focused beam.

Now, a very similar expression obtains, except for some factors of two, if you look at the threshold for buildup of stimulated Raman scattering in the focus.

So, we have, as I say, a relatively good idea of what γ is, both from experiment and from calculation, and I think I mentioned this is for a rotational transition in nitrogen. It's a small shift, something like eighty wave numbers involved, and it's a narrow line. We can plot minus the log 10 of the conversion ratio β as follows:

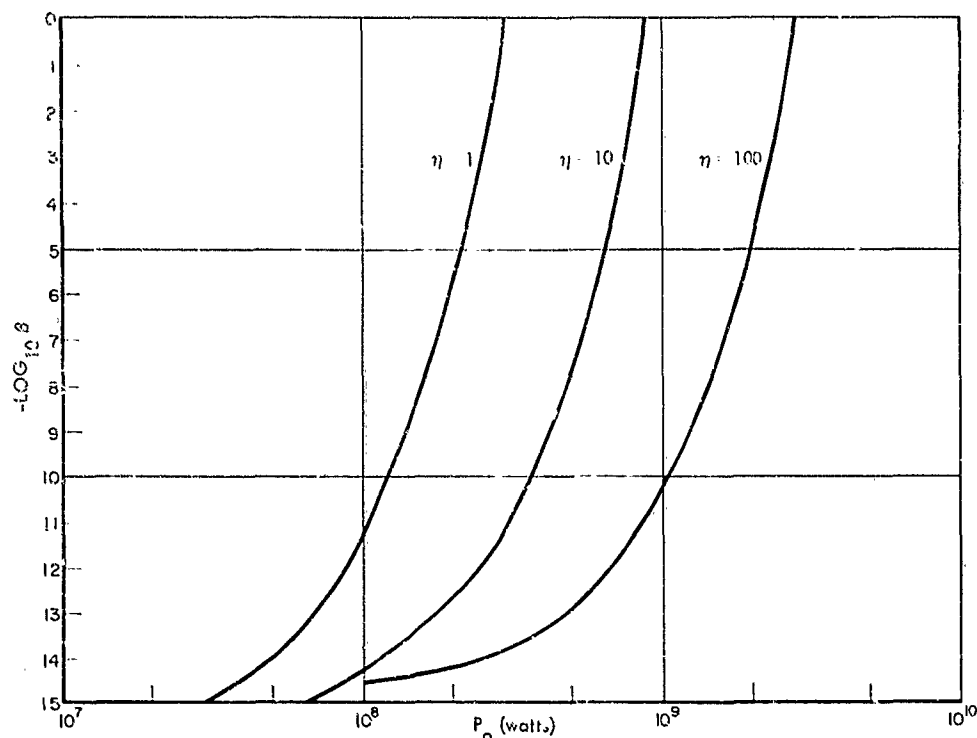
Now, if η is one, this power is something like 10^8 watts; and if η is 100, this power is something like 10^9 watts; but this has to be power within the linewidth of the transition, of course. So that's the conclusion that one arrives at.

As far as we know, there is no laser operating right now which would be capable of causing stimulated Raman scattering in the open air in an unfocused beam.

However, the inference is that we are not far from the point where this will be seen, and this is obviously something that has to be kept in mind.

I might point out that we saw in the two photon absorption that there was a number which characterized the point at which the two photon absorption would essentially limit the propagation of a beam in oxygen.

We had γ here of 1.85×10^{-11} , the corresponding figure for the two photon absorption from the numbers given is something like 10^{-13} , so it would appear that this would be the phenomenon which would enter first.



Buildup of SRS in Distance in Which Beam Diameter Doubles.
Raman Conversion Ratio β vs. Power P_0 For Several Values of Etendu η .

PROF. SUBRAMANIAN: Do you have some number on this power that you are talking about? What is the power level that we will be able to observe the Raman scattering?

DR. GLASS: This is it, 10^8 with an etendu of 1; 10^9 at 100. I took some numbers from talking to various people who had obtained big lasers commercially and put in these numbers, and find they all tend to fall just short of the threshold. The factors that come in, you need to know the power, you need to know in what linewidth this power is concentrated, and you need to know the beam divergence in effect.

PROF. SCHAWLOW: Has Terhune measured the stimulated Raman effect at a pressure low enough so that the rotational structure is resolved?

DR. GLASS: Yes, he has measured it. Well, he feels that he has. Now, I am taking advantage of some conversations with Dr. Terhune, and the work is very preliminary insofar as the experiment goes. Their laser pooped out, is the way I think you have to put it, but they are getting a new laser which ought to be capable of pinning this down, and there are some other experiments in progress at other places which may also shed some light on it.

DR. QUELLE: That's with nitrogen. The point is with going to hydrogen or something like that, a gas has a much lower threshold, you have plenty of power so as to see these things in focus.

PROF. SCHAWLOW: Of course, in the oxygen case it was a vibrational transition. The atmosphere is not composed of hydrogen.

DR. GLASS: There are a number of questions involving what the true nature of the focused beam experiment is, because at the focus the rotational Raman scattering is accompanied by breakdown, and it's not simply nitrogen gas in which this is occurring, but it appears to be something with a lot of free electrons.

DR. CULVER: Although we may not be running into applications of the particular lasers that are going to break down, yet, such as using them as radars, this might be observed by running it through a series of focus. At each focus you ought to be able to get the gain that you got at the preceding one, if you can reproduce the focus, and then you ought to be able to perhaps confirm these results except for multi-mode effects.

That would be rather interesting, in fact.

MODERATOR SOULES: Our next speaker is Professor Subramanian, of Purdue University, who has been doing some experiments on higher order effects of laser.

PROF. M. SUBRAMANIAN: My problem is something similar to what Braunstein told in his presentation of how he is trying to get started in a new place, and it's about the same for me, too.

For the past year and a half I have been establishing a laboratory, for conducting experimental research at Purdue's School of Electrical Engineering. I think I might probably be a little bit of a misfit because most of the people here are physicists, and in fact, my talk will also be more towards engineering oriented.

The primary work on the nonlinear objects at Purdue now is having two phases: One is the dc polarization which I have been working on for the last couple of years, and the second phase is subharmonic generation which we recently started within the last few months. Essentially what I will do now is give you a brief progress report on what we have achieved in terms of the dc polarization, and then describe the preliminary work that we have started on the subharmonic generation.

The dc polarization was observed, two years ago, and it was reported by Bass and Frank, from Michigan University, and also we presented a paper on it in Brooklyn Polytechnic Symp. on Optical Masers. Actually, I will show you a couple of slides borrowed from that conference to orient the people who are not familiar with the dc polarization.

May I have the first slide, please?

$$p = a_1 E + a_2 E^2 + a_3 E^3 + \dots$$

$$p = a_1 E_0 \cos t + \frac{a_2}{2} E_0^2 (1 + \cos 2t) + \frac{a_3}{4} E_0^3 (3 \cos t + \cos 3t) + \dots$$

The dc polarization that I am talking about essentially corresponds to this term here. For the sake of educational purpose, I am presenting the polarization equation in the scalar form. The rest of my talk on the dc polarization is essentially concerned with this term over here. My calculations are for the case of the propagation through a uniaxial crystal along the direction of optic axis. For this case we can find out that the dc polarization is given by the term, that is shown in the next slide.

Plane polarized light:

$$|p| = \frac{\alpha}{2} (a_x^2 + a_y^2)$$

Circularly polarized light:

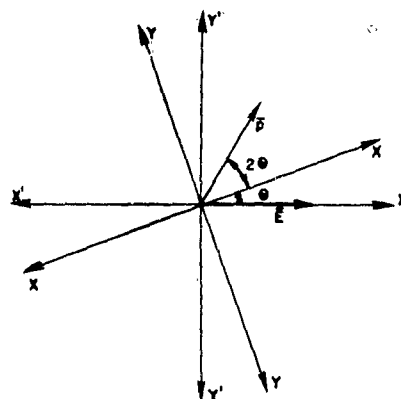
$$|p| \equiv 0$$

For the plane-polarized beam, this is what we get which essentially shows that the magnitude of the dc polarization would be directly proportionate to the power in the laser beam.

This led us to the interesting idea that we could see this dc polarization as a meter for measuring the power in high-power lasers and the further work that we were in was toward this goal. Let me point out one more fact here which is probably the question that many of you may ask about the material we have chosen. The material I chose was quartz crystal, which has low nonlinear polarization coefficient compared to KDP. Now-a-days, we have cadmium sulfide which has a much larger magnitude. The reason for this choice is that the major problem was of getting rid of the pyroelectric effect in these crystals. Since quartz has the least amount of pyroelectric effect, my first choice was this.

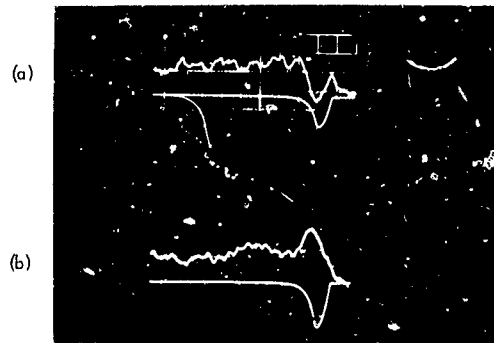
Initially, I took the electrodes away from the quartz crystal, and this way I reduced the heating effect considerably. I was also able to overcome the problem of building an amplifier, even though it was of low sensitivity. Our present work now is just getting started with the other crystals.

So, with this introduction on the material, if we actually plot the polarization direction with respect to the incident polarization of the radiation field, we would get a figure of something like the one that is shown in the next slide here. The X and Y are the principal axes, and if you choose the incident polarization to be polarized along the X prime axis, then the dc polarization is oriented with respect to the X axis of the crystal at an angle 2θ . This provides us with a very interesting proof that we are observing the dc polarization and nothing else. If we rotate the crystal through an angle θ , keeping the polarization constant, then we would observe the dc polarization to rotate through an angle 2θ -- that means if we rotate the crystal through 90° in a positive direction, we should be able to observe the dc polarization rotated in a negative direction through 180° . This is the first conclusive proof that we had for the dc polarization.



For measuring this, I have given to -- chronologically put the subject in the conference here. I also give the old setup we had to measure this with.

May I have the next slide, please?

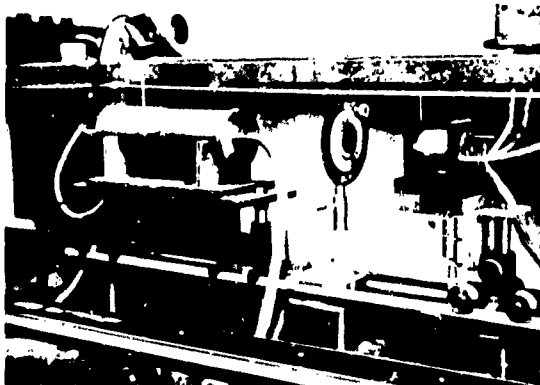


So you can see, this is typically 18th Century setup in the University, and the universities are poor. That's a laser which is using a helical flash tube and is capable of giving kilo-watts output. At that time we didn't have a ninety degree-ruby rod and, hence, to get linearly polarized output we had to use a polarizer. This is the initial quartz mount we had, and the major problem in building this amplifier (which probably took around three or four months) is getting the high input impedance and at the same time wide band and high sensitivity.

The quartz crystal itself has very high input impedance and very low capacitance, and anything you put into your detector from this side is going to be divided according to the ratio of the capacitances.

Input capacitance was a major problem to me, and so we had to devise a special setup which was balanced. All the components were built inside the unit. Incidentally, even though the DC polarization is caused by the same term as the second harmonic, there is actual power transfer to the second harmonic. By adjusting the phase conditions we could increase the output of the second harmonic. However, in the case of DC polarization there is no power transfer. All we see is a pulse in the condition of the field while being set up or decaying.

I have in the next slide the output that we got out of our system. May I have the next slide, please?



You see, this sensitivity here is a 50 microvolts per centimeter, and the noise of the amplifier itself was fifty microvolts per centimeter. We had a hard time in getting any decent output at all with this system here, and --

MODERATOR SOULES: Can you tell us what impedance you were able to achieve?

PROF. SUBRAMANIAN: The input impedance of the detector was ten megohms with, if I remember right, about eight or nine picofarads.

MODERATOR SOULES: Could this be improved considerably with the now-a-days transistors?

PROF. SUBRAMANIAN: Probably not as much as the ones we built recently. This is using RCA nuvistor tubes.

MODERATOR SOULES: The field effect transistor has a fraction of the picofarads onto ten to fifteen megohms, that's why I wondered.

PROF. SUBRAMANIAN: You can't go too high in impedance. In that case, we can use an electrometer amplifier.

MODERATOR SOULES: This is a relatively high band. Good.

PROF. SUBRAMANIAN: We can see clearly here that for a ninety degree rotation the DC polarization goes from a negative value to a positive value. I also have a curve which was presented at the laser conference which shows the linearity of the power content of the beam with respect to the DC polarization.

By the way, that was assuming a circular beam which is very normal in the case of most of the ruby lasers. The DC polarization is only a function of the beam intensity and not a function of the diameter. There is normally the divergence of the beam and one of the major worries is whether this would affect the reading that we would get, and in doing some specific experiments with defocusing and focusing the beam, we found that there was absolutely no difference at all in the output, which confirmed the first order analysis that I made on this system.

The next point that I wanted to investigate was if to increase the DC polarization output by using high power laser beam and observe the spiking phenomenon. Other people have looked into the spiking phenomenon in the second harmonic with respect to the fundamental, and I wanted to do a similar experiment with the DC polarization and see what kind of correlation exists between the fundamental and DC. And to achieve this goal, since I didn't have money to buy a new laser which costs about \$25,000.00, I built a laser myself, and this was almost a six months project in building the laser.

The major difference in the laser that I built from that of the commercial lasers is that I used two linear flash tubes connected in series in a double elliptical cavity instead of in parallel, which is the common way you would have seen in all the commercial lasers. The reason for doing it is that it turned out to be economical, and efficient.

I wasn't sure, initially that this would be the case. Hence, I made some preliminary experiments and it showed that I wouldn't be at any disadvantage, and so we went ahead and built a laser which is giving more than a hundred joules output.

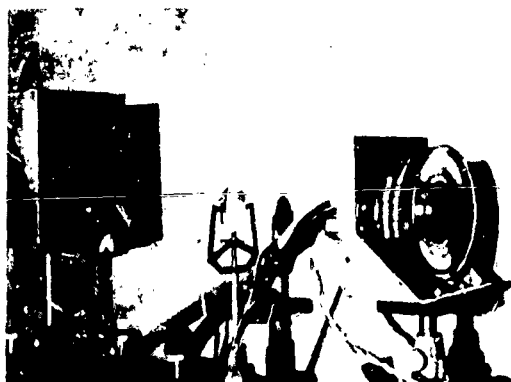
I am still not operating at the peak output that it can give. I think it will give around 200 joules maximum. The period of the pulse would be somewhere in the order of 600 microseconds.

We finished building this laser last summer, and we have been operating continuously so far, and we have not had any bad luck at all with the laser, so essentially we can probably build much cheaper lasers now, high powered lasers, with this technique available.

Of course, we have, now, less stringent restriction as far as building the amplifier is concerned, since we have a higher output of the laser available. So I went ahead and build a new amplifier using RCA nuvistor tubes. Essentially it's a difference amplifier at the input stage.

Now, in the previous case there was no gain at all in the system, whereas now in the new amplifier we have a gain of twenty. The new set up now makes possible for us to observe the spikings.

May I have the next slide?

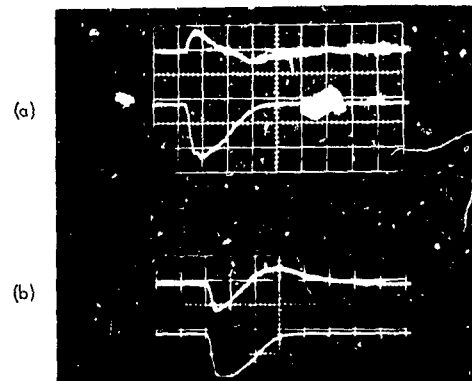


That's the new setup we have, and I should also warn you of the fact that these are all raw. It took a while for us to get this amplifier built, and it was done only about a week or ten days ago, so you see the amplifier is built in a coffee can still in its preliminary condition, with seven nuvistor tubes. This is the laser we have which is capable of giving 400 joules. There is still the problem of the beam diameter (the ruby diameter is 5/8 of an inch). When it comes out, even though the crystal that I am using, is two centimeter in diameter, I have the problem of the beam hitting the plate, so I have to use the lens to contain the beam within the crystal to reduce the noise pickups. The results are shown on the next slide.

See, now, we are having a very high output with very less noise here.

I should have explained what these two curves are. The bottom one actually represents the output from a photo-tube. That shows the laser pulse. This is the laser pulse now, and this is the DC polarization pulse

that we see, and there is a residual effect which I am not positive whether it is due to overshoot or due to the pyroelectric effect. There is remnant pyro effects still present, but we can see that this noise level is considerably reduced.

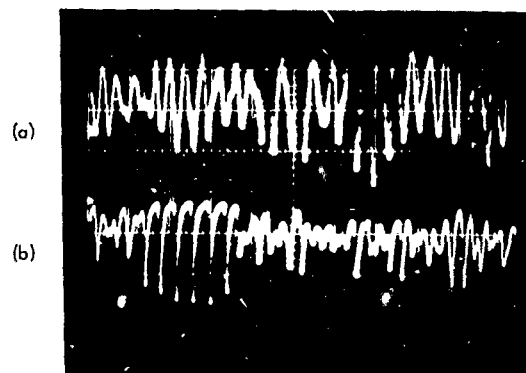


The sensitivity of this scale is two milli-volts per centimeter, so we have a very efficient system of measuring the DC polarization.

The technique being more perfect, we get a large signal on the DC polarization, and so the next logical step is to try to see whether the spiking phenomena can be observed in the DC polarization.

MODERATOR SOULES: Are those two ninety degrees out of phase?

PROF. SUBRAMANIAN: Yes, they are ninety degrees out of phase. This is the spiking on the laser pulse you see on the bottom trace, and the spiking that we see on the upper trace is due to the DC polarization.



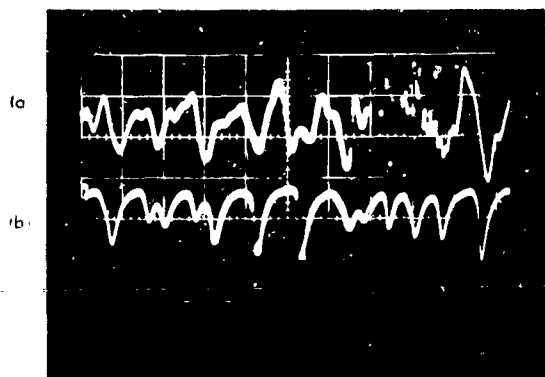
You can see that the bandwidth of the amplifier is limited, so you don't get the correct spikings from the DC polarization. They are kind of rounded off.

In all these cases, (even though the comments I make are not conclusive now), as it is, we don't see any correlation between the two. We see in this region there seems to be a correlation, but in those regions actually here we have the maximum coming in unless there is some noise that is actually introduced, but corresponding to these levels here, power output of the laser is very small as apparently there is no correlation.

I have a few more pictures that I have taken. These were all taken only during one day, and as somebody else was saying, laser went kaput. So far, one of the major problems of the laser that we have come across (twice) is the burning of the coil.

Actually, it's not the coil itself that gets burnt, but it's the connection to the coil because of the large amount of (about three thousand amperes) current flowing through that for each shot. This is a very minor problem as far as the operation of the laser is concerned.

The next slide shows actually the same kind of picture with one micro-second time scale. We see actually the laser pulse spiking process corresponds to approximately one micro-second which is what people have observed earlier.



Again, the correlation is not too rigorous between the two pulses, but I have to do more experiment on this. In fact, if we go ahead and do this with a high power laser and with a crystal which has high nonlinear coefficient, we should expect better results.

MODFRATOR SOULES: What is the time constant of the pyroelectric effect? Does it follow these rapid changes?

PROF. SUBRAMANIAN: No. The rise time seems to be almost following the pulse, but the falling time seems to be very slow. In fact, even in this I think there is still a little bit of pyroelectric effect which I can show by the slide which is showing the two pulses, the positive and negative.

See (ref. slide 5), in the first slide the two peaks, that is, the peak and this peak actually corresponded when I did the initial experiment, but in this high powered laser, you see, it is not actually closely followed. There is a little bit of lag which I think is due to pyroelectric effect, this is the laser pulse here, whereas the pyroelectric pulse here occurs this way. There is a lag on the DC pulse which may be due to that pyroelectric effect which still has to be investigated and that's about the progress we have achieved in this DC polarization so far.

I think I will talk about our efforts on the subharmonic project. In the meantime, if anybody has any question on this, I will be glad to answer it.

MR. WHITE: What did you decide finally about the feasibility of a power meter, using the DC polarization?

PROF. SUBRAMANIAN: If you want to observe this spikings in the power, then I am not sure that we can use it, but if you are interested only in following the envelope of the pulse in the high power laser (anything above fifty joules seems to be a very nice figure to use on this) then you can very definitely follow it.

One of the configurations I used in the earlier setup was to actually put in some numbers on this. Without making any approximations, I put in the electrodes exactly corresponding to equipotential lines, which simplified the problem very much. You can actually build a power meter using this idea.

On the subharmonic generation, people have already talked about this, (starting from Bloembergen and Armstrong's article). Franklin also put forth a traveling wave mode of parametric subharmonic generation, and I think he came up with a number of twenty thousand centimeters for using a power of ten kilowatts, and a nonlinear coefficient of the order of ten ESU.

This doesn't seem to be practical. However, Kingston came up with the idea that you can use a cavity mode and this increases efficiency much higher, and in fact some of his ideas have just come out in the latest January issue of the proceedings of the I. E. E. E., where he comes out with a number of two hundred kilowatts. If you have a two hundred kilowatt pulse of laser, then you can actually build a subharmonic generator.

However, until today, nobody has come out with a device that produces a subharmonic generation.

I have been thinking about this for the past four months or so, and I am trying to approach this subject from a slightly different viewpoint.

The point that I am taking actually is an extension of the circuitry concept that people have extensively worked out in detail as far as generating parametric subharmonics at circuitry frequencies. The basic difference between the two methods is that one considers the transfer of power from the fundamental to the subharmonic by harmonic balancing scheme, (that is, the total power constant, and certain power is transferred to the subharmonic) whereas in the case of the other approach (which is dealt mainly by mathematical formulation), a resonant circuit at some frequency ω connected to a variable capacitor which has a frequency of 2ω . Unfortunately I don't have any slides on this and so I will describe it for on the blackboard.

$$\begin{array}{|c|c|c|} \hline \text{---} & \text{---} & \text{---} \\ \hline \end{array} \Delta C \cos \omega t$$

If you have a tank circuit with a certain loss element G , and connect across this a capacitor ΔC that is driven at $\cos 2\omega t$ where $\omega = \frac{1}{LC}$. Then, under

certain conditions you can observe the system to be unstable and subharmonic to be developed.

The way to analyze this is to write the equation for this system in terms of charge.

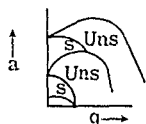
$$\frac{d^2 Q}{dt^2} + \frac{G_e}{C} \frac{dQ}{dt} + \omega^2 \left(1 - \frac{\Delta C}{C_0} \cos 2\omega t\right) = 0$$

We can make some substitutions in this equation and reduce this equation to a set of Mathieu's equations. The Mathieu's equation would be of the form

$$\frac{d^2 U}{dT^2} + (a - 2q \cos 2\omega t) U = 0$$

The details on this can be found out from the book by Chang on "Parametric and Tunnel Diodes."

If you plot the stability diagram for this with the axes as q and a , then we get the figure



something of this form where these correspond to the stable region, and this corresponds to the unstable region. It has been observed that a large amount of power can be transferred from the fundamental to the subharmonic at the circuit frequency.

Now, the question is whether such a system could be used, applying this concept to the light frequency. At optical frequencies, we have the same sort of system wherein we are changing the dielectric constant with the radiation field and hence, we should get the same sort of behavior. If we could also analyze this from the quantum mechanical concept.

The phenomenon of the interaction of radiation with the nonlinear dielectric medium will be illustrated by considering a one-dimensional anharmonic oscillator that is subjected to the forcing field caused by the radiation. In the absence of radiation, the Hamiltonian of the system is of the form²

$$H = \frac{p^2}{2m} + m\omega_0^2 x^2 - \frac{1}{3} \lambda x^3 - \frac{1}{4} \eta x^4 \quad (1)$$

where m is the mass, p the momentum of the particle, λ and η constants of the system, and x is the displacement of the particle from its equilibrium position. In the electric dipole approximation, the interaction of the system with radiation is

$$H_{int} = exE_0 \cos(2\omega t + \phi) \quad (2)$$

where e is the electronic charge and $E_0 \cos(2\omega t + \phi)$ is the incident monochromatic radiation. From Eqs (1) and (2) the equation of motion, including a dissipative term, for the system can be written, which will assume a general form as below

$$\frac{d^2 x}{dt^2} + \alpha \frac{dx}{dt} + \beta x + \gamma x^2 + \delta x^3 = B \cos 2\omega t \quad (3)$$

Following the procedure of Hayashi³, we can transform Eq. (3) into the form

$$\frac{d^2 \xi}{dt^2} + \alpha \frac{d\xi}{dt} + 3x^2 \xi = 0 \quad (4)$$

Letting $\xi = e^{-\epsilon t} U(t)$, and assuming a solution of the form

$$x(t) = x_0 + k_1 \sin \omega t + k_2 \cos \omega t + k_3 \cos 2\omega t \quad (5)$$

we can obtain from Eq. (4) the following Mathieu equation

$$\frac{d^2 U}{dT^2} + \left[\theta_0 + 2 \sum_{\nu=1}^4 \theta_{\nu} \cos(\nu \omega t - \delta_{\nu}) \right] U = 0 \quad (6)$$

This is exactly the same type of equation that we saw earlier (equation), and here we can put in the various values that we have, and this would give exactly identically. So, the idea that I am thinking of is if there is going to be a good transfer of power in the case of circuit relationships in terms of transferring from the fundamental to the subharmonic, then we could approach the subject exactly in an identical manner and get some results also using this approach, instead of using the harmonic balance approach.

So, the work on this is based on the approach that I have given, and we have also set up the initial experiment, I think, that is shown in the next slide. I have two slides on this.



This is the laser we have, and it's interesting to also mention here that this was taken with no external lights at all, and just by firing the laser so the external lights for taking the exposure was given automatically by the laser light, so you can see the intensity of the laser pulse in here.

It was also interesting because people have tried very hard to take pictures of the lasers.

You can see the beam coming, and this is a glycerine tank we have for filtering out any infra-red that comes out of the laser originally, and I think in the next slide the system is shown very clearly.

This is the laser, that we built, and you can see the size of reduction in this compared to all the commercial lasers. A commercial laser would probably fill up half the room with capacitor banks, whereas all the capacitor banks and circuits, everything, are in there, and there is the laser cavity. Incidentally, there is a trick in building a laser cavity, if anybody is interested.

For infra-red furnaces, they build cavity by extrusion process and you can get it at six dollars per inch. It cost us a thousand dollars, including all the crystal and flash tubes as compared to the ten thousand dollars that you would pay in the market. (I may be killing somebody's business!)

There is the crystal mount. I am using the same crystal mount that I had for the DC polarization, even though I don't need these cables.

Here is the detector. One of the major problems that one encounters in this measurement is to filter out the hundred joule laser pulse from entering the infra red detector. We have one of the best and cheapest ways of doing this, to use a silicon crystal. It seems to be a very efficient system, even though still we have some problems in terms of defocusing, etc.

We also don't want any of the infrared, that is, coming out of the laser to enter the infrared detector. A glycerine solution would be useful for this purpose. We are now taking the bugs out of the detector. We haven't done any actual experiment to see whether we can observe any subharmonic or not, and that's about all of the problem in the subharmonic generation.

MODERATOR SOULES: Any questions or comments?

PROF. SCHAWLOW: Where do you get your reflectors?

PROF. SUBRAMANIAN: Reflectors? Which ones?

PROF. SCHAWLOW: The elliptical, double ellipses.

PROF. SUBRAMANIAN: There is a company in Minnesota who distributes this. It's some research corporation. I can give you the name.

PROF. DAW: Did you polish the interior of the cavity?

PROF. SUBRAMANIAN: You can buff it, that is all, the best you can do. Actually, you lose a certain amount of efficiency in this, but I think the reflections of the aluminum is to the order, this is an aluminum cavity, is about seventy percent, also at the frequency of 4100 angstroms, whereas the silver cavity you can get a ninety percent, so you would lose a certain amount of efficiency, but the cost is well worth it.

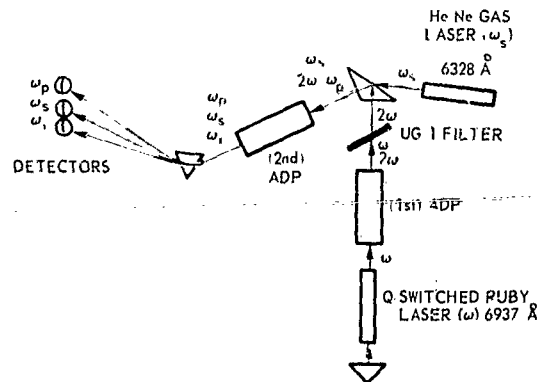
MODERATOR SOULES: Dr. Charles Wang, of the Philco Applied Research Lab at Blue Bell, Pennsylvania, would like to make some comments on this area.

DR. WANG. I understand it is lunch time, so I will only spend a few minutes to describe some progress that we have made in attempting to observe optical parametric interaction, specifically the parametric amplification and the difference frequency generation.

The parametric amplification that I am talking about here is a little different from what you would encounter in the case of Raman amplification. There you have second order resonance. The thing I have here is off resonance.

I don't have. I suppose, to review the theory of parametric amplification, particularly after both Professor Shen and Professor Subramaniam have discussed that in length.

If I could have the first slide. This is the experimental setup that we have for the observation of this parametric interaction. It is essentially the interaction between two light beams generated by two separate sources, and the idea is, in using layman's language, to use a blue beam to amplify a red beam; this understandably is possible if the blue beam is strong enough.



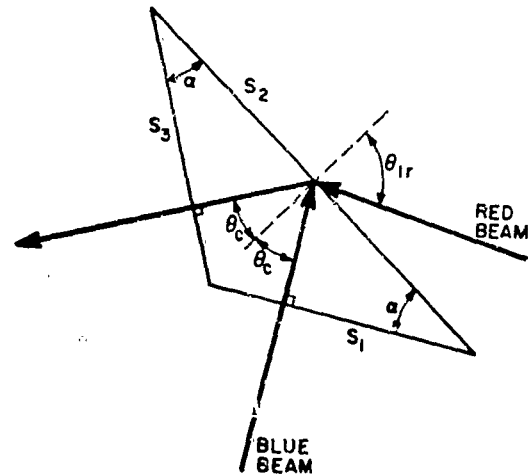
So what we have then, we use a Q-switched ruby laser which generates about thirty megawatts to the best of our estimate, in a time of about thirty nanoseconds, and this output goes into a piece of ADP crystal about eight centimeters long.

The ruby laser beam passes through the ADP crystal in a parallel beam geometry, that is, without focus. At the output we observe the second harmonic of the ruby source, as well as the ruby radiation itself. This, of course, is done at the index matching direction; and the angular dependence of second harmonic generation, using this parallel beam geometry, is about five minutes half width. We found this is primarily due to the divergence of the ruby beam itself, because if you use the index data of ADP, you will find that the width of the angular dependence should be something like four seconds of arc instead of the five minutes which we obtained.

The maximum second harmonic we have obtained to date is something like three megawatts from a thirty megawatt at the fundamental frequency. This is

something like ten percent instead of twenty percent that a lot of people claim that they have been able to achieve.

We have, then, the second harmonic generated this way pass through a UG-1 filter which takes off the ω (beam), but passes 2ω (beam). The 2ω passes through a calcite prism which is shown over here to have the 2ω (beam) colinearized with the so-called signal beam, (if I may use the terminology of parametric amplification here) which is obtained from a gas laser operating at a 6328 Å. At the moment, -- may I have the second slide?



The second slide here shows a little bit more clearly how the two beams can be combined without the use of dielectric coated dichroic mirrors.

We initially were using that, and it turned out that each mirror could stand only one shot, and it was too expensive to do it that way.

The way we have been doing it successfully now is to use a calcite prism, and having the optic axis perpendicular to the plane there so that you can make use of the birefringence and as a result the blue beam will undergo total reflection at the back face, whereas the red beam goes into the calcite prism at that face and it comes out parallel to the blue beam.

This is done. The red beam, it turns out, can be made parallel to the blue beam with about eighty percent transmission from one side of the prism to the other side of the prism.

May I now have that first slide, again? Back to the first slide, now. We have the two beams made parallel. This is assured by observing the burn spots due to the 2ω beam on a piece of polaroid film and spaced over two meters away to be sure that the two beams are aligned.

This way the alignment was made to be about two or three minutes of arc. Incidentally, this is bigger than the beam divergence that we have at the 2ω beam.

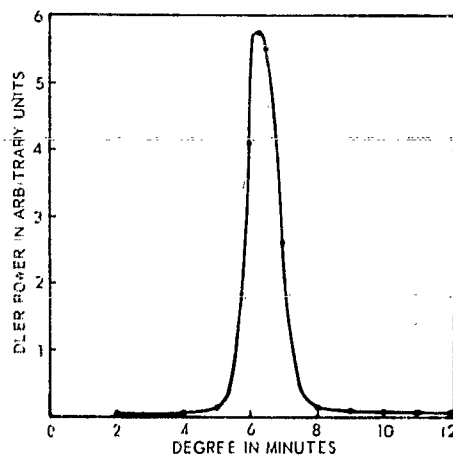
The 2ω beam which is shown here at the second ADP crystal, has a intensity of about three megawatt per square centimeter. We estimate that this is about

the intensity you need in order to get a 3 db gain for the signal. 3 db means that you have one photon in and two photons out. After we pass through the second ADP, we have the pump light beam, we have the signal light beam, and also as a result of this parametric interaction you will have a difference frequency; for our choice this difference is at 7600 Å. At this point, of course, the problem is to tell whether or not you have observed, whether or not you really have had any amplification.

In the second ADP, the problem here is complicated, and if I may go back to the beginning here again, the problems associated with this kind of experiment essentially are the following: (1) you need high enough power; (2) you have to align the two beams to a decent degree of accuracy; and (3) the problem of detection.

I presume most of you gentlemen here are familiar with nonlinear optical phenomena. Essentially all glass filters fluoresce, either because of multiphoton absorption, or simply because of the UV radiation at 2 ω frequency, so that the way to get rid of this is to use a glass prism to disperse the beams out, and to detect them at a distance about sixteen meters away from the second ADP.

The next slide shows the difference frequency that we observed in this experimental arrangement, as you can see here the difference frequency has an angular dependence of about one and half minutes of arc.



This is achieved, again, under parallel beam geometry, and the maximum you can get is at a direction that corresponds to phase matching; and phase matching direction for this particular process is twelve minutes away from the direction corresponding to maximum second harmonic generation; this we calculated to be about fourteen minutes of arc from the second harmonic generation.

In view of the fact that we have two or three minutes of arc uncertainty in alignment, this should be regarded as a good agreement. The maximum difference frequency we have generated this way is about 1.2 milliwatt when we have the pump beam at about three megawatt per square centimeter, and the signal beam at 6328 Å about eight milliwatts.

This is about an order of magnitude below what we would expect, say, in using the nonlinear susceptibility equal to 3×10^{-9} esu, and this I suppose is again due to the multi-mode effect which I believe is actually the subject for the Harvard theoreticians to work on. This is all.

MODERATOR SOULES: Any questions?

PROF. SHEN: May I comment that the parametric amplification is exactly the same as Raman amplification, only the difference is optical and you don't have to worry about the phase matching, I mean the Raman effect, since the dispersion is a straight line, is a constant frequency ω .

MODERATOR SOULES: May I ask, did you get three db gain?

DR. WANG: No, we did not get 3 db gain. I was saying it was down by about an order of magnitude from what I expected. What we observed was that with a three megawatt per square centimeter and eight milliwatt at the signal, the difference is about 1.2 milliwatts. This corresponds to about 117 percent out and 100 percent in at the signal. In terms of db, this is about one db.

Someone asked if we have really seen anything at a signal frequency. Yes, we have, because of the full saturation, due to the DC component we could not really tell just exactly how much we have, but I can show you what we observed on the oscilloscope where we have a pulse on the signal channel although we have only DC signal goes in. This occurred only during the time of giant pulse when you see any different signal generated, and the signal channel shows nothing unless you have amplification, because amplification shows up as pulse and we did see a little pulse here under, as I said, the saturated condition of the photomultiplier.

DR. QUELLE: Shouldn't you be able to look at the idler frequency and tell exactly how much conversion you have?

DR. WANG: This is what we did, but some people were more interested in knowing if we did see a little more photons at the signal in addition to the evidence that you get by observing the idler frequency.

Session III Moderator: F. T. Byrne, ONR

Part 1 Gas Breakdown

Tuesday Afternoon
23 March 1965

Haught	United Aircraft Corp.
Phelps	Westinghouse

DR. BYRNE: The first subject this afternoon is gas breakdown. To start off this part of the program we have Dr. Haught from the United Aircraft Corporation.

DR. ALAN HAUGHT: At the United Aircraft Corporation Research Laboratories we have been involved, for the past two years, in an experimental study of the ionization of gases by the focused high-intensity beam of a giant pulse laser -- a research program supported in part by Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense. In Figure 1 is shown a picture of the breakdown phenomena observed. The laser light in the picture is incident from the left and focused by the lens. At the lens focal point, breakdown of the test gas is observed for suitable conditions of laser beam power and gas pressure.

PROF. SCHAWLOW: What is the lens focal length?

DR. HAUGHT: In this case, approximately 3 cm. The breakdown shown here is occurring in air. You will notice a rather characteristic shape of the breakdown region, blunted on the end toward and lobed on the end away from the incident laser beam. This shape is a consistent one for breakdowns produced by focused high-intensity radiation and as yet is one for which there is no adequate explanation. There is undoubtedly some very interesting fluid dynamics associated with the development of this characteristic shape; however, our attention on the gas breakdown problem has been directed toward an understanding of the development of ionization in the breakdown.

In Figure 2 is shown a schematic diagram of the apparatus used for studying the breakdown. A giant pulse ruby laser system is used as the light source in these studies, and both flat-ended and Brewster-angled ruby rod configurations have been employed. With either configuration the giant pulse laser output was of the order of 30 M watts peak power with approximately a 30 nsec duration. In the diagram, the laser light is incident from the left on the focusing lens which forms one window of a test cell containing the gas under study. The test cell was designed for both vacuum and high-pressure use and permits the study of a variety of gases under high-purity conditions at pressures up to 2000 psi. A set of charge collection electrodes are located within the test cell for measurements of the ionization produced in the breakdown, and aperture windows were provided to permit observation of the breakdown luminosity.

Observations of the breakdown luminosity were carried out, and it was established that the breakdown light was not scattered radiation from the incident giant pulse. In the first place, the breakdown luminosity is readily observed through the laser protective goggles which are specifically designed to exclude the incident laser radiation. In addition, it was observed that the breakdown luminosity lasts for a time long compared with the duration of the incident laser pulse. Shown in Figure 3 is a dual trace record of the laser giant pulse and breakdown luminosity. The laser giant pulse lasts approximately 30 nsec, while the breakdown luminosity is present for some 600 nsec.

The pair of charge collection electrodes described previously were placed on either side of the lens focal point and used to determine that electrical breakdown, that is the production of ion pairs, was achieved. The electrical circuit associated with these electrodes is shown in Figure 4. The breakdown was formed between the electrodes and both the instantaneous current and the total charge collected were measured. About one half of the total charge was collected very quickly over a time of about $.5 \mu$ sec, resulting in a current of approximately 5 amps through the circuit. The remainder of the charge collected was received over a very much longer time interval.

To compare the phenomena observed here with existing theories of the electrical breakdown in gases, measurements have been made of the optical frequency electric field required for breakdown as a function of pressure for a number of gases. The electric field strength at the point of breakdown was determined from calorimetric measurements of the energy in the giant laser pulse, the time duration of the pulse obtained from photodiode measurements, and the diameter of the focused beam. For a typical case, the energy of the giant pulse is one joule and its duration is 30 nsec, giving a peak power in the incident beam of 30 Mwatts. The diameter of the focus point has been obtained by three techniques: measurement of the hole size produced in extremely thin metal foils by the focused laser beam, the product of the measured laser beam divergence and lens focal length, and ray-tracing through the focusing lens.

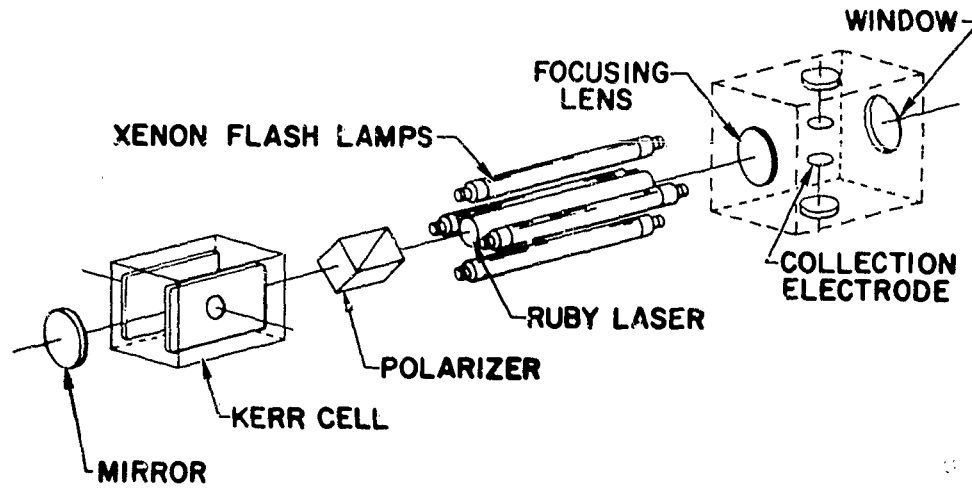
The first of these techniques involves the burning of a hole in an extremely thin metal foil by the focused laser beam. The incident beam is first attenuated to the point that the beam intensity is just below the threshold of damage for the foil used. By then removing an attenuation of 50% from the beam, the signal at every point is doubled and the half power point of the incident focused beam will be at the threshold of damage of the foil. The diameter of the damaged foil area is then the diameter at half power of the focused laser beam. The focal diameter is determined by this technique is approximately 0.2 mm, which, it should be noted, is much larger than the diffraction limit for the beam diameter and lens focal length used.

The laser beam output in the giant pulse mode is not fully collimated but, in fact, has a small divergence. From geometric optics, a lens will focus this slightly divergent beam to a focal diameter given by the product of the lens focal length and the angle of divergence. The divergence is first determined from the diameter of the focal spot produced with an extremely long focal length lens. From the laser beam divergence and the focal length of the lens used in the breakdown experiments, a focal spot size of 0.18 mm is obtained, a result in substantial agreement with that determined from the thin foil experiments previously described.

Evaluation of the focal spot size by ray-tracing the slightly divergent laser beam through the particular lens configuration used in these experiments gave a focal spot size of 0.17 mm, in good agreement with those determined from the hole burning and focal length divergence techniques.



Q - SPOILED LASER SYSTEM



LASER
GIANT PULSE

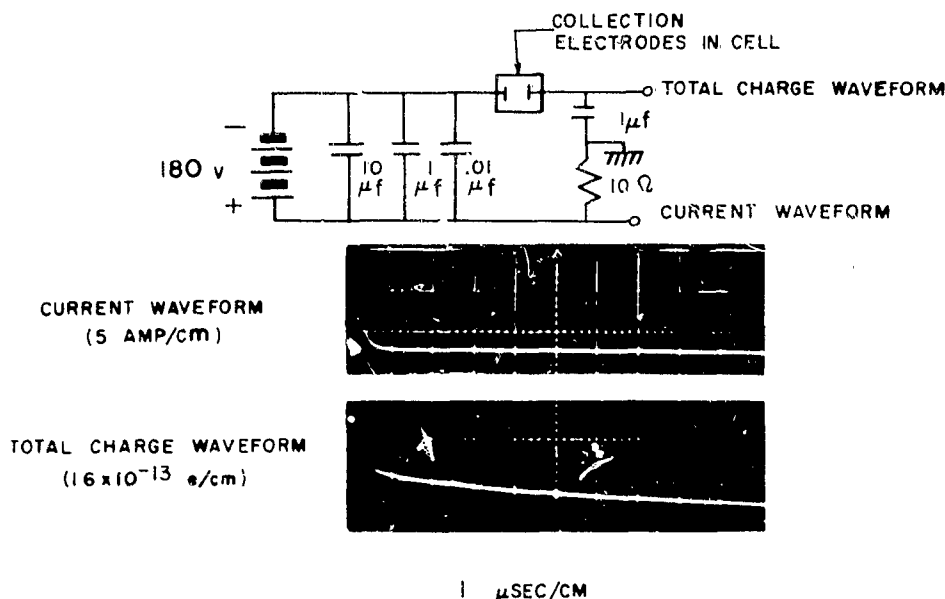


BREAKDOWN
LUMINOSITY



200 nsec/cm

CHARGE PRODUCTION IN BREAKDOWN



Using these focal spot size measurements, the giant pulse time history, and the laser energy required for breakdown, the breakdown threshold electric field strength was determined for a number of gases over the pressure range from one atmosphere to 2000 psi. The data obtained are presented in Figure 5. The values plotted in the slide are threshold electric field strengths; i. e., for a given gas if the electric field strength and pressure lie below the curve breakdown does not occur, and for field strengths and pressures which lie above the curve breakdown is observed.

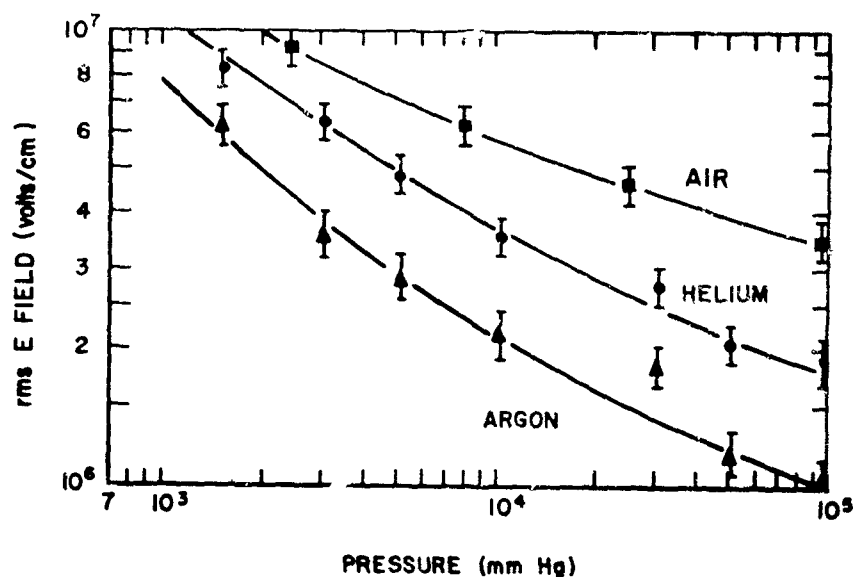
Shown in Figure 5 are the threshold electric field strengths required for breakdown in argon, helium, and air. In all cases, the breakdown threshold electric field decreases with pressure approximately as one over the square root of the pressure. Of the gases studied, argon requires the lowest electric field for breakdown at a given pressure. Helium, which has an ionization potential somewhat greater than that of argon, requires a higher threshold electric field for breakdown. The constituents of air have ionization potentials comparable with that of argon, and yet the electric field required for breakdown in air is substantially higher even than that for helium, indicating that the molecular gases of which air is composed have energy loss mechanisms in addition to those associated with the inert gases.

During the experiments on gas breakdown, it was observed that the incident radiation as it passed through the breakdown region was attenuated by the plasma formed at the lens focus. The apparatus used for these attenuation measurements is shown in Figure 6. Two photomultipliers (A and B) monitor the radiation both before (A) and after (B) it has passed through the breakdown plasma. A partially reflecting glass plate

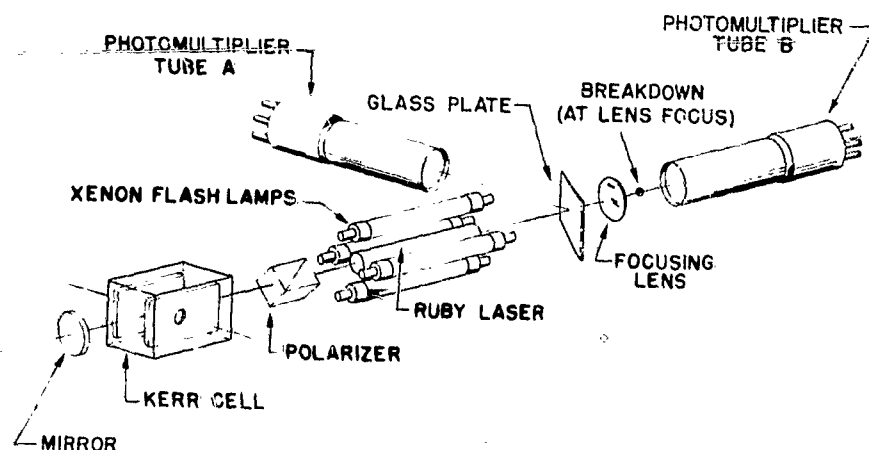
is used to divert a small fraction of the incident laser beam onto photomultiplier A, which is used to observe the wave shape of the incident laser radiation. With both photomultipliers filtered so that they are sensitive only to the 6943 Å ruby laser light, it is observed that when breakdown occurs the transmitted laser radiation is severely attenuated during the later portions of the laser optical pulse. A double exposure of the transmitted laser radiation with and without breakdown is shown in Figure 7. When no breakdown occurs the transmitted light has the time history of the upper trace and is identical to the wave shape observed by the monitor photomultiplier A. When breakdown does occur the laser beam is significantly attenuated, as shown in the lower trace. For these experiments, the beam power is slightly above the breakdown threshold for the argon test gas, and over one half of the one-joule incident optical energy is removed from the transmitted beam. At times shortly after the initiation of the breakdown, approximately 90% of the incident radiation is being withdrawn from the transmitted beam by the plasma.

It is possible that the energy withdrawn from the transmitted beam could be scattered by the breakdown plasma or reradiated at wave lengths other than the ruby radiation. If the radiation were scattered at the ruby laser frequency, this radiation should be observed at angles other than those of the cone of the transmitted radiation. A series of photomultiplier measurements have been carried out covering the entire solid angle subtended by the breakdown region. It was observed that increased scattering of the 6943 Å ruby laser radiation was present when breakdown occurred. However, even integrating over the total solid angle, it was found that the increased scattering was negligible compared with the one-half joule of energy removed from the incident laser beam.

BREAKDOWN FIELD STRENGTH AS A FUNCTION OF PRESSURE



ATTENUATION BY BREAKDOWN PLASMA

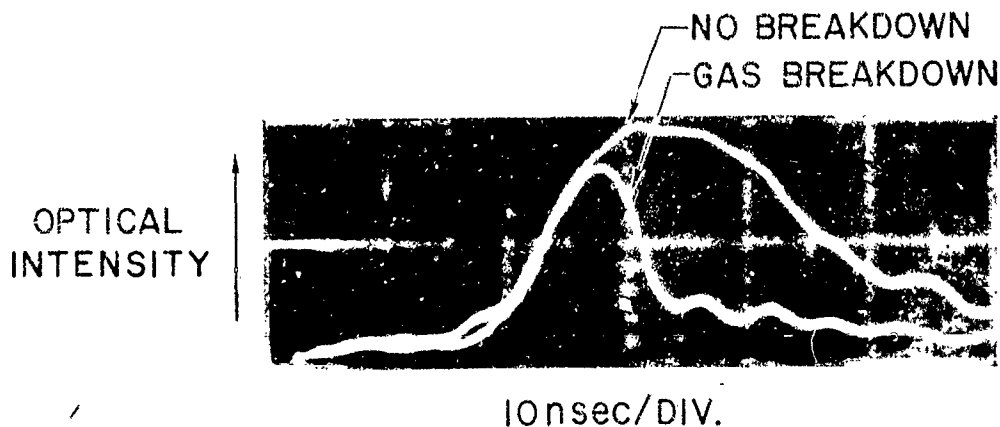


If the energy lost from the laser beam were absorbed in the plasma, this absorption should be observable as a temperature and pressure rise in a fixed volume test gas. To test for such an absorption, the breakdown was produced within a small, closed cell connected to a sensitive pressure transducer as shown in Figure 8. Operating just below the breakdown threshold, no breakdown was formed and no pressure change within the cell was observed. When the incident laser beam power was increased just slightly above threshold, breakdown was observed and a 2 psi pressure rise was measured. This pressure rise in a cell volume of 23 cm^3 corresponds to an energy increase of the gas within the test cell of approximately

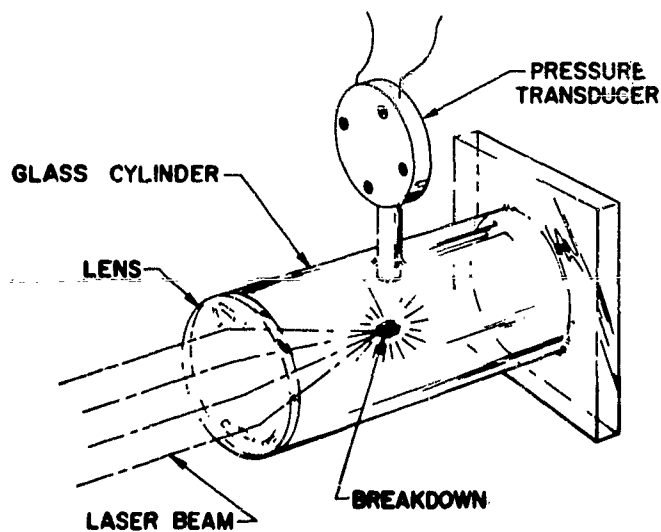
one-third of a joule, and this, within the accuracy of the experiments, is the amount of energy withdrawn from the incident beam by the breakdown plasma.

A number of mechanisms, shown in Figure 9, have been offered in the past to explain electrical breakdown in gases. Over the range of pressures studied in our experiments, the breakdown field strength ranges from 10^6 to 10^7 V/cm or less than 0.1 volt across the dimensions of an atom. This field strength is less by about two orders of magnitude than the 10 eV required for the ionization of a typical atom, and, therefore, direct electric field stripping of an electron from an atom is not likely to be a significant process in the

ATTENUATION OF LASER BEAM



BREAKDOWN IN CLOSED VOLUME



development of optical frequency breakdown. Simple calculations using the cross section for Compton scattering and the energy transfer in a Compton collision show that the energy transferred to the gas by this process is negligible compared with that required to explain either the development of the breakdown or the attenuation of the incident laser beam. Direct photoionization of the gas atoms by the incident radiation is not possible, since the laser photon energy is only 1.78 eV and gases with ionization potentials ranging from 10 to 24 eV have been successfully ionized by the laser beam. There does exist the possibility of multiple photon absorption. A consideration of this process will show, however, that straight forward multiple photon absorption will not account for the phenomena observed. The atoms in the gas are initially in the ground state. Upon absorbing a photon, the bound electron of the atom is raised to a virtual state which persists for a time interval of the order of 10^{-12} to 10^{-13} seconds. During this time, there is a finite probability that a second photon will be absorbed,

POSSIBLE BREAKDOWN MECHANISMS AT OPTICAL FREQUENCIES

DIRECT ELECTRIC FIELD STRIPPING
COMPTON SCATTERING
PHOTOIONIZATION
MULTIPLE PHOTON ABSORPTION
MICROWAVE BREAKDOWN THEORY
INVERSE BREMSSTRAHLUNG

raising the electron to a still higher virtual state. By a succession of such absorptions, the electron could reach the first excited state from which, by further multiple photon absorptions or photoionization to higher energy levels, the ionized state is eventually reached. However, to reach even the lowest lying levels of argon and helium would require, respectively, 7 and 12 successive photon absorptions. Assuming even a 10% probability for each absorption process, this would imply a 10^5 order difference between the intensities of the laser radiation required for breakdown in argon and helium. The experimentally observed ratio of laser beam intensities is only a factor of three, and, on this basis, the simple multiple photon absorption processes described here will not account for the development of optical frequency breakdown. Note added in proof: Tozer in a recent article (Phys. Rev., Vol. 137, March 15, 1965) discusses a multiphoton absorption theory in which account is made of statistical fluctuations of the irradiating beam photon density. Tozer predicts a focal volume dependence of the breakdown threshold which varies as $V^{-1/2N}$, where N is the number of photons required to raise the atom to its first excited state. For argon, N is 7, giving a predicted focal volume dependence of $E \propto V^{-0.07}$ while, as will be described, a volume dependence of $E \propto V^{-0.2}$ was obtained experimentally. From this lack of agreement, it would appear that multiphoton processes are not the rate limiting step in the development of optical frequency breakdown.

Cascade theories have been developed to explain gas breakdown at microwave frequencies and employed by some to explain the optical frequency breakdown. As will be discussed, however, the microwave and optical frequency regimes lead to entirely different pictures of the breakdown process, and it will be of importance to examine both in detail so as to demonstrate their differences. In the microwave case, free electrons gain energy from the applied electromagnetic field as a result of collisions between the electrons and the atoms or ions of the breakdown gas. For an applied oscillatory electric field of amplitude, E , the periodic force on an electron will be of the order of E times the charge of the electron. The resulting acceleration of the electron will then be of order $\frac{Ee}{m}$, where m is the electron mass. At low pressures where the collision frequency of the electrons in the gas, ν , is much less than the radian frequency of the applied field, this acceleration will be experienced by the electron for a time of the order of $1/\omega$ and results in an oscillatory component of the electron velocity of $\frac{Ee}{m\omega}$. The oscillatory energy of the electron is then $\Delta E = 1/2 m (\Delta v)^2 = 1/2 m \frac{E^2 e^2}{m^2 \omega^2}$. The oscillating electron will make

collisions with the background gas atoms, changing its phase with respect to the applied field. Such a collision randomizes the ordered oscillatory motion of the electrons, and, on the average, the electron gains an amount of energy equal to ΔE per collision. With ν collisions per second, the rate of power gain by the electrons is $\Delta E \nu$ or $P = 1/2 \frac{E^2 e^2}{2m\omega} 2\nu$. This result holds when the collision frequency is very much less than the radian frequency of the applied field, that is at low pressures. At microwave frequencies, it is possible to have a sufficiently high pressure in the gas that many collisions occur per oscillation of the electron. While the acceleration of the electron remains

as before, $\frac{Ee}{m}$, the electrons, making many collisions per cycle, experience this acceleration only for times of the order of the reciprocal of the collision frequency,

resulting in a Δv between collisions of $\frac{Ee}{m\nu}$. The energy

gain per collision is then of order $\Delta E = 1/2 m (\Delta v)^2 = 1/2 m \frac{E^2 e^2}{m^2 \nu^2}$. This energy is gained on the average

in every collision, and, with ν collisions per second, the rate of power gain by the electrons at high pressures where $\nu \gg \omega$ is $P = 1/2 \frac{E^2 e^2}{m \nu^2} \nu$. At microwave

frequencies then, if a given rate of power input is required for breakdown, the threshold electric field would vary inversely as the square root of the gas pressure at low pressures, and at high pressures the electric field breakdown threshold would vary directly as the square root of the gas pressure.

At optical frequencies, the interaction of the electron with the applied electromagnetic field is no longer simple, and the concept of an electron oscillating in response to the incident field is no longer valid. Under conditions appropriate for microwave breakdown, the oscillatory energy of the electron in the applied field corresponds to a kinetic energy of the order of 10^{-3} eV, while typical microwave photon energies are of the order of 10^{-5} to 10^{-6} eV. Thus, an electron oscillating in the electromagnetic field absorbs and emits many microwave quanta every cycle, and the motion of the electron may be considered to be classical. At optical frequencies, for the field strengths used in these experiments the oscillatory energy of the electron calculated classically is again of the order of 10^{-3} eV, but the photon energy in the case of a ruby laser is 1.78 eV. Therefore, the oscillatory energy of the electron is small compared to the photon energy, and one might expect that the motions of the electron and its subsequent interaction with atoms in the radiation field is governed by quantum effects.

During an atomic collision, an electron may emit a photon by the process of Bremsstrahlung. From detailed balance considerations, the reverse reaction, inverse Bremsstrahlung, must also exist in which a free electron gains energy by absorbing a photon from the radiation field during a collision with an atom. From a detailed calculation of the energy gained by free electrons in an applied electromagnetic field, including an appropriate balance between stimulated Bremsstrahlung and inverse Bremsstrahlung, a numerical result is obtained which is identical with the energy gain rate associated with the microwave picture at low pressures.

DR. SOULES: If you were to apply large dc magnetic fields into the region in which the breakdown occurs, wouldn't this rather directly sort out these two processes?

DR. HAUGHT: We have carried out experiments observing the breakdown thresholds in magnetic fields as high as 30,000 gauss and have found no effect on the breakdown threshold.

DR. SOULES: What happens in the microwave case?

DR. HAUGHT: I do not know. Perhaps Dr. Meyer and could comment on this.

DR. MEYERAND: To produce any appreciable effect, sufficiently high magnetic fields would be required that the gyro-frequency of the electrons becomes comparable to the radian frequency of the incident electromagnetic fields. Such fields would be of the order of hundreds of kilogauss. For lower magnetic fields and at gas pressures above atmospheric, the electron collision frequency is sufficiently high that the trajectories of the electrons are a series of straight lines and no magnetic field effect would be expected.

DR. HAUGHT: It should be pointed out that while the 30,000 gauss sounds like an extremely high magnetic field, it is, in fact, very nearly equal to the oscillating magnetic field associated with the focused optical radiation. An electron in a plane electromagnetic wave will interact primarily with the electric field of the applied radiation, and any interaction with the magnetic portion of the incident wave will be smaller than this by a factor of v/c , where v is the electron velocity. Thus, for electrons with energies even as high as 10 eV, the effect of a 30,000 gauss magnetic field is negligible compared with the electric field portion of the applied optical radiation.

DR. SOULES: My thought was that the application of a magnetic field would sort out or differentiate any microwave type interactions.

DR. HAUGHT: I do not think that with reasonable magnetic fields any such sorting out would occur; and, in fact, as will be discussed, such a differentiation is really not necessary.

DR. KIDDER: These two processes, microwave absorption and inverse Bremsstrahlung energy absorption are, I think, the same thing. I guess other people are going to say that. In fact, we have done free-free absorption calculations at optical frequency for helium, and the way we did it was to make use of very good elastic scattering calculations and use phase shift methods. Under certain conditions, it can be shown that a calculation of free-free absorption, which you call inverse Bremsstrahlung, at optical frequency amounts to a calculation of microwave absorption. There is a regime where they are essentially the same process.

DR. HAUGHT: They are indeed the same process. However, I think that it is important to draw a distinction between the picture of the two cases. At microwave frequencies one thinks of phase mixing collisions and physical oscillation of the electrons in the applied magnetic field. In the optical frequency case, one no longer considers the existence of such electron oscillations and the collisions themselves are viewed in an entirely different fashion. At low pressures and electron energies greater than the photon energy, the numerical results obtained are the same, and, under these circumstances, the physics involved in the microwave and optical frequency regimes are basically identical. However, the picture of the process in the two cases has relevance in considering the pressure dependence of the breakdown at optical frequencies for extremely high densities and also in determining whether or not a minimum in the breakdown threshold exists at optical frequencies as it does in the microwave case.

DR. MEYERAND: Should not the distinction between electron energies that are very low and those that are

much higher than the photon energy be emphasized. For electron energies below 1.7 eV, stimulated Bremsstrahlung emission of a ruby laser frequency photon is not possible; and, in this case, the energy absorption results differ considerably from those obtained from the microwave picture.

DR. HAUGHT: Such an effect will result in a rapid initial energy input to the electrons and lead to a faster early heating than would be expected on the basis of the microwave picture. In addition, with optical frequency incident radiation, rapid photoexcitation and eventually photoionization can occur once the electron reaches the first excited state of the atom. However, at microwave frequencies the gap between energy levels in the atom is very much larger than the microwave photon energy, and such rapid excitation and ionization does not occur. Here again is a distinct difference between the microwave and optical frequency regimes.

At microwave frequencies, the breakdown threshold electric field at low pressures varies as one over the square root of the gas pressure and at high pressures varies directly as the square root of pressure for a given rate of power input, assuming no loss processes. If diffusion losses are present, the breakdown threshold at low pressures decreases inversely as the pressure. At high pressures the major energy loss mechanism is that resulting from elastic collisions between the electrons and gas atoms and results in a threshold electric field which varies directly as the pressure. The decreasing breakdown threshold as a function of pressure at low gas densities, where $\nu \ll \omega$, coupled with the increasing pressure dependence of the threshold at high pressures, where $\nu \gg \omega$, results in a minimum in the electric field required for breakdown. The minimum occurs at the point where the collision frequency in the gas is equal to the radian frequency of the applied electromagnetic field. This condition extrapolated to the optical frequency gas would require a gas pressure of the order of 30,000 psi, substantially above the measurements which we have conducted to date.

As shown in Figure 5, at optical frequencies the breakdown threshold electric field varies approximately as one over the square root of the gas pressure, which would suggest that diffusion losses do not play a significant role in the development of optical frequency breakdown over the pressure regime of our studies. Experimental measurements have been made to test this conclusion, and it has been found that this is, in fact, not the case. The magnitude of any diffusion losses present will vary as the surface-to-volume ratio of the region in which the breakdown occurs and can be changed by varying the focal volume of the breakdown. In our experiments, the focal volume within which the breakdown is formed has been varied and the breakdown threshold electric field strengths examined as a function of the dimensions of the focal volume for a given gas at a fixed pressure. If diffusion losses are not important in the development of breakdown, then it would be expected that the threshold electric field would be independent of the size of the focal region.

The dimensions of the focal region, as discussed before, are given by the product of the focal length of the focusing lens and the divergence of the incident laser radiation. The divergence of the laser beam remains essentially constant from pulse to pulse, and

the dimensions of the breakdown region can be simply varied by changing the focal length of the lens used to focus the radiation. Experimentally, over a range of lens focal lengths from 3 to 7 cm, the threshold electric field required for breakdown decreases with lens focal length. A higher electric field strength is required for breakdown within the smaller focal regions, indicating that diffusion-like losses play a significant role in the development of the optical frequency breakdown over the pressure volume regime studies.

For the case where diffusion losses dominate, the breakdown threshold electric field should vary as the reciprocal of the lens focal length. Experimentally, however, the threshold electric field varies inversely as the 0.6 power of the lens focal length. It is possible that this 0.6 power focal length dependence corresponds to breakdown near the minimum in the breakdown threshold curve. At microwave frequencies, the breakdown threshold curve differs appreciably from the asymptotic low-pressure and high-pressure dependences over a pressure range of only one or two orders of magnitude. The measurements that we have made at optical frequencies, however, span more than two orders of magnitude in pressure and are yet more than a factor of ten in pressure below that at which the collision frequency equals the radian frequency of the applied field. It would appear then that the pressure dependence of the breakdown threshold at optical frequencies is substantially different from that obtained in the microwave case, and further measurements of the effects of diffusion-like losses on the breakdown are necessary. In our experiments, we plan to extend these measurements to still longer focal lengths until the breakdown threshold electric field no longer decreases with increasing focal volume; i. e., the point at which diffusion-like losses are no longer significant in the development of breakdown. Since the magnitude of the losses is not known, the loss-free breakdown threshold thus

determined is the significant one for testing proposed theories of the optical frequency breakdown process.

Measurements have been made of the electric field strength required for breakdown as a function of the frequency of the incident radiation using both ruby and neodymium laser radiation. With ruby incident radiation, the breakdown field strength varied approximately as the square root of pressure over the range from one atmosphere to 2000 psi. With neodymium incident radiation, a similar dependence of the breakdown threshold on gas pressure was observed, and it was determined that the breakdown field strength for a given gas and pressure lies slightly below that required for ruby radiation.

The neodymium laser beam used in our experiments has a divergence somewhat less than that of the ruby radiation, and the diffusion loss effects associated with the smaller neodymium spot size has been taken into account in these measurements. The measurements from which this correction is derived, however, have been made at present only for atmospheric pressure breakdown, and it is uncertain whether the same diffusion loss correction would apply at the higher pressures. Measurements are currently in progress to determine the focal spot size corrections required at higher pressures, and, on the basis of these measurements, a more valid comparison of the neodymium and ruby radiation results will be made.

The neodymium laser output is at a lower frequency than that from the ruby, and, as predicted by the inverse Bremsstrahlung picture of the breakdown process, the threshold electric field for breakdown should scale inversely with the frequency of the applied field. Experimentally, the neodymium breakdown threshold lies below that for ruby incident radiation, and the ratio of the threshold electric fields is in substantial agreement with the ratio of the frequencies of the neodymium to ruby laser radiations.

MODERATOR BYRNE: Were there any further comments? Then Dr. Phelps from the Westinghouse Lab at Pittsburgh, I believe, has a few comments.

DR. A. V. PHELPS: In this discussion I will concentrate primarily on the theoretical questions associated with the breakdown of gases by lasers.

As Dr. Haught indicated, several mechanisms have been proposed for ionization of the gas processes which I have come to call direct ionization processes. These include photoionization, multiphoton ionization, and electric field stripping. The last two are usually called nonlinear processes.

People in the field are satisfied with the terminology "nonlinear" for these processes but as soon as you get out of the field it bothers people considerably. We had a whole session on nonlinear processes this morning, so we are then to consider this possibility.

A second type of process with which we are very familiar in the field of gaseous breakdown is that of electron impact induced processes.

Some of the arguments regarding the relative importance of these have been given by Dr. Haught. I would like to summarize briefly by saying that to me the principal arguments which indicate that the bulk of the ionization is not due to the direct interaction of the photons with the gas by some multiphoton photoionization or stripping process are a) the small increase of laser intensity required to break down argon relative to helium, and b) the relatively rapid variation in the threshold intensity required to break down the gas. As Dr. Haught indicated, the threshold varies roughly as the inverse square root of the pressure. If we were dealing with a multiphoton process, for example, one would expect a very slow variation of threshold intensity of the laser with pressure. This has been discussed by Tozer. We therefore believe that the bulk of the ionization is probably by some other process, and the question we have been asking is, can one account for the bulk of the ionization by an electron impact process.

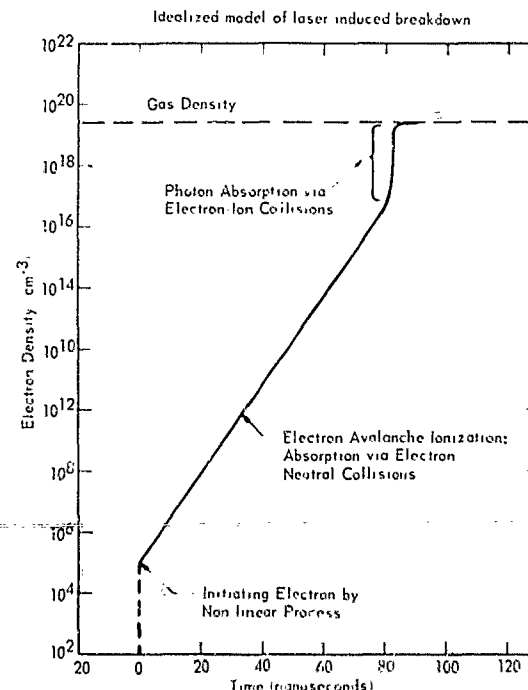
It turns out that one in general cannot account for the bulk of the ionization by the normal electron impact ionization process in the sense of ionization directly from the ground state. However, if one considers ionization as a two-step process in which one first excites the atom or molecule to some excited level, then photoionizes from that level, one can account for the ionization. When I say that, I mean that all of the experimental data available to me at this time is consistent with ionization rates which fall between these two limits.

Let's look at the model which we will use to talk about laser breakdown in gases. This is a rather idealized model. I assume that our laser intensity is zero up to time equal zero, and is constant from there on. It is not and this is a source of a great deal of difficulty in analyzing the data.

If we are going to use electron impact ionization or excitation followed by photoionization to account for the results, we need an electron to start things off. This electron may be residual in the gas; I don't think it is, but it may be. This electron may be produced by the laser.

Let's skip that point for the moment and discuss what happens after we get this first electron. According to the electron impact mechanism, the first electron will gain energy from the radiation field, will excite or ionize an atom or molecule. When ionization occurs, we have two electrons. These two electrons collide, produce four, and we have an electron avalanche type mechanism.

We expect that the electron density will start off at some value corresponding to roughly one electron in the focal volume. Now, the focal volume is of the order of 10^{-5} cubic centimeters in these experiments, so that one electron corresponds to an initial density of around 10^5 cm^{-3} . This is shown in Slide 1.



If we have an electron avalanche ionization process, we expect a density to increase, we eventually get to the point where we find that the mechanism of absorption of energy changes from the free-free absorption involving neutral particles to one involving ions. Because of the larger cross section for electron-ion scattering, once the gas is more than about 0.1% ionized, one expects a very sudden increase in the rate of absorption of energy and presumably a correspondingly rapid increase in the rate of ionization of the gas.

Our interest, then, in discussing the electron avalanche process is to follow the electron density from the point of initiation up to the point of this very rapid absorption.

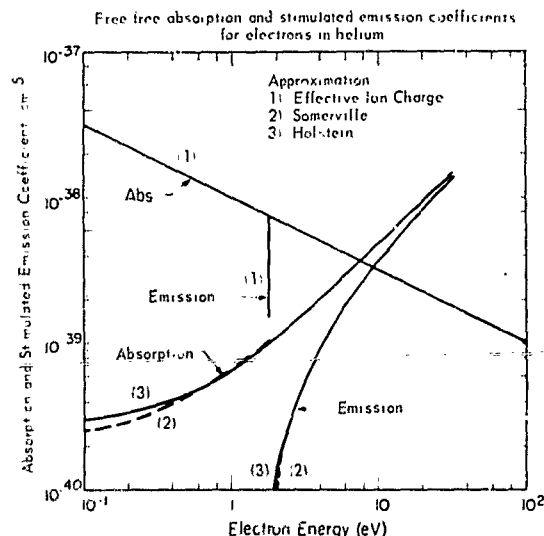
Once we have reached this point, the gas is effectively broken down. There are lots of interesting processes occurring at the high fractional ionizations, but we are not going to consider them.

Now, I have left out several complications which we have investigated briefly. One of them is that as the electron density increases, we produce positive ions.

This begins to set up space charge fields. Eventually the density reaches the point where the Debye length is comparable with the size of the focal radius, and so there is a reduction in the loss of electrons by diffusion. If diffusion is an important loss mechanism, the decreased loss will cause the electron density to rise more rapidly. We will neglect this effect in this discussion today.

Let's now consider in detail the process by which the electrons gain energy and ionize the gas. I would like to do this by showing first the results of some theoretical calculations of the free-free absorption coefficient in the case for helium.

In Slide 2 I have shown several approximations which have been used in discussing free-free absorption. The curve marked (1) is what I call the astrophysicist's way of doing it. In the past, it has been customary to reduce the results to an equivalent ionic charge, and to express the cross section for the process.



If one assumes that this effective charge were independent of the electron energy, then one would find that absorption cross section in a typical electron-ion fashion, dropping with increasing energy. However, this is not the case in neutral gases. The absorption coefficient has been calculated at very low energies, starting with Chandrasekar and Breen, then Somerville, and more recently Holstein. Holstein has shown that the free-free absorption coefficient is very simply related to the cross section for momentum transverse scattering. If one knows that cross section from theory or experiment, one can calculate directly this cross section. The curve labeled (3) shows the calculated cross section for helium.

The work of Somerville suggests a slightly lower curve (2) but I don't think in this stage ten percent is going to bother anybody. Dr. Kidder mentioned that they had done calculations in helium using phase shifts for free-free absorption coefficient.

Dr. Ashkin of our laboratory has just completed some calculations using the Holtzmark model for argon in order to check the Holstein theory. It's not intended that the cross sections calculated using

the Holtzmark model for scattering be accurate, but that the calculation provide a comparison of the cross section obtained by a proper integration of the wave function and the cross section one gets using Holstein's theory. It turns out Holstein's theory is very good. I therefore feel that we know free-free absorption coefficients quite well. Uncertainties in the cross sections may be ten percent or twenty percent. This is probably as well as they can ever be known from theory. Maybe somebody will think up an experiment to check them directly.

I have also shown in Slide 2 the stimulated emission cross sections which, of course, have to be taken into account in the laser problem.

Now that we have what we believe is an accurate free-free absorption coefficient, we want to use this to calculate the rate of energy gained by the electrons and the corresponding rates of electron excitation and ionization. I won't go into details. Basically this involves setting up the Boltzmann transport equation, substituting in the free-free absorption cross section, programming for computer, putting in realistic electron scattering cross sections (which we have previously derived in other connections), and calculating the excitation and ionization coefficients.

For those not familiar with this, in general what one does is to set up a continuity equation in energy space, and solve this equation for the electron energy distribution function which in general falls off with increasing electron energy.

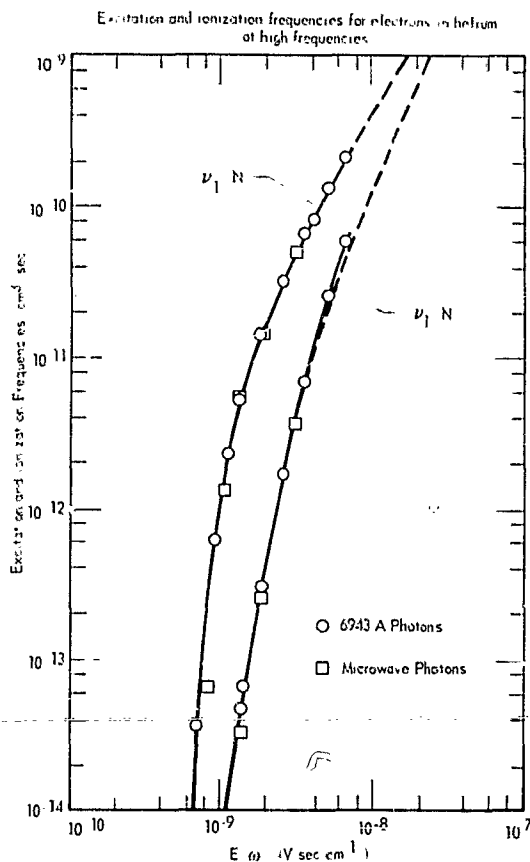
An important question to be answered by these calculations is the applicability of the results of microwave breakdown theory to this problem. Dr. Haught has discussed some aspects of the question of comparison with microwave theory.

The appropriate scaling parameter in theory is the ratio of the electric field strength calculated from the laser intensity to the angular frequency of the optical radiation. The proposal of the proponents of the microwave theory is that if we take the correct value of this ratio, substitute into the microwave theory, we can calculate the rates of ionization and so forth which one needs to compute breakdown conditions. Therefore, what we have done is to make comparisons of the more exact theory with a microwave theory using this same scaling factor.

Now, the distribution function in the microwave case turns out to be a monotonically decreasing function of electron energy, with no particularly interesting structure. When one puts in the finite photon energy of the optical case, one finds that the distribution functions for helium and argon have some small oscillations near zero energy and a few more starting at the excitation potential. Other than that it's very close to that calculated using the microwave theory.

To calculate excitation and ionization rates, we multiply the distribution function times the cross section and velocity and carry out an integration over energy space. The rates of excitation and ionization collisions are shown in Slide 3. Here we show for helium the excitation and ionization frequencies (the rate per unit time per atom) as a function of the parameter electric field strength to angular frequency. The square

points are calculated using microwave theory, that is, making the assumption that the photon energy is so small that we use the classical theory of electron acceleration. If we use the cross sections which I have just presented for optical photons, one calculates the circular points. We see that they agree to within the accuracy of the calculation.



Therefore, even though one may be unhappy with some of the concepts of the microwave theory applied to the optical regime, we feel that we have shown that a properly scaled microwave theory, using the parameter E/w does lead to the correct rates of excitation and ionization.

Now, in any comparison with experiments, in particular in the optical region, we have to worry about this possibility of multiphoton processes. We feel that the evidence available at present strongly favors the presence of multiphoton photo-ionization of excited states. By that I mean that the evidence suggests that if an electron excites an atom to the first excited state, then three photon photoionization occurs very rapidly.

We have obtained what we feel is direct evidence for this in the form of observations of broadening of spectral lines during the laser pulse. However, this information has not been made very quantitative yet.

Now that we know rates of production of electrons, we have to balance this against a loss rate and the rate

of production required to build up the ionization so as to essentially completely ionize the gas.

The continuity equation which we have to consider is

$$\frac{\partial n}{\partial t} = (\nu_x + \nu_i) n - D \nabla^2 n$$

Here n is the electron density, ν_x and ν_i are the excitation and ionization coefficients, and D is the electron diffusion coefficient.

It's difficult to solve this equation to any degree of precision; just within the last few months it dawned on one of our mathematicians that this equation can be reduced to the Schrödinger equation and that therefore techniques for solution are available in many, many books. We are currently in the process of trying to take advantage of this. So far we have used the approximate solution used by those concerned with high power radar transmission. Here one essentially considers that one has a circular beam of energy passing through a gas and that there is an absorbing boundary essentially at the edge of the radar beam. Unfortunately in cylindrical geometry this approximation leads to an error which could be serious, namely, it predicts a threshold for breakdown.

C. W. Helstrom of our laboratory has shown that if one solves the continuity equation in cylindrical geometry, one finds that there is no threshold for breakdown in the true sense. One always gets some rate of growth of ionization.

For our present purposes we replace the diffusion term by a diffusion coefficient divided by a square of the diffusion length. The diffusion length is the radius divided by 2.405, the first root of the Bessel function. We then assume that the electron density increases exponentially with time and calculate the exponent in the growth equation. This solution can be used along with our condition that the electron density grow from about 10^5 cm^{-3} to that of a completely ionized gas to calculate the time required for breakdowns.

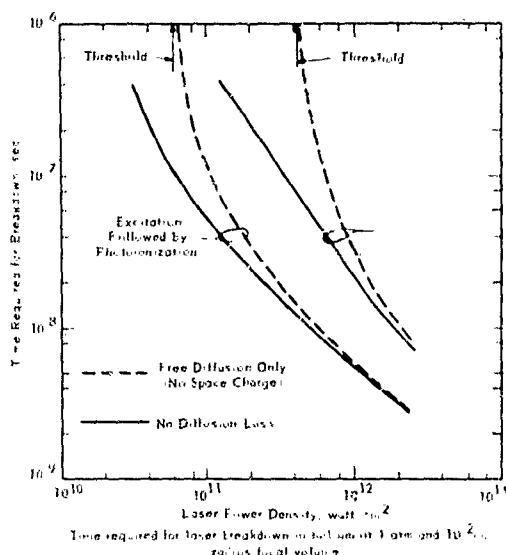
In Slide 4 I have shown some calculations of the time required for breakdown in helium at one atmosphere and for a 10^{-2} cm radius focal spot. As shown by the left hand dashed curve, the predicted threshold in this case is around 5×10^{10} watts per square centimeter when we assume that excitation is followed by photoionization. If we assume that only direct ionization is important, we obtain the right-hand dashed curve.

The solid curves of Slide 4 show curves of the breakdown times with no diffusion. The expected values lie between these curves because of the possible effects of space charge and the errors in solution of the diffusion equation.

Unfortunately, I do not have a slide of any of the experimental data obtained by Wayman and Ramsey. I can show people afterwards a drawing for the case of argon. It turns out that for argon, with a 3.3 centimeter focal length lens, the agreement between theory and experiment is good, probably better than we should expect. For the longer focal length lenses, the agreement is not so good.

I should point out that we have had a great deal of difficulty with changing laser intensity patterns. It has been extremely difficult to keep our calibrations at

all believable, and calibration has really occupied a large fraction of the experimentalist's time. Some of the changes in beam divergence can be eliminated by using a more modern flash lamp and reflector. In spite of these difficulties, I believe the data obtained by Waynant and Ramsey represent a marked improvement in techniques and results over that available previously.



A second point is that the laser intensity is not constant with time assumed in this calculation. One has to take into account the time variation of the laser pulse. We are working on this.

So far I have discussed what we think we understand. Now, I would like to discuss one of the things we don't understand. This has to do with the problem of initiation of the growth of ionization. Before I do that, I would like to show a typical laser pulse and an observation of breakdown.

On the left of Slide 5 is shown a photograph of the laser output as taken with a diode and oscilloscope with a two-tenths nanosecond time resolution. A typical laser pulse in our experiments has a half width about 90 nanoseconds.



On the right-hand side of Slide 5 we have shown the effect of breakdown on the laser energy transmitted through argon. Argon is one of the gases that shows the sharpest onset of breakdown. It is indeed quite sharp with this time resolution. In some gases, such as helium at atmospheric pressure, one has a great deal of difficulty observing the absorption.

This slide is of significance in showing first that we do have the ability to measure the time required for breakdown to occur and, secondly, we do have the difficulty of multimoding in the laser. This also shows up in a very horrible spatial distribution of intensity. Waynant and Ramsey have taken pictures of focal spots using XR film. If these are printed on high contrast paper, the pattern looks like a nebula or something. It's just horrible as far as analysis is concerned. I hope that some day somebody can come up with a technique for producing a more uniform spatial distribution.

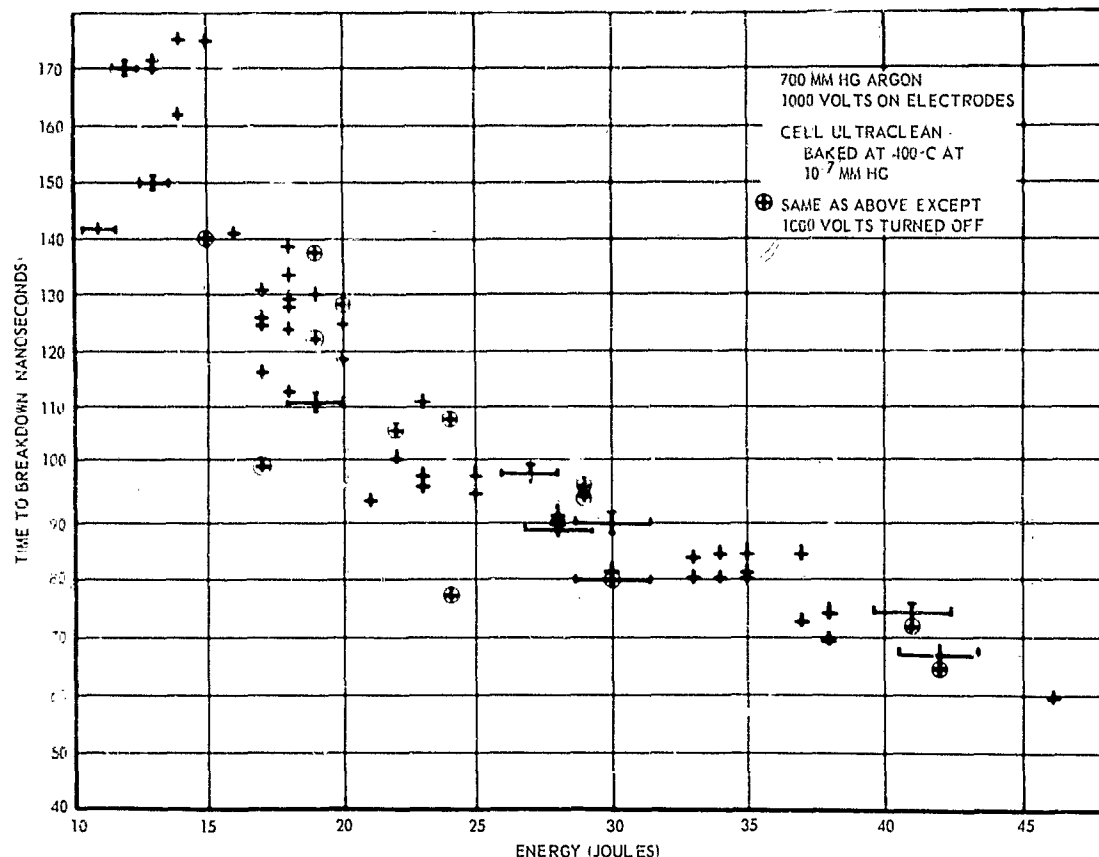
Optical data on breakdown times is shown in Slide 6. Here we plotted the time required for breakdown as a function of the laser energy. The total laser energy is also a measure of the peak intensity of the laser, since the half width of the pulse is fixed. The time shown here is arbitrary in the sense that zero is determined by the synchronization of the oscilloscope. The important point is that breakdown may occur before or after the peak in the laser pulse. On occasion one gets a breakdown at times as large as 180 nanoseconds. The threshold is determined then by finding the minimum intensity or minimum energy which will lead to breakdown.

The data of Slide 6 also shows the effect to the application of a dc field across the breakdown region. We find a thousand volts applied across about a centimeter and a half at atmospheric pressure has no effect. This is the kind of data that one needs for comparison with theory because it can be compared with the calculations that were shown previously in Slide 4.

Now, a rather significant point to be made on the basis of the data of Slide 6 is that if one considers a given laser energy, the spread in breakdown times is rather small. This, we feel, is evidence that the initiation of the discharge is the result of a direct interaction of the laser energy with the neutral particles presumably multiphoton photoionization of the main gas or of impurities. One can account for a portion of the scatter which one sees in Slide 6 on the basis of the nonuniform and nonreproducible laser patterns discussed previously. However, some of the spread is probably due to statistical effects to be discussed below.

Note that I do not believe that multiphoton processes can account for the bulk of the ionization. I don't think there is a factor of a hundred error in intensity as proposed recently in Physical Review Letters by Gold and Beeb. They proposed that all of the observed ionization was due to a multiphoton process and that the reason they didn't get a check between this theory and the experiment was that the experimental measurements of peak intensity were off by a factor of a hundred due to nonuniformities. There may be factors of two error in the peak intensity.

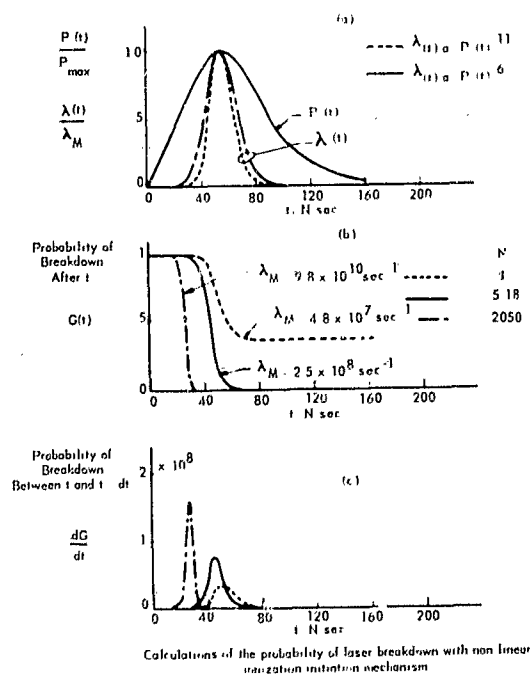
Finally, on Slide 7 I would like to try to present some of the arguments which lead to a prediction of a narrow spread in breakdown time when the initiation process is a nonlinear, or direct one. At the top of the slide the solid line indicates an idealized schematic of the laser intensity as a function of time. If we assume that the initiating electrons are produced by a multiphoton process, then the probability per unit time of producing such an electron will vary as some high power of the laser intensity. This leads to a probability per unit time of production of initiating electrons, such as indicated by the broken curves in the top graph.



The remaining two drawings on Slide 7 are intended to show what one predicts for the probability that the initiating electron will be produced at a certain time during the laser pulse. If the growth required zero time, then this would be the time of breakdown. For the present we will assume that this is a good approximation.

At the lowest intensity the integral under the curve of probability of electron production is unity. In other words, on the average the laser produces one initiating electron. In this case we find that the probability of breakdown after time decreases with increasing time and levels off at about 0.6 as shown by the middle set of curves. In other words, about a third of the time one doesn't see breakdown. If the laser intensity is raised by something like twenty percent, about five electrons are produced per pulse. This gives a rather sharp decrease in the probability of initiation after time which occurs near the maximum of the laser pulse. If the laser energy is doubled, about two thousand electrons are produced per pulse, and the curve representing the probability of initiation is shifted to earlier times.

The derivatives of the middle curves give the probability that initiation will occur between t and $t + \Delta t$ and are shown in the lowest set of curves. From these curves we predict a rather narrow spread in the time of initiation, i. e., some five nanoseconds in the case of our ninety nanosecond half width laser pulse. The time required for the growth of the ionization has to be added onto this time to find the time of breakdown.



Dr. Haught raised the question of the statistics of the growth of ionization. We have investigated this using somewhat simplified models for the free-free absorption and the electron collision cross section. It is our conclusion that although there may be a large statistical fluctuation in the time required for one electron to gain enough energy to ionize, the fact that the avalanche consists of a series of about 30 ionization events reduces the fluctuation in the breakdown time considerably. In the case of helium one might expect as much as twenty percent fluctuation in the time required for the electron density to grow to the value required for the observation of breakdown. This value is probably too large because it was based on the time history of a single electron and does not take into account the averaging effect of the large number of electrons produced in the latter stages of the avalanche. So I think the statistical effects in a gas like helium will in the growth be smaller than, say twenty percent. In a very low ionization potential gas using ruby, they could be quite large.

We have investigated a number of other problems, but I won't have time to discuss them in detail here. We have investigated the effects of transients on the electron energy distribution function. I mentioned that we had investigated better solutions of the diffusion equation and that we had obtained evidence for nonlinear ionization of excited states. This broadening of spectral lines by the laser is very important when one considers the amount of light emitted by the plasma while the laser pulse is on. If the laser reduces the excited state lifetime of about 10^{-10} sec then the amount of radiation emitted in the normal radiation process with a lifetime of, say, 10^{-8} sec is reduced by some four orders of magnitude.

Another interesting nonlinear effect is that in air at high pressures, one observes an absorption of the laser energy which is a cumulative process. This process is in addition to the breakdown process. Breakdown occurs at higher power levels and under these conditions produces a much sharper decrease in transmitted intensity. One possibility is the production of an absorbing species by the laser. I should point out that the experimental work by Waynant and Ramsey and the initial phases of the theoretical work were carried out under Contract AF30(602)-3332 with the Rome Air Force Development Center.

MODERATOR BYRNE: Any questions?

DR. FRED McCLUNG: A question on the broadening of spectral lines. Are you looking at the spectral lines during the emission process that occurs as the result of the ionization, or are you somehow or other trying to do this by excitation or some other means?

DR. PHELPS: We used an IT & T diode to observe the output of a spectrometer. At the center of the line one finds that the light output builds up during the laser pulse and then decays slowly with time. When the spectrometer is shifted 50 Å the amplitude is reduced but the time dependence is unchanged. At 100 Å from the line center the intensity drops off with the laser pulse. The experiment that we would like to do involves a smear camera picture of the output of the spectrometer as a function of time.

DR. McCLUNG: It sounds like you have a black body continually running during the laser pulse itself.

DR. PHELPS: If the spectrometer is set a few hundred Angstroms from the center the intensity is very small.

DR. McCLUNG: There are still a lot of questions.

DR. PHELPS: That's why I say it's not publishable today.

DR. McCLUNG: Tell me more about your laser later, and I will see if I can offer a few suggestions.

DR. PHELPS: This particular laser represented the state of the art at the time the project was started, but certainly could be brought up to date. However, some development would be necessary to obtain a desirable pattern.

DR. CULVER: This absorption at high pressures in air apparently takes place when you do not have breakdowns.

DR. PHELPS: Right, prior to breakdown. If you raise the laser intensity slightly higher the transmitted intensity would show a typical breakdown dropoff.

DR. CULVER: This corresponds to an appreciable absorption out of the beam in the small volume of the focus, and would apparently give rise to an increase in pressure that United Aircraft would measure on the manometer, for instance. This goes actually to heating the air in that region, is that right?

DR. PHELPS: So far as we know. This is an observation which we came across when we were looking at the --

DR. CULVER: It's not the scattering of the beam?

DR. PHELPS: It could be. We did not have sufficient money to investigate this effect further.

DR. CULVER: The way your drawing corresponds to thousands of joules per cubic centimeter.

DR. PHELPS: It's a high intensity, there's no question about it.

DR. HAUGHT: In one of your slides you showed a substantial time delay between the start of the incident giant pulse and the initiation of the breakdown -- a delay which you attribute to a wait for the first electron to be produced by a multiphoton process involving either the background gas or impurities.

DR. PHELPS: Yes, you are referring to the last slide on which the results of our theoretical calculations were shown. They indicate that when the laser intensity is low enough there can be an appreciable delay due to the requirement of producing the first electron. There is, in fact, some very indirect experimental evidence that this may be occurring for breakdowns at high gas pressures and low laser intensities. The whole problem of this nonlinear process is that we have no idea what species are involved.

DR. HAUGHT: That is correct. In fact, that is precisely the point I wish to make here. At atmospheric pressure, there are present in the focal region where the breakdown first develops some 10^{15} gas atoms. The gases used in the experiments have purities no

better than one part in 10^6 , and, therefore, within the breakdown volume there are some 10^9 impurity atoms which may include a substantial fraction of easily ionized sodium atoms from fingerprints, perspiration, or other contamination sources.

We have carried out some experiments in which a cobalt 60 radiation source was used to irradiate the focal region under circumstances which would produce a quantity of initial electrons within the focal region. In these experiments, we found that the cobalt irradiation had no effect whatsoever on the time delay required for the development of breakdown. This indicates that the gas had selected for itself a reaction process both for producing the initial ionization and initiating the avalanche and that the presence or absence of a few additional initial electrons introduced by the cobalt radiation source made no difference whatsoever. These results indicate that the formation of the initial electron is not the rate limiting step in the development of the breakdown. Sufficient impurities are present to provide the initial electrons required for the avalanche process.

DR. PHELPS: That is why I claim we will never understand this process until we put in a mass spectrometer, which is what we would like to do.

DR. MEYERAND: I would like to make a couple of comments emphasizing in particular the areas of agreement between the Westinghouse work and that carried out at United Aircraft. First of all, we are agreed that an avalanche process involving electron-atom ionizing collisions is responsible for producing the bulk of the ionization. This is in distinction to the views of some who are still adhering to the direct mechanisms as Dr. Phelps calls them. We feel, as do the Westinghouse people, that the great bulk of data favors the electron impact cascade mechanism. This is important in predicting the rate of build up of the ionization. Secondly, we feel that an atom is rapidly excited by photoexcitation and photoionization processes after it has been raised to an excited state. This too is important in predicting the rate and magnitude of the ionization occurring. Thirdly, we feel that the question of where the first electron arises is as yet an unresolved problem. Dr. Phelps has tried to remove any residual electrons present in the gas and has observed no effect on the ionization time delay. We have performed experiments in which we produce an initial ionization in the gas by a radioactive source. In these experiments again no effect on the breakdown is observed. We also agree that when the electrons in the breakdown region are hot, that is have an energy in excess of the energy of a photon of the applied field, the balance of photon absorption and emission processes gives an energy gain rate by the plasma that, as Dr. Haught said, relates very closely to that predicted by the classical microwave picture. For low electron energies, the stimulated emission process cannot occur and the absorption may be quite high, much larger than that indicated by the classical microwave picture. Since for many plasmas of interest the electron temperature is low, this large interaction cross section can be extremely important in

determining the absorption of an optical beam and is, in any case, of basic theoretical importance in understanding the interaction of optical radiation with plasmas. I think that at least on these points we are in agreement.

DR. PHELPS: I would like to comment on Dr. Haught's remarks concerning effects to be observed when the electron collision frequency is approximately equal to the angular frequency of the radiation. On the basis of microwave theory, one predicts an increase in the field strength necessary for breakdown at high pressures. It has been pointed out to me by Holstein (whom you will recognize as my chief mentor in this business) that when one gets to this high gas density region and one has to worry about quantum effects, then one is lost. Because what one is asking for is a quantum transport theory for hot electrons. At present there is no useful theory. The difficulty arises from the fact that in this region we are dealing with multiple collisions in which the electron wavelength is comparable with the space between atoms.

This means that, contrary to what I have seen in some reports, the increasing threshold with density predicted by the microwave theory is not an indication of error in the microwave theory. It is probably the only thing we have now that will even come close to predicting what will happen in these high densities. This failure of present quantum theories to predict this effect should be regarded as a deficiency in the quantum theory.

MODERATOR BYRNE: Any further comments?

DR. DAW: I wondered, what about the initial emissions from the breakdown, particularly in the ultraviolet region, the photographs I believe that Dr. Haught was speaking about in which he showed the emission coming from the breakdown region.

DR. HAUGHT: That was in the --- We have not made measurements in the ultraviolet.

DR. DAW: Then both, I think, indicated they had current collectors on the device. Did this make any difference in the breakdown when you were pulling electrons out?

DR. HAUGHT: No, I should have mentioned that we made these measurements with the electrodes. There were potentials on the electrodes actually drawing the current, and without the electrodes there, all in precisely the same cell, we found no difference whatsoever in the breakdown threshold in any of these cases.

It would be very easy to be just a little bit sloppy and have the laser beam hit one of the electrodes in which case the presence of that first electron I don't think would be subject to any doubt whatsoever. This was not the case.

MODERATOR BYRNE: Coffee is available in the back of the room. Let's try to start again in ten minutes.

Session III Moderator: F. T. Byrne, ONR

Part 2 Refractive Index Variation

Tuesday Afternoon
23 March 1965

Izatt NMSU

Daw NMSU

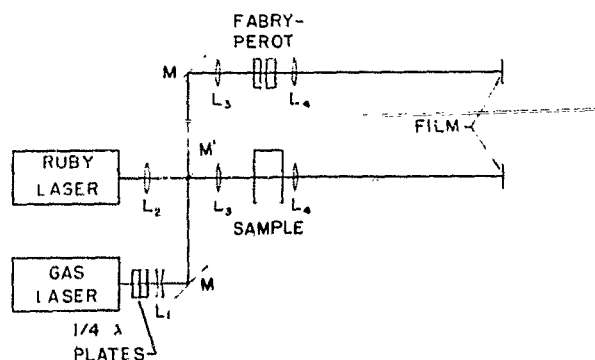
MODERATOR BYRNE: Now we will leave the subject of gas breakdown and go to refractive index variations within the laser material. This work will be presented by Dr. Izatt and Dr. Daw from New Mexico State University.

DR. J. IZATT: We are in the process of making measurements to determine the effect of optical pumping on optical dispersion in the immediate vicinity of the R1 line in ruby.

An obvious first step in doing this is to determine the anomalous dispersion for an unpumped sample. We had expected that when we attempted to do this, we would find close agreement with well-understood physics. We find, however, that our results are a little bit unusual in at least two respects. We would like to describe our experimental procedure in some little detail, and then show results for the unpumped sample in the hopes that you might be able to offer some cogent suggestions in the interpretation of this data or indicate places in the experimental procedure where you think uncertainties might be present.

I am going to talk about the experiment, and then show you some data about the temperature shift of the output of ruby laser at liquid nitrogen temperature, and then Dr. Daw will talk to you about the index measurements on an unpumped sample.

In our experiment we are interested in determining index variations interferometrically, that is, by measuring fringe shifts in an interferometer. The equipment is shown schematically in slide one.



We have two parallel optical channels. We have two lasers, a ruby laser and a gas laser, each of which illuminates two Fabry-Perot interferometers. The beams from the sources are directed by folding mirrors, so that a portion of each of them is incident on a high quality reference interferometer and also on a Fabry-Perot etalon. This etalon consists of a ruby cylinder one centimeter in diameter and one centimeter in length.

The ruby laser is housed in a cavity in such a way that it can be cooled to liquid nitrogen temperature. It has a heating coil associated with it, so that we can vary its temperature over a range around liquid nitrogen temperature. We also pump on the liquid nitrogen in order to achieve temperatures lower than 77 degrees. The temperature of the source laser is measured by means of a thermocouple. The ruby itself is clamped into a copper rod which communicates directly with the liquid nitrogen.

The sample ruby is also housed in a pumping cavity, and it is also cooled to liquid nitrogen temperature. There is also a heating coil associated with it, so that the sample ruby can be varied in temperature. In this case the ruby itself is housed in a sapphire holder, a little spherical holder, which in turn is clamped into a copper rod that communicates directly with the liquid nitrogen.

The procedure for getting data is to illuminate the interferometers with the gas laser. This forms a set of fringes in both of the interferometers which are recorded on film. We then flash the ruby laser and get a second set of fringes in each interferometer. By varying the temperature of the ruby source we scan the source temperature in small steps from well below to well above the sample temperature. From the reference interferometer we get information on the wavelength shift, and from the ruby etalon information on wavelength and index shifts. We use conical Fabry-Perot fringes which were described some time ago by Tolansky.¹ Instead of illuminating the interferometer with diffused light from a collimated beam one has a divergent beam incident on the interferometer. By this means the light can be concentrated into a predetermined number of fringes near the center of the pattern. We illuminate essentially half a dozen fringes with the light. The interferometer is followed with a lens and photographs are made in the focal plane of that lens. We then have fringes whose spacing obeys the normal Fabry-Perot interferometer rules. We use a two-meter lens following the etalon so that the positioning of the photographic plates in the focal plane is not overly critical, and we get good magnification.

The output of the ruby laser is polarized, and we find that upon rotating the sample we get significant variation in the quality of the fringes that are produced by it. Normally, we align the sample so that it produces the best quality fringes. We have a pair of quarter-wave plates associated with the gas laser so that we can rotate its plane of polarization until we get optimum fringes from it also.

PROF. SCHAWLOW: What is the orientation of the C axis of the sample?

DR. IZATT: It is normal to the cylinder axis.

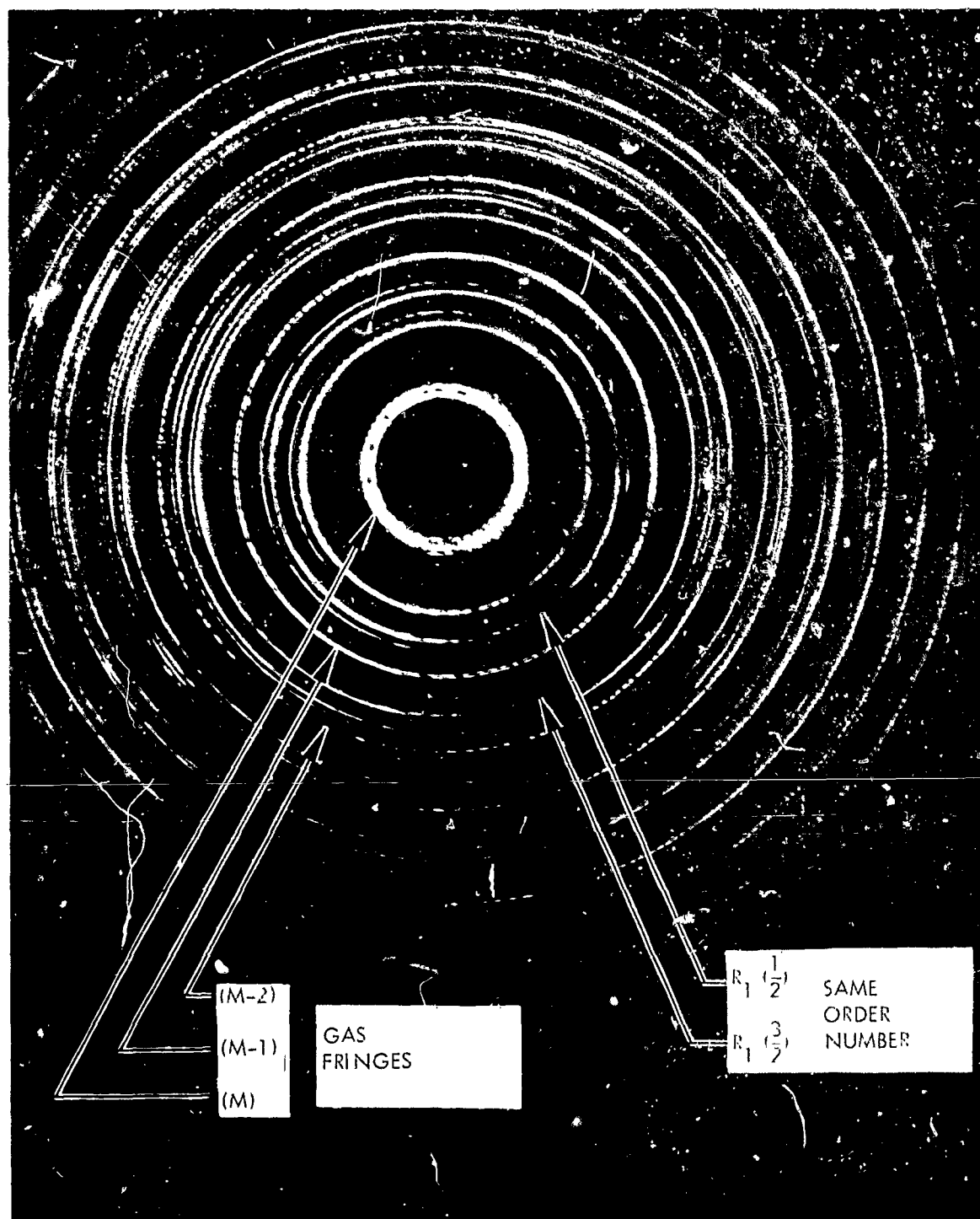
PROF. SCHAWLOW: Do you know how it turns out when you make the adjustment for best fringe quality?

DR. IZATT: Yes, it turns out that the polarization of the laser is parallel to the C axis. We will show you some data in a few minutes that shows the difference upon rotation of the plane of polarization.

PROF. SCHAWLOW: That may account for your weak effects.

DR. IZATT: Yes, we will get to that very shortly.

I believe the first thing, then to be described in further detail is the wavelength shift with temperature. Each time we make an exposure it is a double exposure on each plate. From successive exposures through the reference channel we get a wavelength shift associated with whatever variation in temperature there has been at the ruby source.



The next slide (Slide 2) shows a typical plate photographed through the reference interferometer at liquid nitrogen temperature. The centralmost fringe is a gas fringe; note that it is doubled. The other gas fringes can be identified by this doubling. In between successive gas fringes there are four components representing the output of the ruby laser.

Two of these represent the ground state splitting in the ruby laser, that is, they are separated by 0.38 wave numbers. In making a typical set of measurements, we take densitometer traces in four distinct directions across the plates, and we average the radii that are measured in these directions.

As you will recognize, in a Fabry-Perot pattern, if one takes the squares of the radii of the successive rings, then the difference in the squares should be constant throughout the pattern. If one then divides the square of the radius of a given ring by the difference in the squares of the radii of successive rings, one gets a value for the fractional order number in the center of the pattern. This procedure can be repeated for each ring. We get averages over four different directions of scan, and then over five or six fringes to compute the fractional order number at the center of the pattern. Never in the experiment do we make a measurement of the total order number at the center of the pattern, which is of the order of 50,000. We measure only changes in the fractional order number. This lends some ambiguity to the interpretation of our data that will be brought out later.

Slide 3 represents a similar exposure, but taken now at dry ice temperature. There are probably twenty components in the laser output. It was operated as close to threshold as possible; however, threshold was 1% higher than at liquid nitrogen temperature. In making the wavelength versus temperature measurements, we simply took the center of gravity of all of the fringes.

May we have slide 4, please?

As far as the temperature measurements are concerned, the data is summarized here. The data above about 200° K was reported in 1961 by Abella and Cummin.² The wavelengths are plotted as a function of ruby temperature. This work was done primarily above room temperature, but they also had points below room temperature which scattered rather widely. These were obtained by actually dipping the ruby into liquid nitrogen, then removing it from the nitrogen bath, and putting it back into the pump cavity and exciting it.

The group of points, circles around 100° K, represent points that we have measured. In the case of the temperature measurements, there is no ambiguity in assigning the change in order number from one exposure to another. That is to say, if one considered other possible assignments than the one we have made, even those closest to the ones that have been made here, would either result in a slope to this curve which is even larger than the slope at room temperature, or in a negative slope. There is thus a completely reasonable criterion for assigning order

number changes. The other data represented by circles was obtained at dry ice temperature.

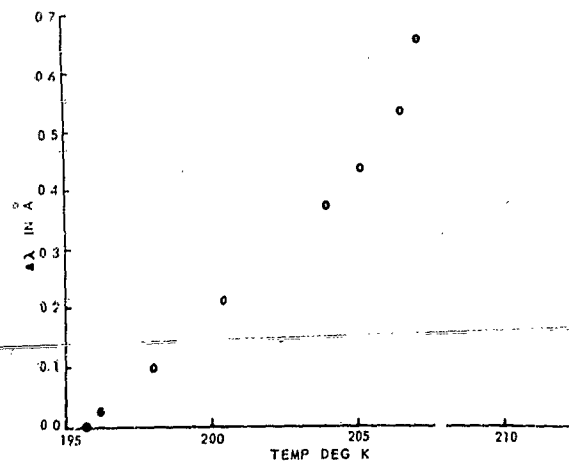
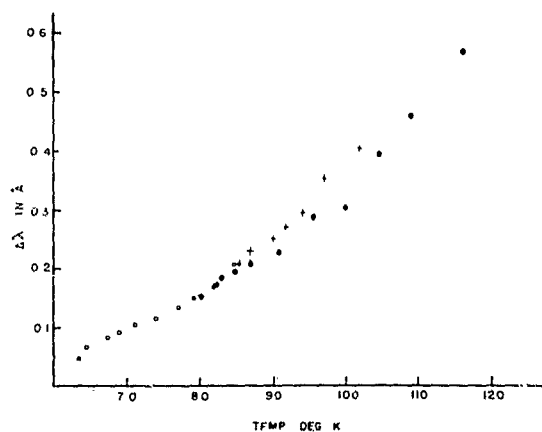
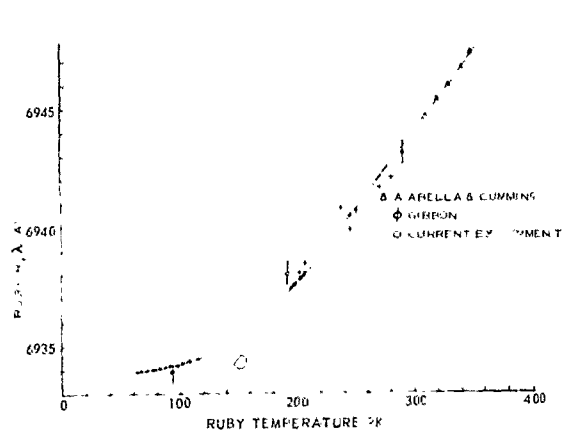
In both cases we don't have a fix on the actual wavelength, but only on the difference in wavelengths between successive points. However, it has been measured by many people that at liquid nitrogen temperature the line occupies a position very close to 6934 angstroms. We have simply fit a smooth curve that fits the curvature of our measured points in both of the regions. The remaining data points were measured by Gibson³ fifty years ago.

Slide 5 simply represents an expansion of the scale in the liquid nitrogen region where the wavelength units are now a tenth of an angstrom, and shows the kind of scatter that occurs in our experiment. The circles and crosses represent the data from which wavelength positions were determined in order to evaluate the index shift data that we are going to show you in just a few minutes. As you see, they follow pretty consistently. We have wondered some if the fine structure in this curve has any significance. The black dots that scatter out further are from a different set of data in which only a single pair of components was present, that is, a single longitudinal mode of the ruby laser. The fringes were so weak that the position measurements on the fringes became very uncertain, and we got a considerable amount of scatter. Those points represent the worst scatter we have seen. The total number of points on this graph, each one of which represents a photographic plate with the averaging that I indicated before, is about 1/5 the total points obtained. They all fall along this same general curve very closely.

Slide 6 is simply an expanded picture of the region around dry ice temperature where we have fewer measurements, but once again it gives indication of the agreement between the points.

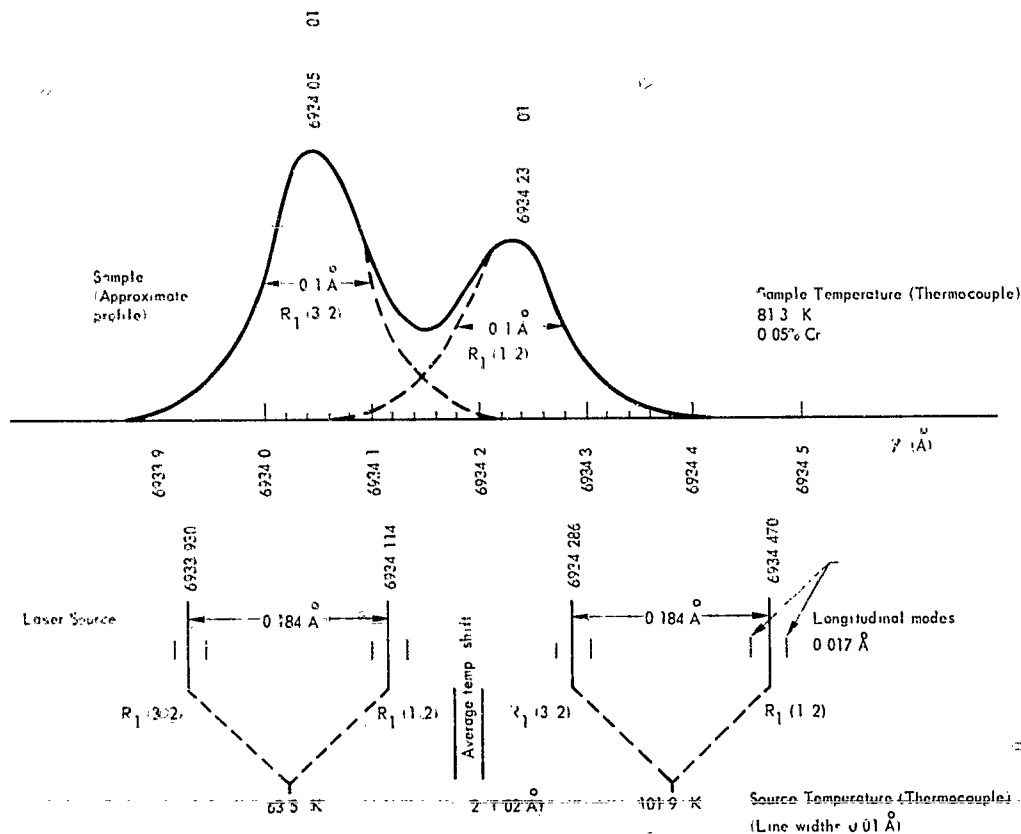
Now I want to say just one more word about the order number assignment. The problem in looking at the fringe patterns is that we simply measure the change in fractional order number from one plate to the next, and there may be integer changes in order number as well. In principle, it might be of almost any magnitude. It's perfectly clear in the case of the temperature data that the assignment we have made is the only reasonable one. However, this represents somewhat more of a problem in the case of the analysis and interpretation of the index shift data, and I will sit down now and ask Harold Daw to talk about that.





PROF. HAROLD DAW: I believe it would be appropriate before discussing the experimental results to sketch on the board the temperature scales with which

we are dealing, the wavelength shifts with which we are dealing, the positions of the lines, and the line half-widths.



The ground state splitting is about .38 wave numbers or .18 angstroms. The width of the lines, is about .1 angstrom. Our "spectrometer" consists of the ruby laser line in which the wavelength shift mechanism is the temperature change. The laser line itself has a half-width, something less than .01 wave number.

It is probably not right to say we have scanned from exactly 6933.9 Å to 6934.5 Å. We have scanned from 63.5°K to 101.9°K, and since the sample may be at some slightly different temperature than the center temperature of our ruby source, the wavelength region scanned could be slid back or forward a few hundredths of an angstrom.

Dr. Izatt has mentioned the problem of order assignments which, in the case of the reference interferometer, was not difficult to do.

In the case of the ruby, we do not really know what to do in terms of order assignment. If you argue that you are in the vicinity of rapidly changing index, it is conceivable that from one picture to another you may change ten order numbers, plus a fraction of an order number.

This is a problem that is not altogether ambiguous because we have measured many points, and have

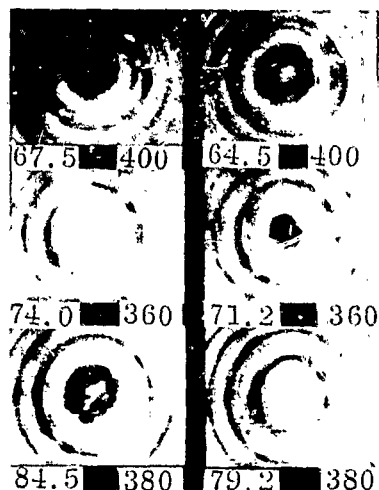
many fractional order number changes, and the temperature intervals are not all equal. They are about 2°, but they are not all equal. If one were supposing they had large order number changes in addition to fractional order number changes, then the fractional order numbers should scatter badly. This is due to the fraction on the large order number change, which would go with different size intervals. We do not find that we have large scatter in the points, and therefore must assume that the order number shift is small.

We have mounted our ruby sample in two different polarizations, and scanned the same region in the two different polarizations. This aids in assigning order number.

The two lines shown in slide 7 scan the region. In places the $R_1(3/2)$ line will overlap the region which has been scanned by the $R_1(1/2)$ line, and so we know that the order number assignments on one must agree with the order number assignment on the other.

If I could have the next slide, please.

These are not the pictures Dr. Izatt talked about which were taken with the reference Fabry-Perot. These are Fabry-Perot fringes through our ruby etalon. We get fine fringes, but they are of relatively low quality compared to those obtained in the reference



interferometer. As an indication of this you can see the ground state splitting, but the lines are fuzzy.

The order number assignment is similar to that shown in Slide 2. However, the longitudinal modes are not resolved.

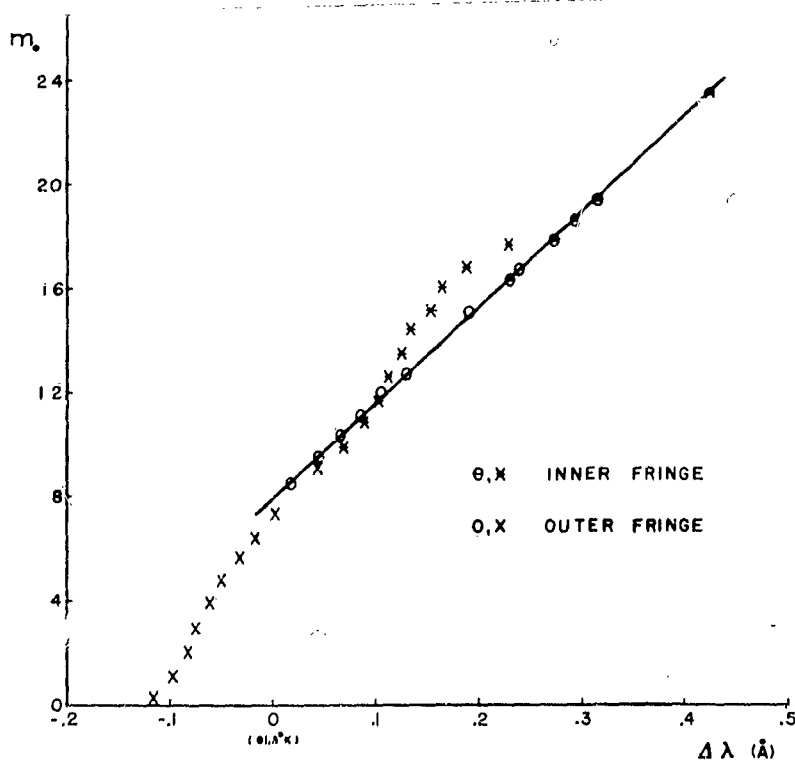
The numbers on the left are the temperatures at which the photographs were taken, and the number on the right indicate the number of joules that were put into the flash lamp. Several fringes were measured in several different directions to obtain the data that were then used for the next step.

One thing that I want you to notice is that you always have fringes. Nowhere are the fringes suddenly getting broad and spreading out, yet it is obvious from Slide 7 we should be somewhere in the regions of the absorption lines. The absorption coefficient reported for liquid nitrogen temperature, and we are indebted to Prof. Schawlow⁴ for this, is on the order of 10cm^{-1} . He tells me there is something more recent in the Journal of Applied Physics that we have missed which reports something like ten per centimeter also.⁵

If we have a coefficient of absorption of ten per centimeter, I believe the number given was thirteen, and our sample is a centimeter thick, the first beam is attenuated by e^{-10} . The second beam must go back through the ruby to the other side and be reflected and come back across, which means it will be reduced in intensity by e^{-20} relative to the first beam, and one will not get very good addition in this case. One would suppose that not only would the fringes be dim, but that they would be washed out since only the initial path would be there, if any at all.

Let us see Slide 9.

Along the ordinate is the order number assignment which we have taken. The changes in wavelength are plotted on the abscissa. There are several sets of data on this slide. The crosses are associated with one of the fringes, and the circles are associated with the other fringe resulting from the ground state splitting. The set of data consisting of crosses which sort of wiggles is associated with one orientation of the ruby, that is one polarization orientation of the C axis of the ruby. The other set of data falls very nicely in a straight line.



The order number shifts are small as pointed out earlier. The order numbers either increase or decrease. We have assumed the order number increases by an interger plus a fraction. This results in the smooth curves shown in the slide. Excuse me. Dr. Izatt, have I said something wrong?

DR. IZATT: Its not a whole order number increase. Its a larger change between successive points than if the order number were allowed to decrease. But between successive points it is less than a whole order number change.

PROF. DAW: We have the fractional order numbers, and we either take them down or up.

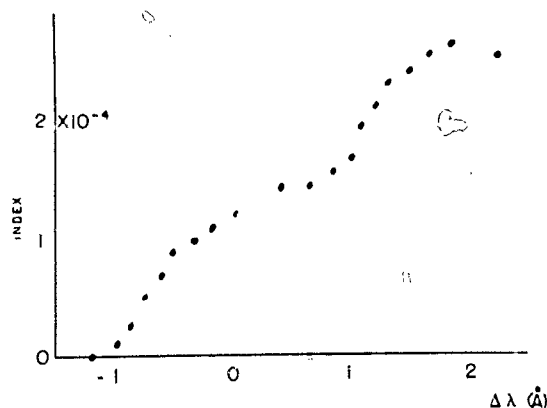
DR. IZATT: That's right.

PROF. DAW: Since the measured fractional order numbers generally decrease, a shift up is larger than a shift down, but both are less than a full order number shift. Since the region scanned by the two lines overlaps, both sets of data must match up. When we assign order numbers such that they do match up, we observe these two curves, and they match up smoothly. If we were to assume that the order number decreased, the curves would go down. In this case, they do not match. There are some jogs that simply do not match.

If we assume that it changes by a little more than an order number going down, the curves again do not match. We have made no other assignments. We do not suppose there are two order changes, since by the time you get two order number changes, the difference in intervals should be enough to begin to produce considerable randomness in the points, and we do not see that.

There is a problem here. This assignment gives a slope up towards longer wavelengths, and that's a little disturbing.

Now, may I have the next slide?



We have taken the difference between the two curves on slide 9, and this, is the difference in those curves. We assume that in the polarization where the lines are weak, we are having no effect from the lines and in

the other polarization where the lines are stronger, we are seeing an effect. What is left is the effect of the absorption line.

Dr. Izatt has plotted some index of refraction curves to compare with the data. The curve in the next slide is the sum of two dispersion curves for a pair of lines separated by .38cm⁻¹ and half width of 0.1Å. This does not represent an attempt to fit the data quantitatively but only to check the general qualitative form. And, I believe that's the last slide. These are the points which you just saw on slide 10 plotted against the sum of the two refractive index curves.

I suppose there will be some questions about that. I will give you an opportunity to ask those in a moment. I would like to point out that we are not through with this work, but there seems to be at least qualitative agreement.

We can answer the question about the ambiguity in order number by changing our temperature intervals and making them smaller. This should settle the question of whether we have whole order number changes or half-order number changes.

It will not presumably settle the question of whether or not we can propagate coherent laser radiation through the middle of this strong absorption. We apparently can, unless one wishes to argue that we have missed the line entirely.

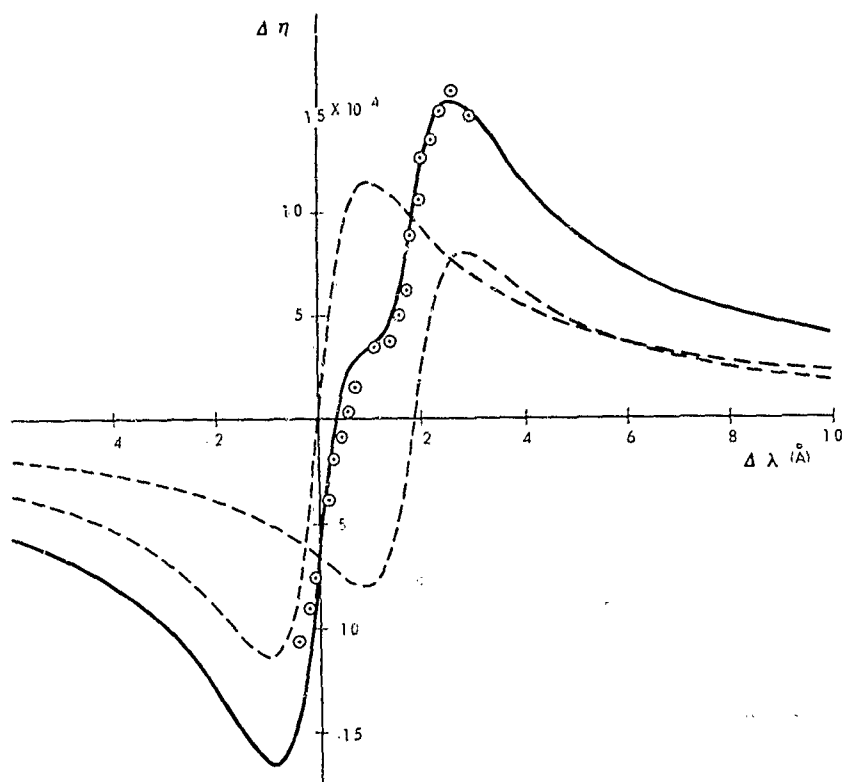
There are some alternate explanations to why we do not observe the strong absorption besides missing the line. We could possibly be bleaching the sample, particularly if we had to bleach only in the very narrow frequency region where the laser line is located. In which case the light could get through. The rest of the line (unbleached) contributes to the index variation.

Since the lifetime for the ruby state is on the order of ten to the minus three seconds, we have supposed that the light the light may go in and be absorbed, and then simply be stimulated out coherently with the incident radiation.

However, every photon is absorbed with an absorption coefficient something like ten per centimeter, essentially ten times in traversing the ruby once. This means many absorptions and reemissions will occur. The probability for stimulating a photon out of an excited state is a good deal less than the probability for its being reabsorbed. This question, so far as we are concerned, is not answered.

We would like to get the index of refraction curves for the unpumped sample and for the sample as the population is changed by pumping. Dr. Izatt didn't mention this, but the sample is mounted in its own pump cavity with a flash tube.

The ruby sample in addition to passing ruby light from the source, will produce fluorescent radiation. Fluorescence radiation will fog the film. We have been controlling the pump light and filtering to see that we don't get enough fogging to spoil the fringes. I have brought along prints of two pictures. (Prints not reproduced here.) These happen to be poor because we had just started the realignment after putting in some light traps at the ruby faces, so the



fringes are not centered. They are not equally intense, but one of these shows the fringes taken through the unpumped sample, and the other shows fringes taken when the sample is pumped about as hard as we will ever pump it. Thus, we have as much fluorescence as we expect and as much background radiation. You can tell very little and I don't want to draw any conclusions from these pictures. I think if you will look at them you will see that in fact the fringes have been shifted significantly by the pump radiation, both in shape and in general quality.

MODERATOR BYRNE: Any questions or comments?

PROF. SCHAWLOW: That bleaching suggestion sounds reasonable to me. Have you made quantitative estimates?

PROF. DAW: We have not made good quantitative estimates, but the reflectivity on the surface of the sample is about 99 percent, and very little of the radiation enters the cavity. However, for those very narrow directions at which it does go into the sample, it enters very well because you get complete transmission where there is coherent addition.

DR. McCLUNG: Are these temperatures that you quote here the starting temperature prior to firing the flashlamp, or the terminal temperature at the end, or what? How are they related to the actual temperature at the time that the ruby is running as a laser?

PROF. DAW: These are the temperatures prior to the flashing of the lamp.

DR. McCLUNG: In other words, the actual temperature may be as much as thirty or forty degrees higher.

PROF. DAW: I would be very much surprised about that, because we would then expect some kind of heat pulse to come up past our thermocouple which we would see.

DR. McCLUNG: Then the thermocouple reads the same temperature at the end?

PROF. DAW: Yes. In our geometry the ruby is fastened into a copper rod, and the thermocouple is located also in the copper rod.

DR. McCLUNG: Yes. And the thermocouple indicates, say 63.5 degrees.

PROF. DAW: Yes.

DR. McCLUNG: I am familiar with the system here. The thermocouple indicates 63.5 Kelvin prior to the time that you fire the flash. Now, what is the temperature of the system as you read it on the thermocouple after, I mean as soon as you can observe it after the process?

PROF. DAW: We don't observe any temperature shift.

DR. McCLUNG: In other words, the copper remains thermally locked to the nitrogen bath, but I don't believe the ruby does.

PROF. DAW: Well, the ruby has a better conductivity than the copper at liquid nitrogen temperature.

DR. McCLUNG: It has a very low heat capacity, and it has a very bad thermal contact with the copper block. Data that has been presented in numerous other places indicate that in the temperature range between helium temperature and somewhere above nitrogen temperature, that it's not at all unusual to see temperature excursions of forty degrees or fifty degrees Kelvin in the ruby, actually, itself, and this is determined by absolute wavelength measurement as compared with fluorescence emission wavelength.

You know that the fluorescence emission can at least be tagged very well to temperature, but you don't know what the temperature of the ruby is at the time that you laser, and so you can actually measure the temperature of the system by using a high resolution spectrograph to locate the center of the line, and thereby identify with no ambiguity at all what the temperature is, and, therefore, the wavelength of the system is.

PROF. DAW: If you actually immerse it in a liquid nitrogen bath, I would argue you also do not know the temperature of the ruby for the very same reason that the heat is delivered into the ruby, but the heat pulse usually sets in at some time delayed relative to the flash.

PROF. SCHAWLOW: Could I make a comment on it?

We have some time ago made some measurements on the output wavelength of a ruby under pumping conditions, and we found that when we cooled it, why, by blowing cold air on it we could never get it down to the temperature of liquid nitrogen. That is, when it lasers, it's always above that.

The wavelengths, this is wavelengths shift, if we immersed the ruby in the liquid nitrogen and didn't hit it too hard, then the wavelengths would be the same wavelengths as we got in low energy fluorescence.

There is one point that I would like to mention without commenting as to whether you actually do or do not have a temperature shift, I don't know. There is the interesting point which you will find in the literature, that the shift in the line position from absolute zero is quite closely proportional to the total heat absorbed.

In other words, at very low temperatures the specific heat is small, and the shift per degree is small. At higher temperatures the shift per degree is larger, but with the shift per calory is constant.

DR. SOULES: Don't you cross-check wavelength shift in the Fabry-Perot alone against the etalon?

PROF. DAW: We have this checked; and the temperature data which we gave, which fits rather nicely, would seem to indicate we do not have that large excursion. Furthermore, the entire scan interval is about forty degrees.

DR. McCLUNG: Yes. So I typically monitor temperature in the system that I work with which isn't that much below room temperature, and see temperature excursions of the order of the magnitude of ten degrees, I might add at relatively low pumping powers.

MODERATOR BYRNE: At what pump power?

DR. McCLUNG: Of the magnitude of 500 joules in input energy.

PROF. DAW: Ours are almost always under 400 joules.

DR. QUELLE: As I recall the curve you had of the anomalous dispersion there, the two peaks on the anomalous dispersion were separated by a small fraction of an angstrom, is that correct?

PROF. DAW: Yes.

DR. QUELLE: Could we have that one? Slide 11. The point that I am getting at is it is my understanding that the anomalous dispersion will peak at the half-widths of the line, which would comply with a rather narrow line, more narrow than I had been led to believe.

DR. IZATT: This is the composite of two lines, which are separated by 0.38 wave numbers, and each of which has a half-width of a tenth of an angstrom. You can see the two index curves that came through from the construction down there in the bottom half. You will notice the peak points are in each case separated by twice the half-widths of the line; the composite curve now has the bumps, as you call them, which are separated by the smaller amount. It is a broadening effect when the two go together.

Incidentally, we never use a temperature measurement in reducing any of the data. We use the wavelength shift that comes from the Fabry-Perot interferometer exclusively. As I pointed out, if we assigned any whole order number shifts there, we would get either a slope to the wavelength-shift-versus-temperature curve, which is even greater than it is at room temperature, or one which was negative.

I think there is no ambiguity there, which once again argues that the wavelength shift that we put in here is pretty reliable.

PROF. DAW: I don't know whether it was pointed out or not, but this is in a vacuum system. We were not dangling it in air or something.

DR. McCLUNG: Oh, no, it's just a problem which has been observed by other people, that when you try going down to these low temperatures, and when you pump the laser system itself, the laser crystal, it takes a certain amount of energy just to invert the populations, and then you can calculate the energy that is put into the lattice to just invert the populations, and this doesn't turn out to be a fantastic amount of energy. It only causes the temperature change to the order of magnitude of three or four degrees, around three or four degrees.

Then you throw in a few other factors to account for the fact that not all of your pumping is in the green band, and you can find --

PROF. DAW: This is why I point out that the temperature interval is not fixed relative to these lines.

DR. McCLUNG: Yes.

PROF. DAW: It can be slid to the right or left.

DR. McCLUNG: Depending upon the system, why, it could be slid by quite a bit, or it could be bleaching, either one, too.

PROF. DAW: Yes. I would think it would be very unlikely that we were shifting sufficiently to miss the lines.

DR. CULVER: Why isn't the output wavelength quite as well defined by the cavity conditions of the laser? It's the output --

DR. IZATT: No. The point is that it is well defined by the other interferometer measurement. I believe the argument that Prof. Schawlow was making just a minute ago indicates that the curvature of this wavelength versus temperature curve should go roughly as T^4 and a T^4 curve is essentially what we have plotted there. If we were to shift those points measured near the liquid nitrogen temperature forty or fifty degrees in either direction, they wouldn't fit the curvature of that curve well at all.

I believe also Dr. Schawlow made the point that when the ruby is immersed in the liquid nitrogen, then the position of the line agrees with the nitrogen temperature. Did I understand you correctly there?

PROF. SCHAWLOW: That wasn't all we did. We also used a clad rod to get thermal ballast. There was about, I think, six times as much sapphire as the ruby.

PROF. IZATT: I might mention that in this clamping arrangement the ruby is clamped tightly into the bottom of the copper rod with an indium gasket so that reasonably good thermal contact can be made.

DR. QUELLE: What fraction of the pumping time did the laser actually lase? What I am getting at is if it lased an appreciable fraction of the pumping time, then if there was a frequency shift, you should see a blurring of the fringes as the frequency changes.

PROF. DAW: It lases for about 200 microseconds.

DR. QUELLE: Then if there was any appreciable shift with temperature, I would assume that you would see a blurring of your fringes.

PROF. DAW: We do not see a blurring of the fringes.

DR. MCCLUNG: That may explain why you have two mounds there instead of one. What is the separation between the two?

PROF. DAW: 0.38 wave numbers. It's just right for the ground state splitting. It could jump from one longitudinal mode to the other, but we do not resolve these in the etalon. These two are resolved.

DR. QUELLE: I would assume that's the maximum amount of -- multiply that by a factor of two or three for the maximum amount of pulling that you might get, due to temperature rises.

PROF. DAW: Anyone can see these pictures if they like. (Refers to prints on pumped sample not reproduced here.)

Note added at time of editing: After the conference it was confirmed by direct spectrographic observation of the laser emission that the measured source temperatures were in error by about 5°K. These measurements were made on a 13-meter Littrow grating spectrograph which provided dispersion of about 6 mm/Å at 6934 Å. This instrument was made available to us by Dr. John Evans, Superintendent of the Sacramento Peak Observatory, Sunspot, New Mexico. Details of the spectrographic measurements are reported in Variation of Refractive Index During Laser Operations, Semi-annual Technical Report No. 3, J. R. Izatt, H. A. Daw, R. C. Mitchell, Contract Nonr 3531(04), April, 1965.

MODERATOR BYRNE: Any further comment?

I have one, and that is I would like to point out that the arrangements for the meeting were made by Lloyd White, and I think that he has done a fine job.

(Applause.)

DR. CULVER: I would like to make one comment before we break up. We all owe ONR quite a debt of gratitude, because I think this has been a very fine meeting all the way around.

(WHEREUPON, at 3:45 o'clock P.M., the meeting was concluded.)

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