AD-A015 587

LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS

James A. Harrington

Alabama University

Prepared for:

Army Missile Command
Defense Advanced Research Projects Agency

August 1975

UAH Research Report No. 177 290116

The University Of Alabama In Huntsville

LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS

by

James A. Harrington, PI

205-895-6404
Department of Physics
The University of Alabama in Huntsville
Huntsville, Alabama 35807

ARPA Order No. 2314 Contract No. DAAH01-74-C-0437

Contractor: The University of Alabama in Huntsville

Amound of Contract: $56,000

Effective Date: 9 Jan. 1974 Expiration Date: 9 Nov. 1975

Semi-Annual Technical Report

9 January 1975 through 9 July 1975

"The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government".

August, 1975

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS	5. TYPE OF REPORT & PERIOD COVERED Semi-Annual Technical Report 9 Jan 1975 - 9 July 1975
	6. PERFORMING ORG. REPORT NUMBER UAH Research Report No. 177
7. AUTHOR(s) James A. Harrington	8. CONTRACT OR GRANT NUMBER(s) DAAH01-74-C-0437
9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of Alabama in Huntsville P. O. Box 1247, Huntsville Al 35807	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Commander, U. S. Army Missile Command Redstone Arsenal AL 35809 Attention: AMSMI-IPBE	12. REPORT DATE August 1975
	13. NUMBER OF PAGES 45
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Commander, U. S. Army Missile Command Redstone Arsenal AL 35809 Attention: AMSMI-RNM	15. SECURITY CLASS. (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release - distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Laser, laser windows, optical materials, chemical lasers, optical absorption, infrared materials.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The optical absorption has been measured at DF and HF wavelengths in a wide variety of materials which show promise for use as windows on high powered chemical lasers. These measurements, which were made using DF-HF chemical laser calorimetric techniques, are compiled in this report in an effort to bring together in a systematic fashion all the absorption data taken to date. Such a compilation of data not only allows a quick determination of the lowest loss materials currently available but also enables one to draw several important conclusions regarding the optical absorption in the 3.8 to 2.7 micron region. One significant but perplexing result is the fact that no total absorption coefficient measured in this region by us to date is less than $10^{-4}cm^{-1}$. This is unusual because most materials studied have intrinsic levels far below this value and some of the same materials have measured absorption less than $10^{-4}cm^{-1}$ at 5.25 and 1.06 microns. The reason for the higher absorptions in the DF-HF laser region is shown to be in part due to the higher surface absorption here than at other infrared laser frequencies. The identification and characterization of these surface absorption mechanisms such as those arising from organic solvents used in surface cleaning and from mechanical polishing, is a major thrust of this report.

The specific materials studied in detail include ZnSe and SrF_2 from Raytheon, Ge and Si from Cal Tech, NaF from NRL, CaF_2 from Hughes Research Labs, Yttralox from GE, and other miscellaneous alkali halides including NaCl, KCl, LiF, and KBr. Since surface absorption has been a prime concern, many of these samples had their surface and bulk absorption measured. ZnSe and SrF_2 showed a high surface absorption ($10^{-3}cm^{-1}$ range) while the alkali halides and some CaF_2 exhibited little. At this point the lowest loss materials at 3.8 and 2.7 microns would be the alkaline earth fluorides and NaCl, ZnSe among semiconductors, and Yttralox among oxides. It is expected, however, that materials will improve and that surface polishing and cleaning techniques advanced to the point that total absorptions less than $10^{-4}cm^{-1}$ will be measured in the near future.

PREFACE

This third semi-annual report describes our continuing study of the optical properties of low loss window materials for chemical lasers. The work described herein was performed during the period from 10 January 1975 to 9 July 1975 on Contract No. DAAH01-74-C-0437, ARPA Order 2614. Participating in the research were, in addition to the principal investigator James A. Harrington, Don Gregory, William Otto, and James Rowe.

LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS

by

James A. Harrington

Department of Physics
The University of Alabama in Huntsville
Huntsville, Alabama 35807

Semi-Annual Technical Report
9 January, 1975 to 9 July, 1975

August, 1975

Prepared for

U.S. Army Missile Command
Redstone Arsenal, Alabama 35809
ATTN: AMSMI-RNM

Sponsored by

Defense Advanced Research Projects Agency
ARPA Order No. 2614

ic

SUMMARY

The optical absorption has been measured at DF and HF wavelengths in a wide variety of materials which show promise for use as windows on high powered chemical lasers. These measurements, which were made using DF-HF chemical laser calorimetric techniques, are compiled in this report in an effort to bring together in a systematic fashion all the absorption data taken to date. Such a compilation of data not only allows a quick determination of the lowest loss materials currently available but also enables one to draw several important conclusions regarding the optical absorption in the 3.8 to 2.7 micron region. One significant but perplexing result is the fact that no total absorption coefficient measured in this region by us to date is less than $10^{-4}cm^{-1}$. This is unusual because most materials studied have intrinsic levels far below this value and some of the same materials have measured absorption less than $10^{-4}cm^{-1}$ at 5.25 and 1.06 microns. The reason for the higher absorptions in the DF-HF laser region is shown to be in part due to the higher surface absorption here than at other infrared laser frequencies. The identification and characterization of these surface absorption mechanisms such as those arising from organic solvents used in surface cleaning and from mechanical polishing, is a major thrust of this report.

The specific materials studied in detail include ZnSe and SrF_2 from Raytheon, Ge and Si from Cal Tech, NaF from NRL, CaF_2 from Hughes Research Labs, Yttralox from GE, and other miscellaneous alkali halides including NaCl, KCl, LiF, and KBr. Since surface absorption has been a prime concern, many of these samples had their surface and bulk absorption measured. ZnSe and SrF_2 showed a high surface absorption ($10^{-3}cm^{-1}$ range) while the alkali halides and some CaF_2 exhibited little. At this point the lowest loss materials at 3.8 and 2.7 microns would be the alkaline earth fluorides and NaCl, ZnSe among semiconductors, and Yttralox among oxides. It is expected, however, that materials will improve and that surface polishing and cleaning techniques advanced to the point that total absorptions less than $10^{-4}cm^{-1}$ will be measured in the near future.

LIST OF TABLES

TABLE OF CONTENTS

I. INTRODUCTION

In past reports on progress in materials for use as chemical laser windows, a large variety of samples have been studied. Over the past few months, we have continued to survey promising candidates for operation at DF (3.8 microns) and HF (2.7 microns) wavelengths but, in addition, we have also taken a closer look at some of those materials which at the moment seem to be the strongest contenders for future use on chemical lasers. In particular, the alkaline earth fluorides and zinc selenide have been more thoroughly investigated especially in terms of the contribution of surface absorption to the total absorption. The amount of surface absorption has been seen to vary greatly among different materials with zinc selenide having the highest surface absorption and the alkali halides and alkaline earth fluorides the least. In almost every case, however, the total absorption seems to be dominated by surface effects and it is for this reason that the primary emphasis of our recent work has been on the characterization and elimination of these absorption mechanisms.

Having surveyed a large number of materials it is now possible to bring together in a systematic way all results of our calorimetric measurements of the absorption coefficient β at chemical laser frequencies. This is done graphically in Sec. 4. One important point can be observed from such a compilation of data: no sample measured to date has a total β less than 10^{-4}cm^{-1} at either HF or DF frequencies. This is rather perplexing in view of the fact that most materials of interest have intrinsic levels far below this value and that, for some of the hosts, β's less than 10^{-4}cm^{-1} have been measured at 5.25[1] and 1.06[2] microns. It is felt that a major reason for this lies in the higher surface absorptions encountered at chemical laser frequencies. In addition to the obvious problem of OH^- contamination at HF wavelengths, it has been found that most organics commonly used to clean surfaces of window samples have strong absorption bands in the DF to HF region. In some cases it has been observed that chemical cleaning with an appropriate solvent just prior to measurement can reduce the absorption by one half its value prior to cleaning. This sensitivity to chemical cleaning is not shared by materials measured at 5.25 or 1.06 microns and it is probably for this reason that absorption coefficients are lower there than at chemical laser frequencies. Efforts will be reported on the methods used to minimize this source of absorption. Hopefully, during the next six months materials will have continued to improve and surface absorption minimized to the point that absorptions below 10^{-4}cm^{-1} will be measured.

A review of the experimental techniques used to measure the absorption as well as the procedures involved in handling and preparing the samples for measurement is given in the next section. Following this, the bulk of the report will consist of a detailed description of our absorption coefficient results arranged in order of individual materials or classes of materials. Finally, a summary of results for all substances studied will be given along with recommendations of the best materials at the present time for use as low loss chemical laser windows.

II. EXPERIMENTAL TECHNIQUES AND PROCEDURES

A. Calorimetry

Standard laser calorimetric methods[3] were employed to measure the small absorption coefficients at chemical laser frequencies. The experimental set-up, which has been described in greater detail in a previous ARPA report[4], consists of an air calorimeter and a small cw DF-HF chemical laser of our own construction.[5] The calorimeter is conventional except for a series of small holes along the bottom which admit dry nitrogen purge gas when the calorimeter is used for HF measurements. In practice, the absorption of HF radiation by air in the calorimeter and subsequent distortion of the heating-cooling curves due to heating of the air has not been detected even without the purge. Purge gas is frequently used, however, to minimize any errors in the temperature-time data and in measuring the laser power.

A three-slope method[3] is applied to the data for the calculation of β. The surface absorption has been measured by two different techniques. The first is an older method in which the total absorption is measured as a function of sample length L. An extrapolation of a plot of βL vs. L to zero length then gives a measure of the surface absorption while the slope gives the bulk β. This method, unfortunately, has the disadvantage that all surfaces for each length should be identically prepared and thus of equal value. Even with this constraint, this method has been successfully applied to various hosts, such as KCl[6], in order to get a good estimate of the surface absorption. Because of the necessity of equal surface conditions for at least three different lengths and the time required to prepare and measure all these samples, a more direct method is desirable. Such a method was developed by Hass[7] and involves measuring the absorption in long, bar shaped samples. With the appropriate sample geometry it is possible to distinguish between surface and bulk absorption directly from slope changes in the temperature-time curves. Strictly speaking this should be done by curve fitting the data to a computer calculated heat flow equation but in practice reliable values can be obtained directly from the raw data. A few of the measurements reported in the next section involve the use of bar type samples but more work with this type of sample will be reported on in an upcoming ONR report and elsewhere.[8]

B. Crystal Preparation

The samples studied have been procured from a wide variety of window material processors. In most cases the samples are received with a good surface finish. When this is the case, the sample is run as-received in order to provide the supplier with a β unbiased by any of our polishing and cleaning techniques. After an initial measurement, the surfaces are examined using Normarski microscopy and then refinished. Mechanical polishing involves a final polish with Linde B and isopropanol with intermediate polishes using diamond grit for the harder substances. For ZnSe the prescriptions of Hughes Research Lab[9] and Raytheon[10] for chemical etching and polishing on pitch laps were utilized. In the future more use will be made of pitch laps not only for ZnSe but for the alkaline earth fluorides as well.

As mentioned in the Introduction, surface cleaning just prior to measurement is one of the most important requirements for a reliable β. Popular CH-bonded solvents like methanol, ethanol, acetone, etc. which have absorptions[11] in the DF-HF region have been found to produce higher absorption coefficients in crystals washed with these than for crystals washed in, for example, carbon tetrachloride. At the present time, all crystals have a final cleaning in spectrograde CCl_4. In the future other solvents, such as Freon, will be evaluated. With a good surface finish and careful cleaning it has, on occasion, been possible to reduce the β of the as-received sample by one half its original value. Cases where this occurs are indicated in the explicit results that follow.

A constant threat to reliable β's at HF wavelengths is hydrolyzing of the surface. The dry N_2 purge minimizes this danger to some extent but greater care is needed. To prepare the sample's surface in a low humidity environment, a glove box has been obtained in which the humidity can be kept less than 10%. A vacuum calorimeter has just been built which can be loaded in the dry box so that the crystal can be both prepared and measured in a low water vapor atmosphere. Several of the samples (KBr and NaCl) have been measured using this apparatus and in the future full utilization will be made of this equipment.

All β measurements have been made using a multiline laser output. This output has been analyzed using DF and HF spectrum analyzers. The frequencies present in our multiline output are as follows (partial list, strongest to weakest):

DF (microns)	HF (microns)
3.75	2.738
3.837	2.906
3.876	2.866
	2.777
	2.818

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Zinc Selenide

An important material at 10.6 microns, zinc selenide holds great promise as a window at chemical laser frequencies as well. In our last report[4], only a very brief investigation was made into its optical absorption at DF-HF wavelengths. Since then we have begun an exchange program with Dr. Robert Donadio at Raytheon Research Laboratories to obtain state-of-the-art CVD ZnSe for more extensive absorption measurements. During the past six months we have received several samples which reflect Raytheon's best fabrication techniques at a particular time, and thus we have been able to monitor the usual evolutionary process of materials' improvement through changes in the optical absorption.

The oldest sample, grown several years ago, was ZnSe-96. This sample had a total β equal to $3 \times 10^{-3} cm^{-1}$ at 10.6 microns but had absorption coefficients almost 10 times greater at DF and HF wavelengths:

$$\beta(DF) = 3.3 \times 10^{-2} \pm 4\% \ cm^{-1}$$

$$\beta(HF) = 2.2 \times 10^{-2} \pm 7\% \ cm^{-1}.$$

These values were obtained from the as-received sample and no further work was pursued on this piece because better material was being received. In particular, ZnSe-96 exhibited the usual light-dark bands which often characterized

Raytheon's early material. It was decided to concentrate on the more recent ZnSe which was free of these obvious bands.

The next sample received for study was part of Raytheon's absorption standard series (No. 40). This sample had a total β equal to $1.98 \times 10^{-3} \pm 4\%\ \mathrm{cm}^{-1}$ at 10.6 microns as measured by us ($1.69 \times 10^{-3}\mathrm{cm}^{-1}$ as measured by Raytheon at 10.6 microns). Our value is that measured after cleaning the surfaces in methanol. On the as-received sample the 10.6 micron absorption was measured to be $2.84 \times 10^{-3}\mathrm{cm}^{-1}$. Here is an example of the effect of a simple chemical cleaning on the total β. In this case the absorption was reduced by about 50% by the methanol wash. The absorption at chemical laser wavelengths was found to be substantially reduced from the high values previously measured in ZnSe-96. The total β's were found to be,

$$\beta(\mathrm{DF}) = 2.2 \times 10^{-3}\mathrm{cm}^{-1}$$

$$\beta(\mathrm{HF}) = 4.0 \times 10^{-3}\mathrm{cm}^{-1}$$

for the sample after the methanol wash.

Even though the absorption was reduced to the low 10^{-3} cm^{-1} region at DF-HF frequencies, this was still far above the intrinsic level for this material. In order to determine how much of this absorption was due to the surfaces a third sample was obtained from Raytheon (Run I-20). This rectangular parallelepiped was cut into four lengths for βL vs. L measurements at 10.6, 3.8, and 2.7 microns.

For the DF-HF wavelength measurements the sample surfaces were mechanically polished using diamond grits with a final polish using Linde B and isopropanol. All surfaces were cleaned prior to measuring with spectrograde CCl_4. For the CO_2 calorimetry, the above finishes were further refined using the chemical etch (potassium ferricyanide) and associated prescription of Hughes Research Labs.[9] An important consideration in all of these measurements was that the surfaces were all treated identically for each series of measurements at a given laser frequency. It was found that mixing of the polishing methods, say one surface chemically etched, one mechanically polished could drastically influence the βL vs. L curve and make the results meaningless. This is because the surface absorption for ZnSe was found to be substantial and each surface preparation technique had to be evaluated individually owing to the fact that each could produce a widely different value.

The βL vs. L plots for all three laser wavelengths are shown in Fig. 1. A least squares fit was made to the data and the following β's extracted are listed in Table 1 along with the earlier ZnSe results which are summarized for completeness. The surface absorption shown is for <u>two</u> surfaces.

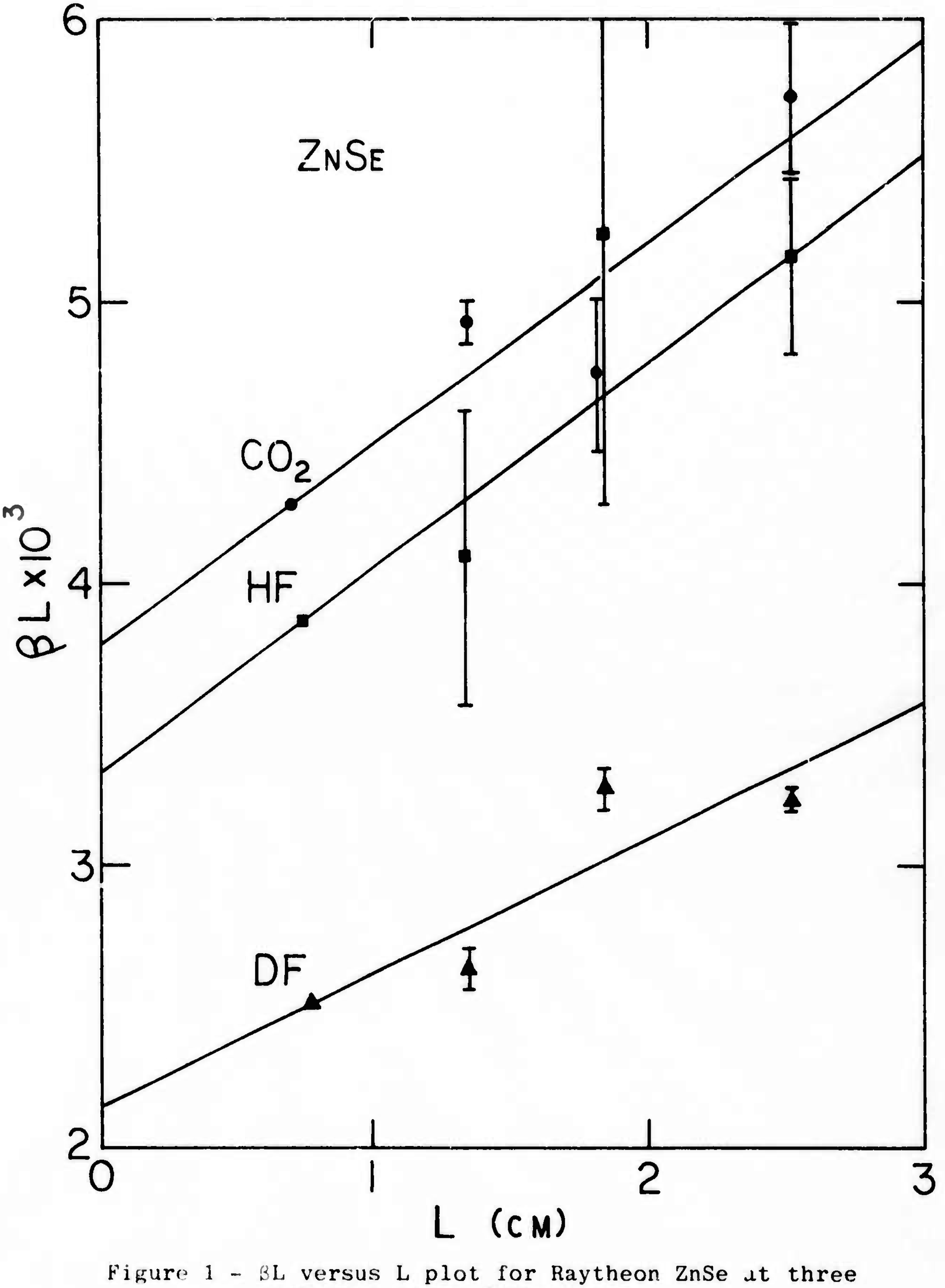


Figure 1 - βL versus L plot for Raytheon ZnSe at three different laser frequencies.

Table 1

Absorption Coefficients for ZnSe at CO_2, DF, and HF Wavelengths

Sample No.	Wave-length (microns)	β_{total}	β_{bulk} (cm^{-1})	$\beta_{surface}$ (cm^{-1})
ZnSe-96	10.6	3.0×10^{-3}	-	-
	3.8	2.2×10^{-2}	-	-
	2.7	3.3×10^{-2}	-	-
Std.No. 40	10.6	$1.98\times10^{-3}\pm4\%$	-	-
	3.8	2.2×10^{-3}	-	-
	2.7	4.0×10^{-3}	-	-
I-20	10.6	2.62×10^{-3}	$7.12\times10^{-4}\pm10\%$	$3.8\times10^{-3}\pm10\%$
	3.8	2.62×10^{-3}	4.8×10^{-4}	2.14×10^{-3}
	2.7	4.05×10^{-3}	7.34×10^{-4}	3.32×10^{-3}

Several important features can be gleaned from the results in Table 1. The first is that for the two most recent ZnSe samples supplied by Raytheon, No. 40 and I-20, the total absorption is about the same for all three laser lines. It is a little higher at HF but this may be due to the presence of OH^- in the bulk or on the surface of the samples. In a further reduction of the data into surface and bulk contributions, we see the surprisingly large surface absorption which dominates the total β. It is clear that a marked decrease in $\beta_{surf.}$ would mean a much improved window material since the β_{bulk} is quite good.

In the future several methods will be applied to ZnSe to try to reduce this surface absorption. A preliminary result has indicated that the chemical etch will lower the absorption at DF wavelengths so that more work will be done with this etch. Pitch laps will be used following the recipe of Raytheon.[10] In addition, use will be made of long bar samples to more easily separate bulk and surface absorption especially when it is desired to try a series of surface preparations. In doing this it is desired to reduce the surface absorption below $10^{-3}cm^{-1}$ into the region where the dominant contribution to the absorption is from the bulk.

B. Strontium Fluoride

Strontium fluoride has the potential of being one of the best window materials at chemical laser wavelengths owing to partially compensating physical parameters. In terms of figure of merit this means a large power may be transmitted before the window fractures or optically distorts the beam.[12] In the last report results were given for all the alkaline earth fluorides.[4] During the past six months our efforts on SrF_2 have been restricted to the cast SrF_2 provided by Dr. Chuck Willingham and Dr. Dick Newberg of Raytheon Research Labs. This material had exhibited low β's in the past so we decided to pursue it further to try to learn about the surface absorption as well as the bulk absorption.

The first sample studied was an irregular shaped piece, No. VHP-275. Unfortunately, inhomogenities in β were detected across the sample but several representative values were as follows for different positions of the laser beam:

$$\beta(\mathrm{DF}) \begin{cases} 7.5 \times 10^{-4}\mathrm{cm}^{-1} \\ 8.5 \times 10^{-4}\mathrm{cm}^{-1} \end{cases}$$

$$\beta(\mathrm{HF}) \begin{cases} 2.1 \times 10^{-3}\mathrm{cm}^{-1} \\ 1.5 \times 10^{-3}\mathrm{cm}^{-1} \\ 7.8 \times 10^{-4}\mathrm{cm}^{-1} \end{cases}$$

This sample was not pursued further due to these and even larger inhomogenities found in β.

The major portion of the effort on this host was devoted to Raytheon SrF_2(VHP-348). This rectangular parallelepiped (0.86 x 1.88 x 4.44 cm) was used to obtain βL vs. L data. The first set of data taken were on the as-received sample. Then due to some unusual discrepancies observed in β for the various lengths (discussed below) and because the surfaces as viewed by Normarski microscopy were rather scratched, the surfaces were repolished. The repolishing involved using Linde B and distilled water followed by a CCl_4 rinse.

The results for the as-received and repolished SrF_2 sample are given below in Table [illegible] each length. From these results it is easily seen that there is consistent

Table 2

Absorption Coefficient for SrF_2(VHP-348) at DF and HF Wavelengths

Sample Surface	Wavelength (microns)	Path Length (cm)	β_{total} (cm^{-1})
As received	3.8	4.44	$7.0\times10^{-4}\pm34\%$
		1.88	$1.0\times10^{-3}\pm14\%$
		0.86	$1.2\times10^{-3}\pm10\%$
As received	2.7	4.44	$6.3\times10^{-4}\pm15\%$
		1.88	$1.6\times10^{-3}\pm28\%$
		0.86	$1.9\times10^{-3}\pm20\%$
Repolished	3.8	4.44	$4.1\times10^{-4}\pm10\%$
		1.88	$7.7\times10^{-4}\pm19\%$
		0.86	1.7×10^{-3}
Repolished	2.7	4.44	$3.8\times10^{-4}\pm5\%$
		1.88	$1.1\times10^{-3}\pm5\%$
		0.86	$2.4\times10^{-3}\pm9\%$

non-uniformity in the β values between the longest side (4.44 cm) and the other two sides at either DF or HF frequencies. This makes a plot of βL vs. L meaningless and thus no such plots are shown of the above data.

The problem remains to understand this peculiar result of an absorption coefficient being significantly different along one direction of cast, polycrystal-type material. It was thought at first that this anisctropy in β was due to surface finishing or residual stress in the sample. From Table 2, repolishing the surfaces has not improved the discrepancy in the absorption coefficient so that it is felt that this is not an effect of crystal polishing. Next, the sample was viewed in crossed polarizers. While the crystal did exhibit the usual amount of stress birefringence observed for polycrystalline materials, there was no evidence for any large or small amount of stress along a preferred direction. Thus stress is not thought to be a significant factor contributing to the anisotropic absorption.

It was suggested by Dr. Chuck Willingham that the effect being observed is due to anisotropic surface absorption. Such surface absorption conditions could occur if different crystalographic directions are exposed at the different faces. For this sample the orientation of the grains is not known at present but this will be determined in the near future. Therefore, while this is a plausible explanation, it is merely conjecture that this is in fact what is happening in our case and more work needs to be done to determine the nature of this anisotropy.

It is unfortunate that a meaningful surface absorption could not be extracted from all of this data. It is still felt that SrF_2 has a low bulk absorption in general and is therefore a strong window candidate. In this next period more SrF_2 from Raytheon will be procured for evaluation. In addition some new single crystal material will also be measured.

C. Silicon and Germanium

To investigate further the optical properties of semiconductors, several samples of silicon and one germanium sample were acquired. Some silicon and the one germanium were kindly provided by Prof. Tom McGill of California Institute of Technology. Their single crystal silicon came from Wacker Chemical Company in Germany and was P type with a high resistivity of 15,000 ohm-cm. The germanium is ultrapure, highly intrinsic material from a source unknown to us (material used in electron-hole droplet studies). A sample of low resistivity (14.5 ohm-cm), polycrystal silicon was obtained for comparison from Unique Optical.

The results of the chemical laser calorimetric measurements are shown below in Table 3. Commercial chemical polishes were applied to both the germanium and silicon samples obtained from Cal Tech. Before and after polish measurements are shown for germanium, only the after polish

Table 3

Absorption Coefficients for Ge and Si

at DF and HF Wavelengths

Sample	Wavelength (microns)	β_{total} (cm^{-1})	Comment
Ge (Cal Tech)	3.8	1.6×10^{-2}	Before polish
		$1.35 \times 10^{-2} \pm 4\%$	After polish
	2.7	1.6×10^{-2}	Before polish
		$1.3 \times 10^{-2} \pm 1\%$	After polish
Si (Cal Tech)	3.8	$7.85 \times 10^{-4} \pm 6\%$	15,000 Ω-cm
	2.7	$5.5 \times 10^{-3} \pm 2\%$	
Si (Unique Optical)	3.8	$2.53 \times 10^{-1} \pm 3\%$	14.5 Ω-cm
	2.7	$1.4 \times 10^{-1} \pm 3\%$	

for silicon. No polish was applied to the silicon from Unique Optical since no polish could reduce this terribly high absorption.

The β values for the Cal Tech silicon are quite low for a semiconductor. This particular material could serve well as a laser window material if absorptions in this range could be maintained. An attempt at using a more inexpensive polycrystalline sample fails badly when compared to this high resistivity Si. For Si then one should use the highest resistivity material available.

Germanium has a disappointingly high β at both chemical laser frequencies. A slightly n-doped material would probably have yielded a lower absorption [13] No further efforts are planned for investigation of this host.

D. Yttralox

Yttralox is a cubic, polycrystalline ceramic (90% Y_2O_3 and 10% ThO_2)[14] which is showing increasing potential as a window for short wavelength lasers. This oxide material is produced by General Electric Corporate Research and Development Laboratories and is kindly provided to us in an exchange program with Dr. Chuck Greskovich. In the last report[4] we had made some initial measurements on this material. The β values for both HF and DF frequencies were about 1.4×10^{-2} cm^{-1} on the as-received samples. (N.B. Due to an error in the specific heat measurements made by GE this value was earlier reported[4] to be $6 \times 10^{-3} cm^{-1}$. All β values quoted in Table 4 incorporate the correct specific heat.) The reason for this high extrinsic absorption was the presence of strong impurity bands lying directly between the 3.8 and 2.7 micron laser lines (cf. last semi-annual report[4]). These impurity bands, which are presumably associated with oxygen or OH^- impurities, are also common to other oxides eg. MgO. The reduction of these bands, which clearly limit the absorption coefficients at DF and HF wavelengths, could lower the absorption to near the intrinsic value of 1 x $10^{-4}cm^{-1}$ at 3.8 microns.

During this past reporting period the emphasis has been on the elimination of this impurity absorption. Dr. Greskovich has suggested that these bands might be associated with oxygen vacancies in the material and that a treatment of the sample in a small amount of oxygen at high temperatures might drive oxygen into these vacancies making the ceramic more stoichiometric. In order to test this idea two previously measured samples ($\beta \sim 1.4 \times 10^{-2}cm^{-1}$) were returned to General Electric for conditioning in a high temperature, oxygen-containing (~ 10 ppm O_2 in argon) atmosphere. During treatment one sample melted but the other survived and was returned to us for further optical measurements.

A most surprising and delightful result occurred on remeasuring the oxygen treated samples. The DF absorption coefficient had been reduced by a factor of 6 and the HF a factor of over 4. The actual values are given in Table 4 below. Further, the sample was measured on the Beckman IR-12 and whereas before the infrared scan quite readily exhibited the impurity bands (cf. Fig. 8 of Ref. 4), this time there was <u>no</u> indication of any impurity absorption. Therefore, both the ir spectrum and laser calorimetry indicate a strong

Table 4

Absorption Coefficients for Yttralox

at DF and HF Wavelengths

Sample	Wavelength (microns)	β_{total} (cm^{-1})
As-received	3.8	$1.4x10^{-2}$
	2.7	$1.4x10^{-2}$
After oxygen treatment	3.8	$2.3x10^{-3}$
	2.7	$3.8x10^{-3}$

reduction of these bands. However, from Table 4 we see that the material is not yet intrinsic. Thus, the treated sample has been sent back to General Electric for another exposure to high temperature oxygen and hopefully another reduction of the absorption.

E. Sodium Fluoride

Sodium fluoride was only briefly investigated in the last report with the study of one sample obtained from Optovac. Since then an exchange program has been initiated with Dr. Phil Klein of Naval Research Laboratory to provide high quality NaF crystals from their extensive NaF purification program. Several of these samples have now been received and measured with more expected in the future.

The two samples reported on here were received polished and therefore measured as-received. One sample had a small amount of Li (1 mole %) added to the melt. The other was a pure, second generation grown ingot. The results for both samples are given in Table 5 below. In each case the values given represent the average value after repolishing the samples and chemical cleaning just prior to measurement.

Table 5

Absorption Coefficients for NaF at DF and HF Wavelengths

Sample	Wavelength (microns)	β_{total} (cm^{-1})
NaF:Li (NRL 960)	3.8	7×10^{-4}
	2.7	9×10^{-4}
NaF (2nd Gen. No. 11)	3.8	2.7×10^{-4}
	2.7	4.3×10^{-4}

Quite clearly, the purer, second generation NaF has lower overall absorption as might be expected <u>a priori</u>. One reason for this is the reduction of the OH^- concentration which occurs in the second generation growth process.[15] A reduction of the OH^- has correspondingly reduced the HF absorption. One can be even more specific and look at the position of the main OH^- band in NaF which occurs at 2.78 microns and compare this with the multiline HF laser output (cf. Sec. 2B). One sees that indeed the strongest HF lines are very near the OH^- line in NaF. The lines at 2.738 and 2.777 microns should be strongly absorbed by the OH^- and thus a measurement of the HF β is an indication of the OH^- impurity content in the crystal. Tunable HF laser calorimetry, of course, would be ideal for a more definitive study (planned for the future) but the multiline output at least gives an average result for the amount of OH^- present. Further work along these lines should be helpful to crystal growers of NaF and many other substances for it will help indicate the OH^- impurity levels.

F. Miscellaneous Alkali Halides

In this section we shall summarize the results of absorption coefficient measurements on LiF, NaCl, KCl, and KBr. These materials have been routinely measured as part of our overall material's characterization program but as yet have not received the large amount of individual attention accorded the previously described measurements. Some of these hosts have shown some very low β's and therefore greater efforts will be devoted to them in the upcoming period.

The LiF was obtained from Mr. Don Leslie at Harshaw Chemical Co. The NaCl measured was Harshaw Polytran^{TM}. Naval Research Laboratory and Dr. Phil Klein kindly provided the RAP grown KCl and the KBr. All materials were polished by us and chemical polishes were applied to the KCl and KBr as required.

The results for these four hosts are given in Table 6. The data for LiF indicate the intrinsic nature of this salt at DF frequencies. Deutsch[16] has published a β versus ω curve for LiF and from this we extract an intrinsic β of $1 \times 10^{-3}\text{cm}^{-1}$ at around 3.8 microns. The frequency spread of the DF multiline output influences the β value measured since our value is an average over this small frequency range. Thus the average DF β in LiF of about $1.8 \times 10^{-3}\text{cm}^{-1}$ is essentially intrinsic with the difference between $\beta_{\text{meas.}}$ $(1.8 \times 10^{-3}\text{cm}^{-1})$ and β_{int} $(1 \times 10^{-3}\text{cm}^{-1})$ being mostly due to the frequency spread of the multiline laser output used in the measurements.

The Polytran^{TM} NaCl has a very low DF absorption - the lowest measured value of any crystal studied to date. For some unknown reason KCl does not measure as low although it should. Both of these hosts as well as KBr are currently being measured in our vacuum calorimeter. This is necessary to minimize surface contamination. It is felt that these salt crystals may exhibit very low β's once surface con-

Table 6

Absorption Coefficients for LiF, NaCl, KCl, and KBr at DF, HF, and CO_2 Wavelengths

Sample	Wavelength (microns)	β_{total} (cm^{-1})
LiF (No. 1)	3.8	$2.4\times10^{-3} \pm 2\%$
	2.7	$7.7\times10^{-4} \pm 7\%$
LiF (No. 2)	3.8	$2.1\times10^{-3} \pm 7\%$
	2.7	$6.4\times10^{-4} \pm 30\%$
LiF (No. 3)	3.8	$1.8\times10^{-3} \pm 1\%$
	2.7	$8.0\times10^{-4} \pm 4\%$
NaCl (poly) (PRN 1)	3.8	$1.5\times10^{-4} \pm 57\%$
	2.7	$1.8\times10^{-3} \pm 10\%$
NaCl (poly) (PRN 2)	3.8	$6.2\times10^{-4} \pm 29\%$
	2.7	2.1×10^{-3}
KCl (NRL-B2)	3.8	$9.5\times10^{-4} \pm 3\%$
KBr (NRL-4)	10.6	1×10^{-3}

tamination can be controlled. One reason for this is that surface preparation, i.e. chemical polishing techniques, are so well understood for these substances that it should be possible to reduce surface absorption to a very low level. Another reason is that these materials are now produced very pure due to the large amount of technology that has gone into the crystal growth methods of salts. Further, more careful studies of these crystals are planned.

G. Hughes Research Calcium Fluoride

In a recent exchange program with Mr. Art Braunstein of Hughes Research Laboratories, several CaF_2 samples have been received for measurement. These samples are in support of a Hughes DF window coating program sponsored by ONR. The samples received were forged CaF_2 and single crystal CaF_2. All were polished and chemically cleaned then potted with a plastic film prior to shipping. Just prior to measurement, this protective coating was removed. It was observed in some cases that on further cleaning the absorption went down. This may be due to the removal of a residue left on the surface by the plastic film.

The results for several samples are listed below in Table 7 along with comments pertaining to the type of surface finish used. From the table it can be seen that the single crystal material has lower absorption than the forged material. In fact the single crystal material is the lowest DF β measured to date in CaF_2. Actually, another piece of forged CaF_2 in the shape of a long bar has indicated, in measurements to be published later, that the β in the forged material is not always so high. In fact the bulk β for the

Table 7

Absorption Coefficients for CaF_2 at DF and HF Wavelengths

Sample	Wavelength (microns)	β_{total} (cm^{-1})	Comments
Forged CaF_2 (Single Crystal)	3.8	$1.3 \times 10^{-3} \pm 8\%$	As received
		$1.8 \times 10^{-3} \pm 2\%$	After mech. polish
		$4.6 \times 10^{-3} \pm 13\%$	After CCl_4 wash
	2.7	$3.7 \times 10^{-3} \pm 7\%$	As received
		$3.0 \times 10^{-3} \pm 4\%$	After mech. polish
		$3.0 \times 10^{-3} \pm 9\%$	After CCl_4 wash
CaF_2 (Single Crystal H1309-07-A)	3.8	$5.5 \times 10^{-4} \pm 11\%$	As received
		$1.7 \times 10^{-4} \pm 9\%$	After mech. polish
	2.7	$9.3 \times 10^{-4} \pm 8\%$	As received
		$4.9 \times 10^{-4} \pm 19\%$	After mech. polish

bar is in the low $10^{-4} cm^{-1}$ range. The β values quoted in Table 7 are for a forged disk and for some reason (maybe surface absorption) this is higher than for a forged bar.

H. Oklahoma State University Potassium Chloride

One sample of OSU KCl was received from Dr. Joel Martin. This sample (OSU-021875) was chemically polished and measured at 10.6 microns in our vacuum calorimeter. The average β measured was $7.4 \times 10^{-4} \pm 2\%$ at CO_2 wavelengths.

IV. SUMMARY OF EXPERIMENTAL RESULTS

In the preceding sections, detailed discussions on many of the most likely candidates for use as chemical laser window materials were presented. It is now possible to collect all of this data, as well as results from earlier progress reports,[4] into two composite graphs which represent at the present time the extent of our DF-HF absorption coefficient measurements. Such a composite will enable the reader to quickly determine the range of β's observed for any particular host studied. It is expected that materials will improve so that this list will be updated correspondingly to reflect these changes as well as additions of new materials.

The composite data at DF frequencies are shown in Fig. 2. The bars indicate the range of total (bulk plus surface) absorption measured. Fig. 3 shows results for the same samples at HF frequencies.

It is possible to cautiously draw some conclusions about the best potential laser window materials from Figs. 2 and 3. Care is necessary because the absorption is only one of

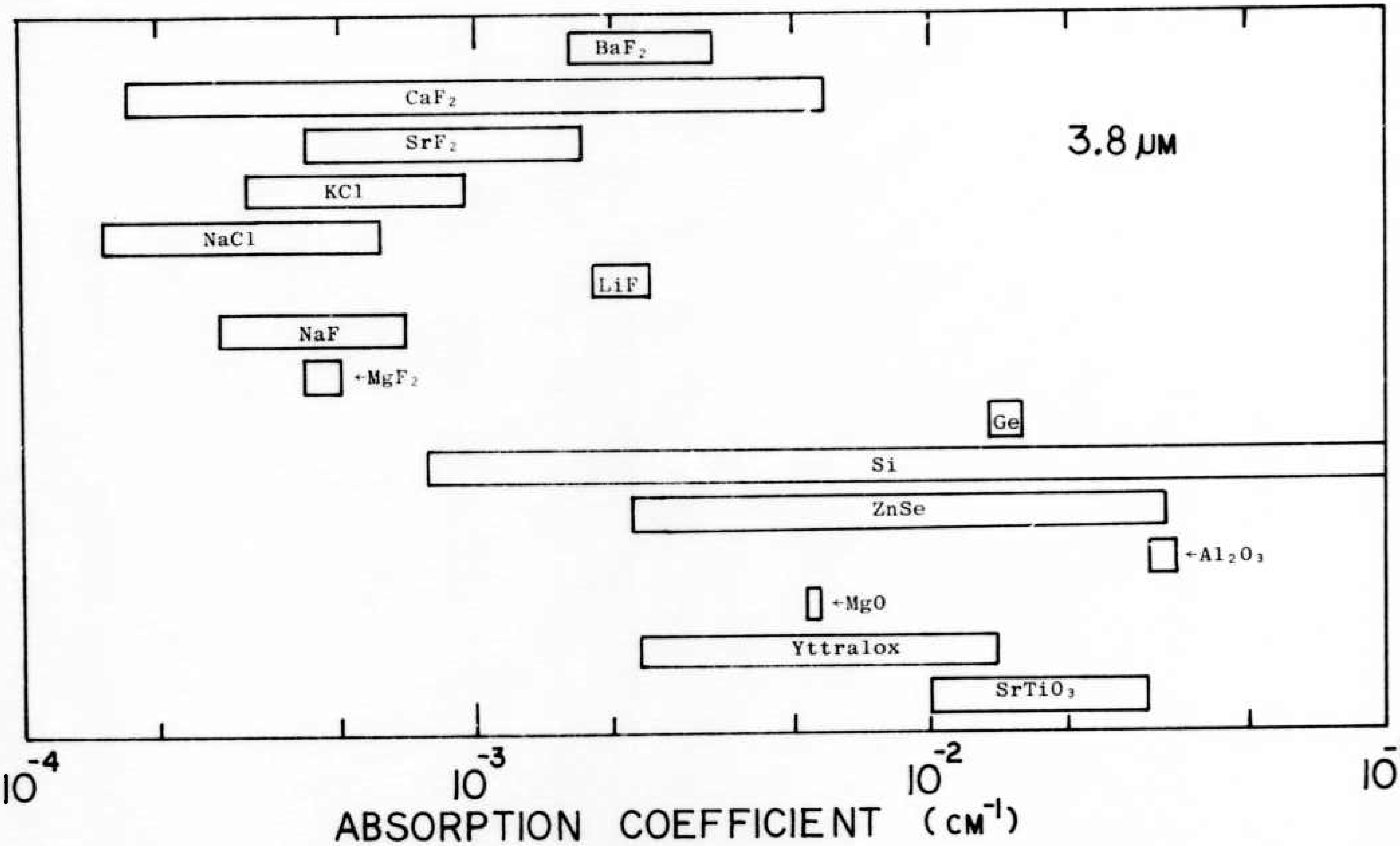


Figure 2 - Absorption coefficients for various materials at DF chemical laser frequencies.

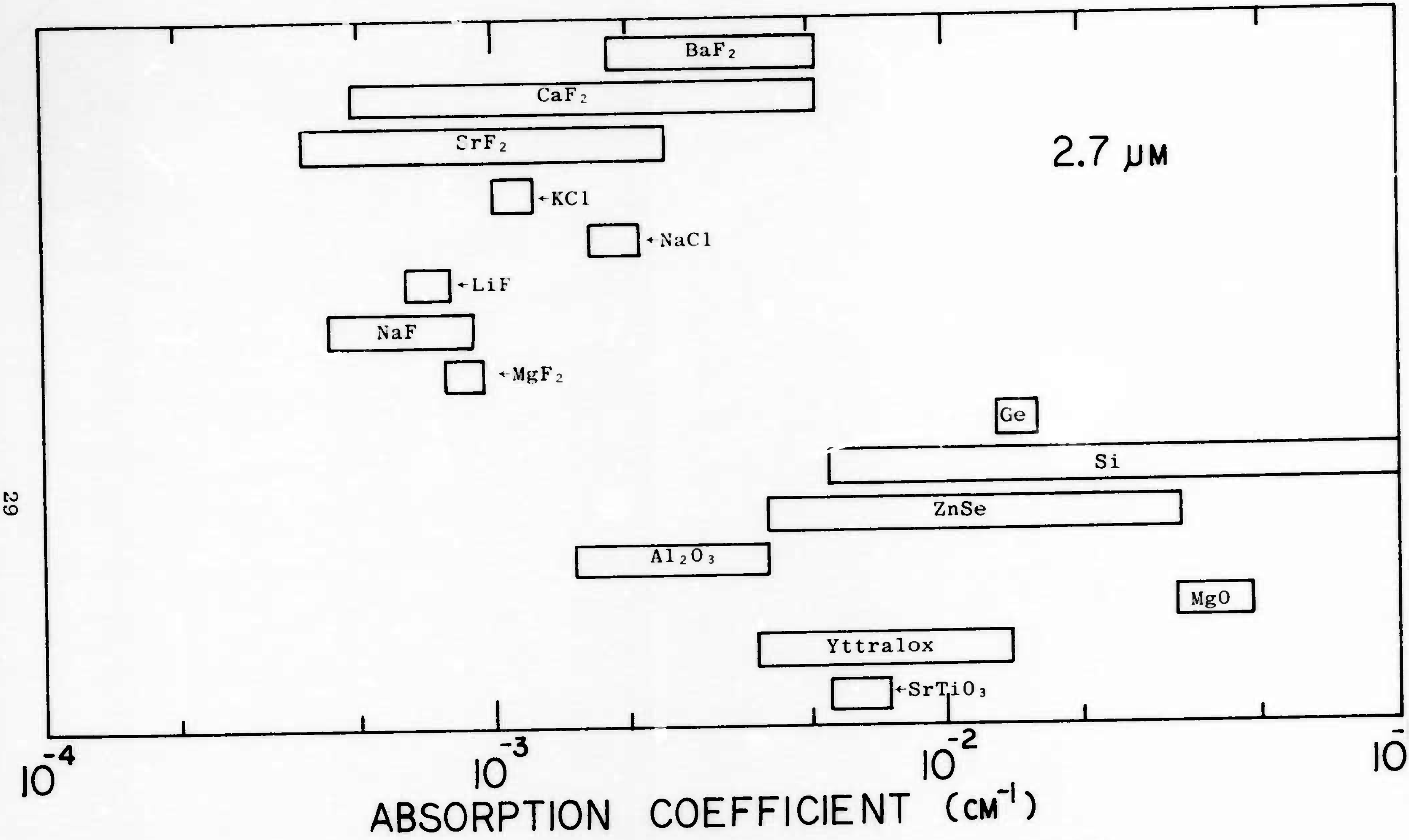


Figure 3 - Absorption coefficients for various materials at HF chemical laser frequencies.

several critical physical parameters which dictate the effectiveness of the material as a chemical laser window. Therefore, from essentially only an absorption coefficient point of view, one can say that the alkaline earth fluorides are one of the best window candidates at this time. Equally good in terms of a low range of β's are NaCl and NaF. The most promising oxide material would be Yttralox while the semiconducting material of greatest appeal would be ZnSe. These recommendations, as mentioned above, would have to be weighted in terms of other physical parameters entering, for example, the figure of merit for the material[12] in order to obtain the best window. In addition, of course, the specific requirements of the application would further limit the choice. In materials research programs across the country efforts continue to improve the above hosts so that it is likely that in the future these materials will continue to be highly recommended as the best window candidates.

REFERENCES

1. T. F. Deutsch in Third Conference on High Power Infrared Laser Window Materials, ed. by C. A. Pitha and B. Bendow, p. 13, February, 1974.
2. M. Hass, J. W. Davisson, H. B. Rosenstock, and J. Babiskin, Applied Optics 14, 1128 (1975).
3. M. Hass, J. W. Davisson, P. H. Klein, and L. L. Boyer, J. Appl. Phys. 45, 3959 (1974).
4. J. A. Harrington, Semi-Annual Technical Report, ARPA Order No. 2614, January, 1975.
5. J. A. Harrington, Final Technical Report, Contract No. DAAH01-74-C-0438, prepared for U.S. Army Missile Command, Redstone Arsenal, Alabama, March, 1975.
6. J. W. Davisson, M. Hass, P. H. Klein, M. Krulfeld in Third Conference on High Power Infrared Laser Window Materials, ed. by C. A. Pitha and B. Bendow, p. 31, February, 1974.
7. M. Hass, J. W. Davisson, H. B. Rosenstock, J. A. Slinkman, and J. Babiskin in Optical Properties of Highly Transparent Solids, ed. by S. S. Mitra and B. Bendow, Plenum Press, New York (in press).
8. J. A. Harrington, et al., to be published.
9. M. Braunstein in Third Conference on High Power Infrared Laser Window Materials, ed. by C. A. Pitha and B. Bendow, p. 863, February, 1974.

10. C. B. Willingham, Semi-Annual Technical Report, ARPA Order No. 2415, March, 1974.

11. Sadtler Standard Spectra, published by Sadtler Research Laboratories, Philadelphia, PA 19104.

12. M. Sparks and H. C. Chow, J. Appl. Phys. 45, 1510 (1974).

13. A. J. Bishop and A. F. Gibson, Applied Optics 12, 2549 (1973).

14. C. Greskovich and K. N. Woods, Amer. Cer. Soc. Bull. 52, 473 (1973).

15. P. H. Klein and J. W. Davisson in Fourth Conference on Infrared Laser Window Materials, ed. by C. R. Andrews and C. L. Strecker, p. 465, January, 1975.

16. T. F. Deutsch, J. Phys. Chem. Sol. 34, 2091 (1973).

Multiphonon Absorption of Alkali Halides and Quasiselection Rules

J. A. Harrington
University of Alabama in Huntsville, Huntsville, Alabama 35807
C. J. Duthler*
Xonics, Incorporated, Van Nuys, California 91406
F. W. Patten and M. Hass†
U. S. Naval Research Laboratory, Washington, D. C. 20375

A well-defined band has been observed in the low temperature infrared spectrum of KI, KBr, NaI, and RbCl in the region corresponding to the sum of three optical branch phonons and no corresponding band in the two- and four-phonon regions. These results can be accounted for by deducing an odd-even quasiselection rule for crystals having a gap between the optical and acoustical branches of the vibration spectrum.

The infrared absorption spectrum of alkali halides in the multiphonon region has received a great deal of experimental and theoretical attention in the past few years. For all alkali halide crystals which have been studied previously, the experimental results consist of an exponentially decreasing absorption as a function of frequency which contains no resolved structure in the three-phonon and higher multiphonon regions.[1] The theoretical interpretation of these results has been accounted for by a number of different approaches which have generally assumed that anharmonic coupling of the phonons to the reststrahl mode is the main source of the multiphonon absorption.[2-8] The present experimental results provide the first evidence for structure in the multiphonon absorption of alkali halides. A well-defined band has been observed in the low-temperature infrared spectrum of KI, KBr, NaI, and RbCl in the frequency region corresponding to the sum of three optical branch phonons. No corresponding bands have been observed in the two- and four-phonon regions.

Boyer et al. predicted structured absorption in these crystals for both even and odd sums of optical branch phonons. This structure arises from peaks that occur in the multiphonon density of states of these crystals which have a gap or near gap between the optical and acoustical branches of the phonon spectrum.[8] To account for the missing even sum bands observed experimentally, one must use a theory that takes proper account of transition matrix elements rather than simply using an average matrix element along with the multiphonon density of states.

A general theory of multiphonon absorption based on actual phonon interactions and dispersion relations has been presented by Sparks and Sham.[2] By proceeding along the lines of Sparks and Sham for the two-phonon case, Duthler and Sparks calculated the two-phonon absorption of NaI, which has a gap, to deduce a quasiselection rule.[9] This rule states that the two-phonon band associated with the sum of two optical branch phonons would be expected to be much weaker than the sum involving one optical and one acoustical branch phonon. The extension of a calculation of this nature and the generalization of the quasiselection rule to higher sum bands is presented here and can be applied to explain the present experimental results.

The experimental results for the infrared multiphonon spectrum for KI, KBr, RbCl, and NaCl are shown in Fig. 1 along with a comparison with the theory of Boyer et al.[8] and the results for NaI are shown in Fig. 2 along with a comparison with the present theory. Results have been taken on different crystals with different spectrometers and a correction for low temperature emittance of the sample was employed. Consequently, it is believed that the observed spectral structure is indicative of the bulk crystal and not associated with impurities or with the instruments. Some difficulty in reproducibility was found at lower absorption coefficients which is believed to be associated with surface effects, but spectra in this region are not essential to our argument.

The results for NaCl are typical of many crystals which have been studied previously in that the absorption coefficient decreases exponentially as a function of frequency with little or no structure in the three- and higher n-phonon regions, even at lower temperatures.[10] The calculations of Boyer suggest that some slight structure might be present at low temperatures for NaCl even beyond the two-phonon region. While the experimental results might be regarded as showing some structure, this would be difficult to confirm without additional measurements.

On the other hand, for KI, RbCl, NaI, and KBr, a definite band appears at low temperatures and some trace of this may exist at room temperature. The position of this band is in quite good agreement with an approach based upon a multiphonon density of states with a position for these gap crystals corresponding to the sum of three optical branch phonons. Furthermore, no corresponding band appears in the frequency range corresponding to two- and four- optical branch phonons. It can be seen in Fig. 2 for NaI that theoretical calculation by the approach to be described succeeds in reproducing the main features of the experimental data of NaI and is in accord with the quasiselection rule deduced from these calculations. As is evident from the data, the quasiselection rule appears to hold for the other gap and near gap crystals studied here.

In calculating the absorption coefficient, we include only the anharmonic contribution to the absorption in which a photon is absorbed by virtual excitation of the fundamental reststrahl mode which decays by emission of n final-state phonons. The contributions to the absorption from higher-order dipole moments is neglected, although there have been recent estimates that this contribution may be large.[11] As the transition matrix elements for both mechanisms are similar, the quasiselection rule and general shape of the absorption may have many common features using either mechanism.

In the following, we present a new form for the Sparks and Sham expression for the absorption from n-phonon absorption processes. At least for crystals having a gap, it is possible to show the existence of an n-phonon quasiselection rule which states that the splitting of the fundamental reststrahl phonon into an odd number of optical phonons is a strong process, while the splitting into an even number is a weak process.

Using the results and notation of Sparks and Sham, the "anharmonic" contribution to the absorption coefficient β as a function of frequency ω is

$$\beta(\omega) = \frac{4\pi N e^{*2}}{c\, m_r n_r \Omega} \; \frac{\omega \omega_f \Gamma(\omega)}{(\omega^2 - \omega_f^2)^2 + [\omega_f \Gamma(\omega)]^2} \quad , \tag{1}$$

where N is the number of unit cells in a crystal of volume Ω, e^* is the Born effective charge, c is the speed of light, m_r is the reduced mass of the two ions in the unit cell, n_r is the refractive index at frequency ω, ω_f is the frequency of the fundamental mode, and $\Gamma(\omega)$ is the relaxation frequency of the fundamental mode. The contribution of the n-phonon summation process to the relaxation frequency Γ is obtained in Ref. 2 from straightforward perturbation theory which yields

$$\Gamma_n(\omega) = \frac{2\pi}{\hbar^2}\,\frac{1}{n!}\left(\frac{\hbar}{2m_<}\right)^{n+1}\left(\frac{m_<}{m_r}\right)\omega^{-1}(n_\omega+1)^{-1}\left(\phi^{(n+1)}\right)^2\Lambda_n^2\,\Sigma_n\ , \tag{2}$$

where

$$\begin{aligned}\Sigma_n = N^{-n}\sum_{Q_1\cdots Q_n} N\Delta\left(\sum_{j=1}^{n}\vec{q}_j\right)\ \delta\left(\omega - \sum_{j=1}^{n}\omega_{Q_j}\right)\\ \times\prod_{j=1}^{n} 2\left|U_x(Q_j)\right|^2\,\frac{\left[n(\omega_{Q_j})+1\right]}{\omega_{Q_j}}\left[1+(-1)^{n+1}\cos\left(2\sum_{j=1}^{n}\varphi_{Q_j}\right)\right]\ ,\end{aligned} \tag{3}$$

and where

$$U_x(Q_j) = w_{<Q_jx} - (m_</m_>)^{1/2}\, w_{>Q_jx}\, e^{iq_x a_{nn}} = \left|U_x(Q_j)\right| e^{i\varphi(Q_j)}\ . \tag{4}$$

In Eqs. (2)-(4), $m_<$ and $m_>$ are the smaller and greater ionic masses; $n(\omega_{Q_j})$ is the Bose-Einstein occupation number of the phonon mode Q_j having wave vector $\vec{q}_j$, branch b_j, and frequency ω_{Q_j}; $w_{<Q_jx}$ and $w_{>Q_jx}$ are the x-components of the polarization vectors representing the displacements of the smaller and greater ions; a_{nn} is the spacing between nearest-neighbor ions; and $\varphi^{(n+1)}$ is the (n+1)th derivative of the assumed nearest-neighbor, central-force potential. In Eq. (2), Λ_n is a vertex correction factor to the simple vertex where the fundamental mode splits directly into n final-state phonons which is considered explicitly in writing Eqs. (3) and (4). The sum over phonon modes Q_j in Eq. (3) is unrestricted.

We have chosen to write the Fourier transform of the x-component of the relative displacement $U_x(Q_j)$ in Eq. (4) in terms of a magnitude and a phase φ_{Q_j}, which is slightly different than in Ref. 2 where Σ_n was incorrectly written into terms of the two products of the real and imaginary parts of the U_x term. The principal term involved in deduction of the quasiselection rule is the phase factor φ_{Q_j}. For a given branch, the phase factor φ_{Q_j} tends to remain constant through the Brillouin zone with $\varphi_{Q_j} \cong 0°$ for optical branches and $\varphi_{Q_j} \cong 90°$ for acoustical branches. This result has been calculated directly for the simple case of the linear diatomic chain with nearest-neighbor interactions. In the present calculations, the values of φ_{Q_j} were taken from lattice-vibration calculations for NaI using the deformation dipole model of Karo and Hardy[12] where the mean value of φ_{Q_j} was found to be 3°, 3°, and 4° for the three optical branches of NaI and 71°, 106°, and 115° for the three acoustical branches. By approximating the phase factor by 0° for optical branches and by 90° for acoustical branches, it is possible to arrive at the odd-even quasiselection rule for sums of optical branch phonons in gap crystals by insertion in Eq. (3). The slight departure from an exact value of 0° or 90° will result in a weakening of this selection rule for higher multiphonon processes. In the case of NaI, it would be expected to hold to about seven optical phonons.

Another simplification results from the realization that the magnitudes of $U_x(Q_j)$ for a given type of branch (optical or acoustical) are fairly constant throughout the Brillouin zone, at least for gap crystals, except for the relatively unimportant case of acoustical phonons near the zone center. This result is obtained using either a one-dimensional diatomic chain, or using the Karo and Hardy polarization vectors for NaI. If this approximation is made, the complicated $\vec{q}$ dependent sum in Eq. (3)

is reduced to a thermally weighted density of states in which the branches are kept distinct. These approximations also allow one to easily calculate vertex corrections, which are found to be negligible for NaI.

Details of the multiphonon absorption calculation using the quasiselection rule will be published elsewhere.[13] In the present calculation, it has been assumed that the width of the final-state phonons is less than the width of the histogram bins used in Fig. 3. This is a fairly good approximation at 80 K, but there is experimental evidence from inelastic neutron scattering data indicating that the phonons are broadened at room temperature, especially for the longitudinal optical branch where there is considerable broadening. Consequently, the room temperature theoretical curve is much sharper than the experimental curve where no distinct three-phonon peak is observed.[14] Incorporating a phonon linewidth in the present theory would improve the agreement.

In conclusion, the first experimental evidence for a well-defined band in the three-phonon region of an alkali halide has been found in KI, RbCl, KBr, and NaI, all of which have a gap or near gap between the optical and acoustical branches. This band, which corresponds to the sum of three optical branch phonons, can be accounted for by a generalization of a quasiselection rule which states that the odd sum band of optical branch phonons in the multiphonon spectrum is much stronger than the even sum. This quasiselection rule has been deduced for a crystal having a gap, but is believed to apply to some extent to all of the alkali halides.

We should like to thank L. L. Boyer for permission to use his unpublished calculated spectrum of RbCl, and M. Sparks for discussions concerning the theory of multiphonon absorption. One of us (JAH) would like to thank Mr. Don Leslie of Harshaw Chemical Co. for kindly providing the samples used in this study.

REFERENCES

*Research supported by the Advanced Research Projects Agency of the Department of Defense and monitored by the Defense Supply Service, Washington, D. C.

†Visiting Associate, California Institute of Technology, 1974-1975.

1. T. F. Deutsch, J. Phys. Chem. Solids 34, 2091 (1973).
2. M. Sparks and L. J. Sham, Phys. Rev. B 8, 3037 (1973).
3. D. L. Mills and A. A. Maradudin, Phys. Rev. B 8, 1617 (1973).
4. (a) T. C. McGill, R. W. Hellwarth, M. Mangir, and H. V. Winston, J. Phys. Chem. Solids 34, 2105 (1973); (b) T. C. McGill in "Proceedings of the International Conference on the Optical Properties of Highly Transparent Solids, 1975," edited by B. Bendow and S. S. Mitra (Plenum, New York, to be published).
5. A. K. Nedoluha in "Proceedings of the International Conference on the Optical Properties of Highly Transparent Solids, 1975," edited by B. Bendow and S. S. Mitra (Plenum, New York, to be published).
6. B. Bendow, S. C. Ying, and S. P. Yukon, Phys. Rev. B 8, 1679 (1973).
7. K. V. Namjoshi and S. S. Mitra, Phys. Rev. B 9, 815 (1974).
8. L. L. Boyer, J. A. Harrington, M. Hass, and H. B. Rosenstock, Phys. Rev. B 11, 1665 (1975) review the experimental data as well.
9. C. J. Duthler and M. Sparks, Phys. Rev. B 9, 830 (1974).
10. R. W. Pohl in "Proceedings of the International Conference on the Optical Properties of Highly Transparent Solids, 1975," edited by B. Bendow and S. S. Mitra (Plenum, New York, to be published) reports results for the gapless crystal NaF at low temperature.

11. See references cited in Refs. 4(b) and 8.

12. A. M. Karo and J. R. Hardy, Phys. Rev. 129, 2024 (1963).

13. C. J. Duthler (to be published).

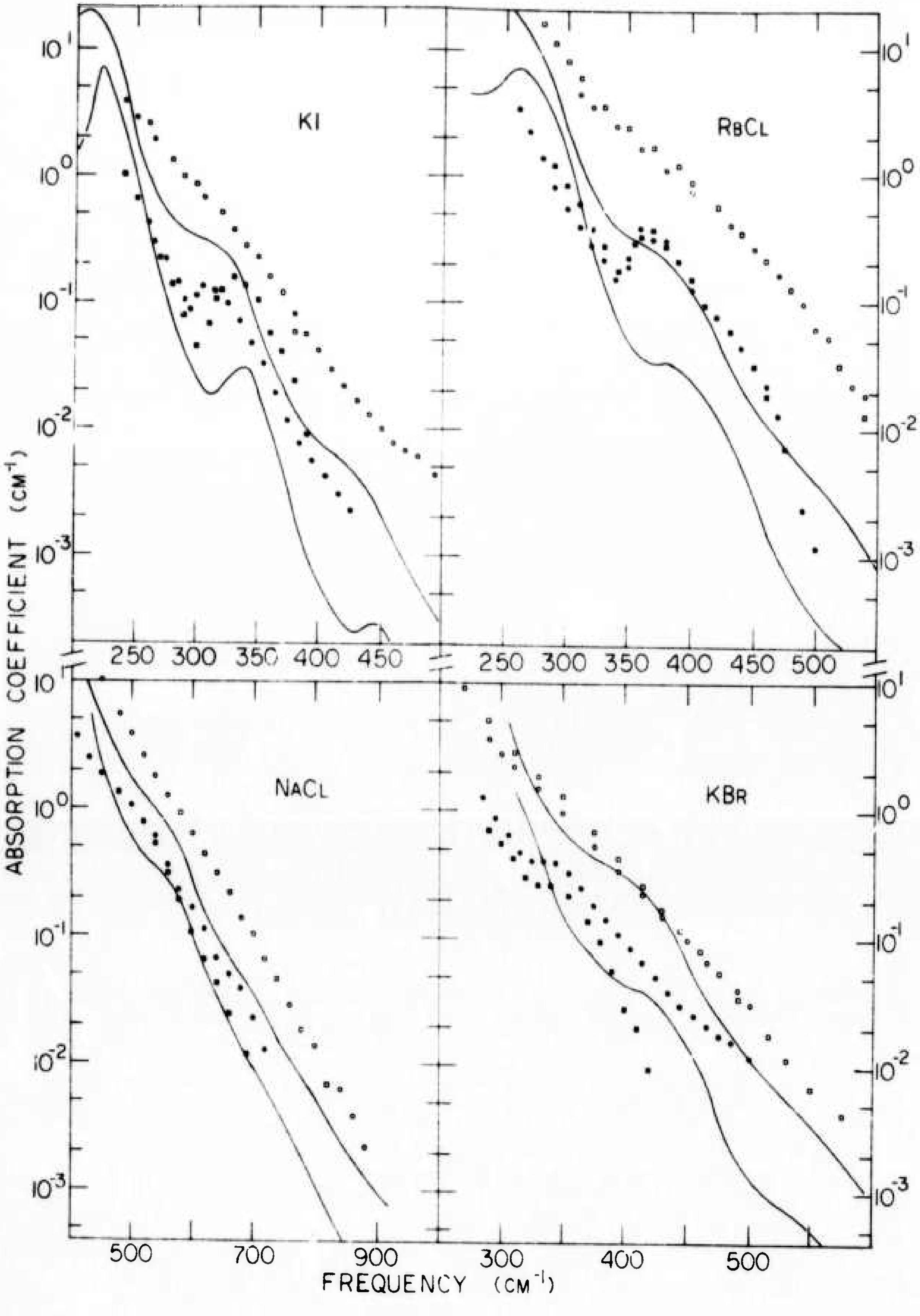
14. A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. 131, 1025 (1963); E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. London Ser. A287, 259 (1965).

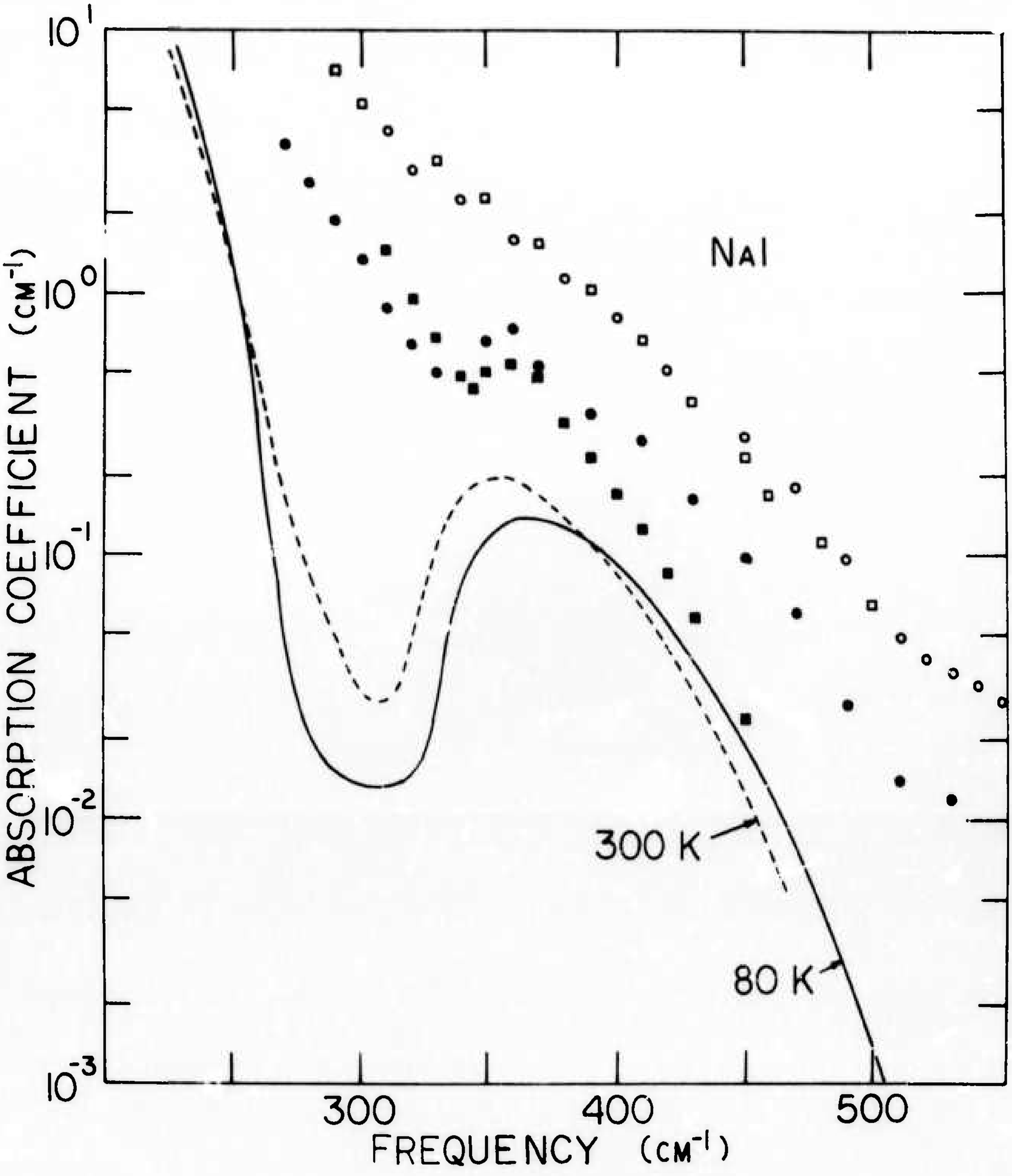
FIGURE CAPTIONS

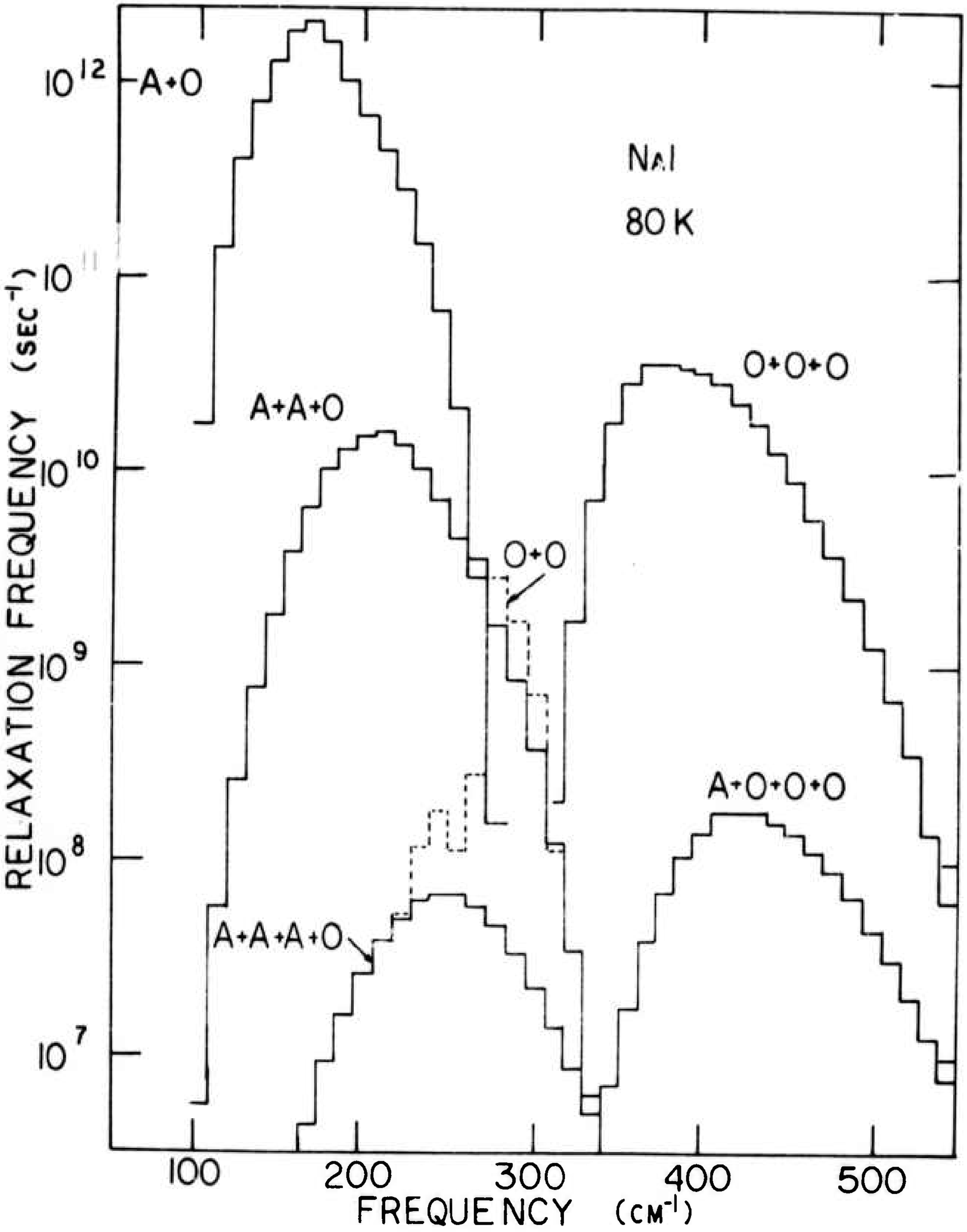
FIG. 1 Absorption coefficient as a function of frequency for some alkali halides compared with calculations (upper curve, 300 K, lower curve, 50 K) of Boyer, et al., Ref. 8. Upper data points are at 300 K (□ , UAH; ○ , NRL) while the lower set are at 80 K (■ , UAH; ● , NRL). For crystals with a gap or near gap (KI, KBr, RbCl), the band corresponds to the sum of three optical branch phonons. For NaCl, which lacks a gap, no well-defined structure is observed at low temperature.

FIG. 2 Absorption coefficient as a function of frequency for NaI compared with present calculations (solid and dashed curves). As in Fig. 1, the upper data are at 300 K (□ , UAH; ○ , NRL) and the lower data are at 80 K (■ , UAH; ● , NRL). The band corresponds to the sum of three optical branch phonons.

FIG. 3 Contributions to the relaxation frequency Γ of NaI as a function of frequency ω for quasiallowed combinations of phonons. The relatively small contribution made by the quasiunallowed sum of two optical phonons is shown by a dashed line to illustrate the validity of the quasiselection rule.


KI
RbCl
NaCl
KBr
ABSORPTION COEFFICIENT (CM⁻¹)
FREQUENCY (CM⁻¹)
10¹
10⁰
10⁻¹
10⁻²
10⁻³
250
300
350
400
450
500
500
700
900
300
400
500


10^1
10^0
10^-1
10^-2
10^-3
ABSORPTION COEFFICIENT (CM^-1)
NaI
300 K
80 K
300
400
500
FREQUENCY (CM^-1)



A+O
NaI
80 K
A+A+O
O+O+O
O+O
A+O+O+O
A+A+A+O
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
RELAXATION FREQUENCY (SEC^{-1})
100
200
300
400
500
FREQUENCY (CM^{-1})