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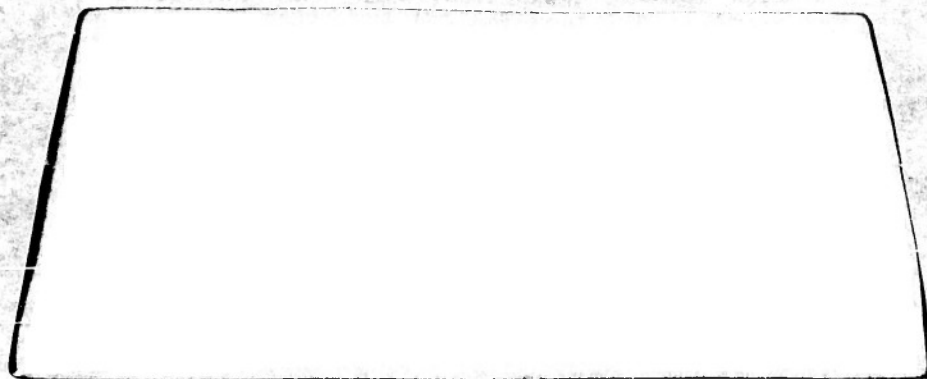
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INSTITUTE OF INDUSTRIAL RESEARCH

DEPARTMENT OF PHYSICS

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Bibliographical Control Sheet

1. Originating Agency: Syracuse University, Syracuse, New York
Monitoring Agency: Solid State Sciences Division, Office of
Scientific Research
2. O.A. report #3
M.A. OSR-TN-54-274 /
3. Title: The Influence of Lattice Vibrations on Electronic Transitions
in Solids
Title is unclassified
4. Author: Melvin Lax
5. Date of report: October, 1954
6. Pages: 47
7. Illustrative material: 8 figures
8. Prepared for Contract No. AF 18(600)-651
9. Prepared for Project RDO No. R-355-40-5
10. Security Classification: Unclassified
11. Distribution Limitations: None
12. Abstract: A summary is given of our present state of knowledge concerning optical and thermal transitions of electrons or holes trapped in solids. Among the topics covered are integrated intensities for absorption, the breadth of absorption lines and the rates for thermal ionization and capture. The relation between the latter and photoconductive lifetimes is discussed briefly.

The Influence of Lattice Vibrations

On Electronic Transitions in Solids

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Technical Report No. 5

Contract No. Nonr 669(04)

Project No. NR 017-419

with the U. S. Office of Naval Research

Technical Report No. 3

Contract No. AF 18(600)-651

Project No. R-355-40-5

with the Office of Scientific Research
of the U. S. Air Force

Abstract

A summary is given of our present state of knowledge concerning optical and thermal transitions of electrons or holes trapped in solids. Among the topics covered are integrated intensities for absorption, the breadth of absorption lines and the rates for thermal ionization and capture. The relation between the latter and photoconductive lifetimes is discussed briefly.

I. Introduction

The scope of the present paper will be limited to those electronic transitions in solids that involve lattice vibrations in an important way.¹ The simplest category is that of radiation-less transitions--the thermal ionization of a trapped electron (or the inverse process of thermal capture). In this process the trapped electron through its interaction with the lattice acquires energy by absorbing one or more phonons and is released into the conduction band. For impurities in germanium or silicon, the ionization energy of .01 or .05 e.v. is less than the Debye energy $k\theta$ for these materials, so that, in principle, a one-phonon transition can take place. For an F center, however, the ionization energy^{2,3} of ~ 2 e.v. in KBr is many times larger than the energies of the phonons $\sim .03$ e.v., so that thermal ionization can only occur as a multi-phonon process. In sections 2 and 3 an explanation will be given of the way in which multi-phonon transitions are made possible.

Although optical absorption by trapped carriers can occur without lattice vibrations, such absorption would have a line spectrum. The broadening of such a line into a band is of obvious importance for photoconductivity, and for this lattice vibrations are essential.

¹ An attempt will be made to summarize the present state of our knowledge concerning such transitions. References will be given to the previous literature to facilitate the reader in following our discussion, but no attempt will be made to review all of the previous literature, and significant references will undoubtedly be omitted--with apologies to the authors concerned.

² R. W. Pohl, Proc. Phys. Soc. 49, (extra part), 3 (1937).

³ B. Szigeti, Trans. Far. Soc. 45, 155 (1949).

Mott and Gurney⁴ using the classical Franck-Condon principle suggested that the broadening should increase in proportion to the square root of the absolute temperature. Many experiments⁵⁻¹¹ indicate good agreement with this suggestion at high temperatures. At low temperatures, however, the line width did not approach zero, but reduced to a constant value.⁵⁻¹¹ For KBr, the residual line width of about .2 e.v. is one order of magnitude larger than the Debye energy!

Schon¹² suggested that the residual line width was produced by the zero-point oscillations of the lattice. Calculations based on a simple configurational coordinate model (for different materials) were made by Williams,¹³⁻¹⁵ Klick,¹⁶ and Vlam¹⁷ to obtain more detailed information concerning the shape of the bands and the way their width changed with temperature.

⁴ N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford Press, New York, 1940, p. 117.

⁵ C. C. Klick, J. Phys. Chem. 57, 776 (1953).

⁶ C. C. Klick, J. Opt. Soc. 41, 816 (1951).

⁷ C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. 40, 509 (1950).

⁸ H. Brinkman and C. C. Vlam, Physica 14, 650 (1949).

⁹ C. C. Vlam, Physica 15, 609 (1949).

¹⁰ H. F. Hamelka and C. C. Vlam, Physica 19, 943 (1953).

¹¹ D. D. Johnson and F. J. Studer, Phys. Rev. 82, 976 (1951).

¹² M. Schon, Ann. Physik Series 6, 3, 343 (1948).

¹³ F. E. Williams, J. Chem. Phys. 19, 457 (1951).

¹⁴ F. E. Williams, Phys. Rev. 82, 281 (1951).

¹⁵ F. E. Williams and M. H. Hibb, Phys. Rev. 84, 1181 (1951).

¹⁶ C. C. Klick, Phys. Rev. 85, 154 (1952).

¹⁷ C. C. Vlam, "The Structure of the Emission Bands of Luminiscent Solids Thesis, University of Groningen, July 1953.

In Section 3 we shall discuss the configurational coordinate model in the light of a generalized Franck-Condon principle.¹⁸ In particular, we shall discuss the band shape and width at low, high and intermediate temperatures. We shall also explain the observation¹⁹ that total intensities of absorption (or emission) are essentially independent of temperature.

¹⁸ M. Lax, J. Chem. Phys. 20, 1752 (1952). Equations quoted from this paper will be prefixed by the letter I.

¹⁹ See especially reference 17, figures 9 and 14, pp. 26-32.

2. Optical Absorption by Trapped Electrons: Integrated Intensities

An electron trapped in a crystal will have a wave-function whose extent is small compared to the wave-length of the radiation it can absorb. It will always be permissible therefore to treat radiation or absorption by making a multipole expansion of the electromagnetic field. When electric dipole radiation does not vanish because of a selection rule, it will make the dominant contribution and all higher order effects may be neglected.

For electrons that are closely-bound ("deep traps"), including F centers, the electronic energy will be large compared to the Debye energy of the crystal. The electronic frequencies will then be fast compared to the highest vibrational frequencies and a Born-Oppenheimer treatment of the electronic motion will be valid. In silicon and germanium, however, the (hydrogenlike) impurities have ionization energies of the order .05 e.v. and .01 e.v. which are smaller than the Debye energy and the Born-Oppenheimer approximation cannot be made without further analysis. In treating the broadening of impurity levels in semi-conductors, it was found, however, that the important vibrations are those whose wave lengths are comparable to the Bohr radius, more precisely, whose propagation constant $\tau = (2/a)$ where a is the Bohr radius in the crystal.²⁰ The ratio of vibrational energy to ground state binding energy is then $\hbar\omega/E_g \approx \hbar v_s (2/a)/E_g$ where v_s is the velocity of sound. This ratio is about .1 or .2 in Ge or Si, so that it is still a fairly good approximation to employ the Born-Oppenheimer method.

²⁰ M. Lax and E. Burstein, Broadening of Impurity Levels in Silicon.

To be submitted to the Physical Review.

An analysis of the absorption and emission of electric dipole radiation by an electron trapped in a solid has already been given using the Born-Oppenheimer approximation.¹⁸ The principal result of this analysis is incorporated in the starting equation¹⁸ I(2.1) for the absorption cross-section:

$$\sigma(\nu) = \left[\frac{n}{K} \left(\frac{E_e}{E} \right)^2 \right] \frac{8\pi^3 \nu}{3c} I_{ba}(\nu) \quad (2.1)$$

The factors in the brackets take account of the modification of the electromagnetic field in the crystal: n = optical index of refraction, K = optical dielectric constant, E_e/E = ratio of average electric field at the center to its average value in the crystal.¹⁸ The shape of the absorption spectrum is contained in $I_{ba}(\nu)$ where the subscripts indicate that a transition has taken place from electronic state $\phi_a(r, x)$ to electronic state $\phi_b(r, x)$ (with any accompanying change in the vibrational states). Here r is the electron coordinate and x the set of nuclear coordinates. The electric moment for the transition is given by

$$M_{ba}(x) = \int \phi_b^*(r, x) e r \phi_a(r, x) dr \quad (2.2)$$

The integrated absorption¹⁸ from I(4.3) is given by:

$$\int I_{ba}(\nu) d(h\nu) = A_\nu [|M_{ba}(x)|^2] = \int P_a(x) |M_{ba}(x)|^2 dx \quad (2.3)$$

when $P_a(x) dx$ is the (quantum-mechanical) thermal average probability of finding the nuclear coordinates in dx . To a zeroth

approximation, $M_{ba}(x)$ will not depend significantly on x for the moderate displacements that occur in lattice vibrations. Then (2.3) reduces approximately to a constant value $|M_{ba}(0)|^2$ independent of temperature--in agreement with the widespread observation that the integrated absorption is essentially constant over a wide temperature range even though the breadth and shape of the absorption spectrum may change appreciably. To a first approximation $M_{ba}(x) \simeq C + Dx$ and

$$A_V [|M_{ba}(x)|^2] = C^2 + D^2 A_V(x^2)$$

so that the effect on the integrated intensity is to produce an increase with temperature that is second order in the ratio D/C . (The primary effect of such a linear term is to alter somewhat the shape of the absorption spectrum. Dexter²¹ has found that the usual Gaussian shape can be altered by 20 per cent or more on the wings.)

The integrated absorption cross-section in the presence of vibration can therefore be estimated from the corresponding cross-section in the non-vibrating lattice. We can avoid statements that depend on an explicit choice of electronic wave-functions by introducing the oscillator strength

$$f_{ba} = (2 m^* / \hbar^2) (E_b - E_a) (1/3) | \underline{\mu}_{ba} |^2 \quad (2.4)$$

The electronic (rigid-lattice) cross-section to all possible final states b can then be written

$$\sigma(\nu) \simeq \frac{m}{K} \left(\frac{E_e}{E} \right)^2 \frac{2\pi^2 \hbar e^2}{m^* c} \Gamma(\nu) \quad (2.5)$$

²¹ D. L. Dexter, On the Shapes of Absorption and Emission Lines of Impurities in Solids, Office of Scientific Research Technical Note 54-192.

where
$$\Gamma(\nu) = \sum_{b>a} f_{ba} \delta(E_b - E_a - h\nu) \quad (2.6)$$

and
$$\int \Gamma(\nu) d(h\nu) = \sum_{b>a} f_{ba} \quad (2.7)$$

Each term in (2.6) represents a sharp line because of the neglect of all sources of broadening, however, the corresponding term in (2.7) yields the integrated result for that line, which to a first approximation is valid even in the presence of broadening.

Note that m^* cancels out of the combined equations (2.4) and (2.5), and can therefore be chosen somewhat arbitrarily. For a highly localized electron e.g. in an F center, the first allowed transition (e.g. 1s to 2p) will have an oscillator strength of the order unity (using $m^* \simeq m$) and higher transitions, e.g. 1s to np will be reduced roughly by a factor n^3 because of the reduction in overlap. Thus (2.5) and (2.7) with these assumed oscillator strengths provide a quick rough estimate of the integrated cross-sections for the discrete transitions. Direct calculations of the oscillator strengths are necessary, for a more accurate analysis. Such calculations have been carried out by Dexter²² for the F-center case.

For electrons whose wave functions are sufficiently slowly varying, the Wannier-Slater-James treatment of electrons in perturbed periodic lattices becomes valid. It then becomes possible to represent the wave-function of a trapped electron as a linear combination of orthogonalized atomic (Wannier) orbitals belonging to one band (if no degeneracy exists). The coefficients in this expansion are a slowly varying function of their

²² D. L. Dexter, Phys. Rev. 83, 435 (1951).

argument--the cell position, and when replaced by a single continuous function describe the smooth envelope of the complete wave function whose rapid variations are contained within the Wannier orbitals. This smooth envelope function may be regarded as a macroscopic Schrodinger wave function since it bears the same relation to the complete wave-function as a macroscopic electromagnetic field does to the microscopic field. Indeed, the macroscopic Schrodinger function obeys a hydrogen-like wave function with an effective mass different from the vacuum mass just as a macroscopic electric field obeys a Maxwell equation containing the medium dielectric constant.

A slight extension of the Wannier-Slater-James treatment can be used to show that for electrons with large orbits, the electric dipole matrix element can be calculated to a good approximation directly from the macroscopic Schrodinger wave functions ignoring the periodic substructure.²³ A consequence of this result is that the usual sum rule for oscillator strengths

$$\sum_{\text{all } b} f_{ba} = 1 \quad (2.8)$$

is valid providing that m^* in (2.4) is the effective mass in the crystal. If ellipsoidal energy surfaces are present then (2.8) remains valid provided m^* is interpreted as the harmonic mean of the three masses:²⁴

$$1/m^* = 1/m_1 + 1/m_2 + 1/m_3 \quad (2.9)$$

²³ See for example how the matrix elements of the deformation potential are calculated in ref. 18.

²⁴ A proof of this statement will be included in a paper by E. Burstein and the author on optical absorption by impurity levels in silicon.

If the energy surfaces are spherical and the potential hydrogen-like, then the oscillator strengths are the same as in the original hydrogen atom--the influence of a change in effective mass and dielectric constant cancels out of the oscillator strength formula (2.4) since $E_0 - E_a$ is proportional to m^*/K^2 and r_{ba} is proportional to the modified Bohr radius, or to $(Km^*)^{-1}$.

The absorption in the continuous spectrum also bears a simple relation to that in a hydrogen atom. The contribution of the continuous spectrum to $\Gamma(\nu)$ can be written:

$$\Gamma_{\text{CONT}}(\nu) = \frac{1}{E_g} \frac{2^7}{3} \left(\frac{E_g}{h\nu} \right)^4 \frac{\exp[-4m' \operatorname{arccot} m']}{1 - \exp[-2\pi m']} \quad (2.10)$$

where $n^1 = \left[(h\nu/E_g) - 1 \right]^{-\frac{1}{2}}$ and E_g is the ionization energy of the ground (1s) state. The integral $\int \Gamma_{\text{CONT}}(\nu) d(h\nu) = .436$ represents the fraction of the absorption in the continuum as compared to the total absorption. The contribution to this integral from any region, measured in units of E_g , is identical to the corresponding contribution for the hydrogen atom. However, $\sigma(\nu)$ itself according to (2.5) and (2.10) is proportional to $(n/K)(m^*E_g)^{-1}$ or $K^{3/2}/(m^*)^2$.

For purposes of comparison with experiment, we summarize the most pertinent hydrogen-like oscillator strengths from 1s to np and to the continuum:²⁵

$$f_{2p,1s} = .416, f_{3p,1s} = .079, f_{4p,1s} = .029, f_{\text{cont},1s} = .436 \quad (2.11)$$

²⁵ H. Bethe, Handbuch der Phys. 24/1, Kap. 3, Ziff. 41, Julius Springer, Berlin 1933.

and the integrated absorption cross-section:

$$\int \sigma(\nu) d(h\nu) = \left(\frac{E_e}{E}\right)^2 \frac{m}{K} \frac{m}{m^*} \frac{2\pi^2 \hbar e^2}{mc} \quad (2.12)$$

with
$$\frac{2\pi^2 \hbar e^2}{mc} \simeq 1.098 \times 10^{-16} \text{ e.v. (cm)}^2.$$

Figure 1 and 2 show the optical absorption by Boron-doped silicon. Three absorption peaks can be observed corresponding to the 1s-2p, 1s-3p and 1s-4p transitions in addition to the continuum absorption above about 0.046 e.v. The most striking discrepancy between theory and experiment is that the discrete absorption peaks get about 10 per cent of the total absorption rather than about the 50 per cent to be expected from the hydrogen model. Secondly, the strongest discrete transition is the 1s-3p transition rather than the 1s-2p transition. These discrepancies are related to the fact that the valence band of silicon contains three degenerate bands (six if spin is included), and spin-orbit coupling only partially removes the degeneracy. Thus the wave functions describing an impurity trapped hole involves a linear combination of Wannier functions from several bands, and the elementary treatment given above is not valid.

The integrated absorption should, however, be less sensitive to details of the wave-functions and better agreement should be obtained with the theoretical expression (2.12). The experimental integrated absorption coefficient $\int \alpha(\nu) d(h\nu)$ is $0.90 \text{ (e.v.)cm}^{-1}$. This may be converted to an integrated cross-section by dividing by the concentration of Boron centers. To estimate the latter, we note that the specimen in question has a room temperature resistivity of 1 ohm-cm.

Assuming a mobility²⁶ of 350 cm²/volt-sec, this leads to a room temperature hole concentration of 1.8×10^{16} holes/cm³. Since all Boron centers would be ionized at room temperature, we may take 1.8×10^{16} /cm³ for the concentration of Boron centers--assuming the concentration of other centers to be negligible. Thus we can conclude that

$$\int \sigma(\nu) d(h\nu) \simeq 0.5 \times 10^{-16} \text{ e.v. (cm)}^2 \quad (2.13)$$

with an accuracy no better than 30 per cent.

The theoretical integrated absorption cross-section can be estimated from (2.12) assuming (1) the effective field correction $(E_c/E)^2$ is negligible for a center as large as the one in question (2) the effective mass may be determined from the ionization energy $E_g \simeq .046$ e.v. to be $m^* \simeq 0.45 m$ (3) $n/k \simeq (k)^{-1/2} \simeq (12)^{-1/2}$. The final result of 0.7×10^{-16} ev. (cm)² is in reasonable agreement with experiment.

²⁶

This mobility has been found reasonably representative at Bell Laboratories for estimating carrier concentrations in a group of specimens from which the sample in question was taken.

3. Absorption by Trapped Electrons: Broadening

There are two distinct stages in the calculation of the shape of an absorption curve broadened by lattice vibrations. The first is a determination of the electronic energy as a function of the pertinent nuclear coordinates using either one configurational coordinate or many. The second is the calculation of the spectrum from the known energy vs. configurational coordinate curves using classical, semi-classical, or quantum mechanical methods.

Simple energy level diagrams against a single fictitious coordinate have long been used to give a qualitative understanding of absorption, luminescence, non-radiative transitions, etc.²⁷ The first serious attempt to calculate accurately the energy against a (single) real coordinate was made by Williams²⁸ for thallium activated KCl. Williams used as his coordinate the radial displacement of the six nearest neighbors. His configurational diagram is shown in Figure 3. The remarkable agreement between his calculated spectrum and the observed spectrum is shown in Figure 4. Williams results will be analyzed in more detail later.

²⁷

See for example, H. W. Leverenz, *Luminescence of Solids*, John Wiley and Sons, New York 1950, p. 132, or Mott and Gurney, ref. 4.

²⁸

F. E. Williams, *J. Phys. Chem.* 57, 780 (1953). This paper contains the most accurate calculation of the configurational diagram. More detailed discussion is given in the earlier papers, refs. 13 - 15.

Klick¹⁶ and Vlam¹⁷ have essentially reversed the Williams procedure, by deriving configurational coordinate curves from the experimental data. They assume that an adequate description can be given in terms of one coordinate, and that the energies of the ground and excited states may be approximated by quadratics in the coordinate. No attempt, however, is made to assign a real significance to the "fictitious" coordinate, or to compare the configuration curves with calculations from fundamental principles. Nevertheless, a significant contribution has been made by this reduction of the experimental data to a more basic form. The configuration curves permit the observed absorption (and emission) to be qualitatively understood, and provide an intermediate link between experiment and a fundamental theory. For the many cases in which the basic mechanism for broadening is not understood, or too difficult to treat, the Klick and Vlam procedure is the best that can be done.

Two courageous physicists Huang and Rhys²⁹ in treating the F center problem, attempted the double feat of (1) calculating the F center energy as a function of all the normal coordinates in the lattice (2) making an all quantum mechanical treatment of the many body problem. As we shall see, they were more successful in the second or methodological aspect of their work.

Huang and Rhys pointed out that the energy change of the F center electron would be produced primarily by the long range electrostatic forces present in a polar lattice. Furthermore they noted that large long-range fields are produced primarily by the long-wave longitudinal optical modes. They therefore neglected interactions with all other

²⁹ K. Huang and A. Rhys, Proc. Roy. Soc. (London) A204, 406-423 (1950).

modes, and treated the long-wave longitudinal optical modes by a dielectric continuum model earlier discussed by Huang.³⁰ This continuum model smooths the cell polarization into a continuous function--just as the deformation potential method smooths the displacements in a long wave acoustic mode.³¹

Huang and Rhys²⁹ describe the electron-lattice interaction as the interaction of the continuum polarization with the electric field produced by the static charge distribution associated with the F center electron. Since the electric field decreases very slowly with distance, Huang and Rhys expect a long range induced polarization, which when translated into normal coordinates emphasizes the long wave length modes. Unfortunately, however, Huang and Rhys neglected the fact that the F center is neutral. Stated differently, the only polarization that we need consider is the change compared to the perfect lattice case, and therefore the charge distribution to be used is that of the F center electron minus that of the negative ion it replaces. Such a neutral distribution, however, produces only short range effects and invalidates the continuum approximation made by Huang and Rhys.

One might anticipate that the Huang Rhys procedure of using the static unneutralized charge distribution of the electron would yield too high an answer for the broadening. Actually their parameter S which measures the broadening is calculated to be 3.6 whereas a comparison with

³⁰ K. Huang, Report L/T 239 of British Electrical and Allied Industries Research Association. See also H. B. Callen, Phys. Rev. 76, 1394 (1949) and H. Frohlich, Proc. Roy. Soc., London A160, 230 (1937).

³¹ J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).

experiment yields $S \simeq 22$. Two points are involved in explaining their small result. The first is that the error involved in using a non-neutral charge distribution cancels out of their final calculations since only the difference between the electron-lattice interactions in the ground and excited states is of importance. The second is that their continuum treatment grossly underestimates the contributions of short range interactions.

To explain the latter statement, we note that the electron-lattice interaction used by Huang and Rhys is linear in the normal coordinates and its net effect is to shift the equilibrium positions of all the ions. However, the major shift will take place for the nearest neighbor ions, and such a shift cannot be calculated from a continuum model but must be based on a detailed analysis of all the local forces similar to the one carried out by Williams for KCl:Tl.

Burstein and Oberly³² have suggested a model for the F center based on treating the trapped electron as a particle in a box. This model correlates with the empirical rule suggested by Mollwo³³

$$\nu_{\max} a^2 \simeq .5 \text{ sec}^{-1} \text{ cm}^2 \quad (3.1)$$

relating the maximum absorption frequency $\nu_{\max}$ to the inter-ion distance a for all the alkali halides. The particle in a box model emphasizes the incompressibility of the alkali ions that form the box walls--i.e. it emphasizes short range forces of a sort omitted in the Huang Rhys treatment. A closely related molecular model has been proposed

³² E. Burstein and J. J. Oberly, Optical Properties of F Centers at Liquid Helium Temperatures. Proceedings of Conference on Low Temperature Physics, 1951, National Bureau of Standards Circular 519.

³³ E. Mollwo, Z. Phys. 85, 56 (1933).

by T. Innui and Y. Vemura,³⁴ and a detailed molecular calculation was started by Muto.³⁵ However, an adequate calculation of the configuration energy of the F center does not yet exist.

In the remainder of this section, we shall assume that the energy of the trapped electron as a function of the various configurational coordinates is known, and shall discuss the methods available for computing the shape of the absorption spectrum. The Franck-Condon principle states that we may regard the nuclei as standing still while the electron changes its state due to absorbing the photon. Thus the strength of absorption can be computed for a given configuration and the result averaged over all possible configurations. The shape factor

$I_{ba}(\nu)$ in (2.1) can then be written

$$I_{ba} \xrightarrow{\text{F.C.}} \int |M_{ba}(x)|^2 P_a(x) \delta(\Delta E(x) - h\nu) dx \quad (3.2)$$

$$\Delta E(x) = E_b(x) - E_a(x) \quad (3.3)$$

The squared matrix element $|M_{ba}(x)|^2$ represents the strength of the absorption. $P_a(x) dx$ is the normalized probability of finding the nuclei between x and $x + dx$ (here x may represent a set of nuclear coordinates) and the presence of the delta function factor insures that only those configurations whose energy difference $\Delta E(x) = h\nu$ will contribute to the spectrum at $h\nu$. A "derivation" and detailed analysis of the Franck-Condon principle has been given by the author.¹⁸

³⁴ T. Innui and Y. Uemura, Prog. Theor. Phys. 5, 395 (1950).

³⁵ T. Muto, Prog. Theor. Phys. 4, 181 (1949).

We shall refer to the Franck-Condon principle as classical if classical statistics are used in obtaining the probability distribution:

$$P_a(x)_{\text{classical}} = \exp[-E_a(x)/kT] / \int \exp[-E_a(x)/kT] dx \quad (3.4)$$

and as semi-classical if the quantum mechanical distribution is used:

$$P_a(x) = \frac{\sum_m \exp[-E_{am}/kT] |X_{am}(x)|^2}{\sum_m \exp[-E_{am}/kT]} \quad (3.5)$$

where $X_{am}(x)$ is the m^{th} vibrational wave function when the electron is in state a , and E_{am} is the total electron-vibrational energy in this state. For sufficiently high temperatures, the quantum mechanical distribution (3.5) can be shown to reduce to its classical value (3.4). Such a classical approximation will be valid providing $kT \gg \hbar\omega$ where ω is the frequency of the normal mode or modes important in the broadening. We shall see, however, that the semi-classical method is so easy to apply that little is gained by making the classical approximation.

We shall illustrate our remarks by considering the case where x is a single variable. (For the appropriate generalization to the many body problem, the reader is referred to reference 18). Equation (3.2) can then be reduced to

$$I_{ba}(\nu) = |M_{ba}(x)|^2 P_a(x) \left| \frac{dx}{d\Delta E(x)} \right|_{\Delta E(x) = h\nu} \quad (3.6)$$

and if the states $X_{\text{em}}(x)$ can be approximated by states of a harmonic oscillator of frequency ω and mass M then

$$P_a(x) = [2\pi \langle x^2 \rangle]^{-\frac{1}{2}} \exp[-\frac{1}{2} x^2 / \langle x^2 \rangle] \quad (3.7)$$

where $\langle x^2 \rangle = (\hbar / M\omega)(\frac{1}{2} + \bar{m})$ (3.8)

and $\bar{m} = [\exp(\hbar\omega/kT) - 1]^{-1}$ (3.9)

The combination of (3.6) and (3.7) yields the complete spectral distribution. To be even more specific, I shall assume that the excited as well as ground state configurations can be approximated by parabolas:

$$E_a(x) = \frac{1}{2} K x^2 \quad (3.10)$$

$$\Delta E(x) = Ax - \frac{1}{2} B x^2 + h\nu_{ba} \quad (3.11)$$

where $h\nu_{ba}$ is the energy difference when $x = 0$ i.e. from the equilibrium point of the lower state and $K - B$ is the stiffness of the excited state. (Usually $B > 0$).

The spectrum (3.6) aside from a factor $|M(x)|^2$ can now be written

$$G(\nu) = [2\pi \langle x^2 \rangle]^{-\frac{1}{2}} (A\Gamma)^{-1} \left\{ \exp\left[-\frac{1}{2}(1-\Gamma)^2 A^2 / B^2 \langle x^2 \rangle\right] + \exp\left[-\frac{1}{2}(1+\Gamma)^2 A^2 / B^2 \langle x^2 \rangle\right] \right\} \quad (3.12)$$

where the two roots for x are $x = (A/B)(1 \pm \Gamma)$ and

$$\Gamma = \left[1 - 2B(h\nu - h\nu_{ba}) / A^2 \right]^{\frac{1}{2}} \quad (3.13)$$

If the change in stiffness B is sufficiently small, or the temperature sufficiently low that $B^2 \langle x^2 \rangle \ll A^2$, then it is permissible to drop the second exponential and expand Γ with the result that the spectrum becomes Gaussian:

$$G(\nu) \approx [2\pi \langle x^2 \rangle]^{-\frac{1}{2}} A' \exp \left[-\frac{1}{2} (h\nu - h\nu_0)^2 / A^2 \langle x^2 \rangle \right] \quad (3.14)$$

$$\text{with } \langle (h\nu - h\nu_0)^2 \rangle = A^2 \langle x^2 \rangle \quad (3.15)$$

and a mean energy independent of temperature.

A detailed quantum mechanical analysis of the spectrum¹⁸ showed that the semi-classical spectrum (3.12) has the correct first and second moment:

$$\langle h\nu \rangle = h\bar{\nu} = \langle \Delta E(x) \rangle = h\nu_0 - \frac{1}{2} B \langle x^2 \rangle \quad (3.16)$$

$$\langle (h\nu - h\bar{\nu})^2 \rangle = A^2 \langle x^2 \rangle + \frac{1}{2} B^2 |\langle x^2 \rangle|^2 \quad (3.17)$$

(Note the temperature dependence of the mean energy (3.16)). However, the shape of the spectrum (3.12) depends on the validity of the semi-classical approximation, which we shall now examine, by considering the extent to which the third moment is adequately given by the semi-classical formula

$$\langle (h\nu - h\bar{\nu})^3 \rangle_{s.c.} = \langle (\Delta E(x) - h\bar{\nu})^3 \rangle \quad (3.18)$$

The difference between the quantum mechanical and semi-classical third moments is found¹⁸ from I(4.5) and (4.8) to be:

$$\langle (h\nu - h\bar{\nu})^3 \rangle_{QM} - \langle (h\nu - h\bar{\nu})^3 \rangle_{s.c.} = A_V \left[2\Delta E(T, \Delta E) + (T, \Delta E) \Delta E \right] \quad (3.19)$$

where $T = P^2/2M$ is the kinetic energy, $(T, \Delta E)$ is a commutator, and the symbol $A \bar{\sigma}$ means take an average of the enclosed operator in the state $X_{am}(x)$ and then take a Boltzmann average over the states m . It is not fair to compare the error (3.19) with (3.18) since (3.18) vanishes if $B = 0$. An estimate of the accuracy involved can be obtained by comparing (3.19) with $[\langle (\Delta E(x) - h\bar{\nu})^2 \rangle]^{3/2}$

This criterion was stated in I(4.9). Indeed, the ratio of the third moment to the three halves power of the second moment is called the skewness and denoted γ . (c.f. Eq. I 8.18). Our criterion for validity of the semi-classical approximation is $\gamma_{Q.M.} - \gamma_{S.C.} \ll 1$

If this condition is obeyed then (3.12) will be valid. The spectrum will however reduce to a Gaussian even in the semi-classical case only if the skewness is then sufficiently small: $\gamma_{S.C.} \ll 1$

Evaluating (3.19) and (3.18) and dividing by the three-halves power of (3.17) we obtain respectively:

$$\gamma_{Q.M.} - \gamma_{S.C.} = \lambda(1+\alpha)^2/\alpha^3 \quad (3.20)$$

$$\gamma_{S.C.} = (324)/(329\alpha) \quad (3.21)$$

$$\text{where } \lambda = (16/17) (K/B)^2 / (1 + 2 \bar{m})^2 \quad (3.22)$$

$$\text{and } \alpha = 4 A^2 / (17 B^2 \langle x^2 \rangle) \quad (3.23)$$

The semi-classical criterion $\gamma_{Q.M.} - \gamma_{S.C.} \ll 1$ can be simplified

by considering separately the cases in which λ is greater or less than unity. If $\lambda > 1$, then $\alpha \gg \lambda$ or $A^2(2\bar{m}+1)/(2\hbar M\omega^3) \gg 1$ (3.24)

In this case, it is clear that we must also have $\alpha \gg 1$, so that using (3.21) the spectrum is also Gaussian. Comparing with (3.8) and

(3.17), the condition (3.24) can be written in the more perspicuous form.

$$(\alpha/\lambda)^{1/2} \approx A[\langle x^2 \rangle]^{1/2} / \hbar \omega > 1 \quad (3.25)$$

If $\lambda > 1$, and $\alpha > 1$ it follows, comparing (3.25) and (3.17) that the observed broadening will be large compared to the phonon energy of the ground state. (In the absence of other information the Debye energy $\hbar \theta$ can be used as an estimate for $\hbar \omega$). This latter condition is necessary but not sufficient for the validity of the semi-classical method. Even if $\lambda < 1$, if $\alpha > 1$, the condition (3.25) is sufficient to insure the semi-classical and gaussian nature of the spectrum.

However, if $\lambda < 1$, the semi-classical condition (3.20) merely requires

$$\alpha \gg \lambda^{1/3} \quad \text{when } \lambda < 1 \quad (3.26)$$

so that if $1 > \alpha \gg \lambda^{1/3}$ a semi-classical non-gaussian spectrum can be observed. Under these circumstances the condition (3.26) can be rewritten in the form:

$$A[\langle x^2 \rangle]^{1/2} \gg \hbar \omega / \alpha \quad (3.27)$$

$$\text{or } \langle (h\nu - h\nu)^2 \rangle \gg (\hbar \omega / \alpha) [1 + (2/17\alpha)]^{1/2} \quad (3.28)$$

which is slightly more stringent than (3.25) since $\alpha < 1$. Therefore if (3.25) is disobeyed, a fully quantum mechanical treatment is necessary.

We shall illustrate these criteria by applying them to the problem of KCl:Tl discussed by Williams. From his configuration diagram

(Figure 2) we may deduce that $A = 2.393 \text{ e.v./}\text{\AA}^2$, $B = 8.016 \text{ e.v./}\text{\AA}^2$,

$K = 15.85 \text{ e.v./}\text{\AA}^2$, $\hbar \omega = .0166 \text{ e.v.}$ using his mass of $M = 6$

$[M_{Cl} + (.4264)^2 M_K] = 4.239 \times 10^{-22} \text{ grams.}$ At absolute zero, we

$$\text{have } \langle x^2 \rangle_0^{1/2} = (\hbar \omega / 2K)^{1/2} \approx 2.22 \times 10^{-2} \text{ \AA} \quad (3.29)$$

$$\lambda(0) = 16 K^2 / (17 B^2) \approx 4.16$$

$$\alpha(0) = 4 A^2 / (17 B^2 \langle x^2 \rangle_0) \approx 42.6$$

Thus we have $\lambda > 1$ and $\alpha \gg \lambda > 1$ so that the spectrum will be both semi-classical and Gaussian. In fact $\gamma_{QM} - \gamma_{SC} \approx (\lambda/\alpha) \approx .1$ and $\gamma_{SC} \approx (1/\alpha) \approx .02$ so that the skewness would be quite small. These results could have been deduced directly from the experimental data (assuming $\lambda > 1$) by noting that the r.m.s. width

$$\langle (h\nu - h\bar{\nu})^2 \rangle^{1/2} \approx .125 \text{ e.v.} / (2.346) \approx .0533$$

(where .125 e.v. is the full width at half-power). This width is larger than the Debye energy, and certainly larger than $\hbar \omega \approx .0166$ e.v. In fact $\lambda(0)/\alpha(0) \approx (.0166/.0533)^2 \approx .1$ in agreement with the previously calculated value.

At higher temperatures $\lambda(T) = \lambda(0)/(1 + 2\bar{m})^2$,
 $\alpha(T) = \alpha(0)/(1 + 2\bar{m})$ so that $\lambda(T)/\alpha(T)$ decreases with increasing temperature, and the semi-classical criterion remains valid in William's case. The spectrum will remain Gaussian as long as
 $\alpha(T) = (42.6)/(1 + 2\bar{m}) \gg 1$, i.e. for all measurable temperatures.

As a contrast to the William's case, we shall consider the configurational diagram deduced by C. C. Klick and J. A. Schulman for $\text{Zn}_2\text{SiO}_4\text{:Mn}$. They find $A \approx -.9 \times 10^{-14}$ ergs/cm, $B = 31 \times 10^4$ ergs/cm²,
 $K = 46 \times 10^4$ ergs/cm², $M = 4M_0 \approx 1.057 \times 10^{-22}$ g., $\hbar \omega \approx 6.952 \times 10^{-14}$ ergs $\approx .0434$ e.v. The observed broadening at low temperatures is of the order of .1 e.v. so that one might hope for the validity of a semi-classical treatment. However, the zero pt displacement
 $(\hbar \omega/2k)^{1/2} \approx 2.67 \times 10^{-10}$ and $A(\hbar \omega/2k)^{1/2} \approx 2.4 \times 10^{-14}$ ergs which is only .35 ($\hbar \omega$) so that condition (3.25) is violated. One finds further that $\lambda(0) \approx 2$, and $\alpha(0) \approx .27$. With these parameters, the semiclassical requirement cannot be satisfied at any temperature! The basic reason, of course, is that the two parabolas

of the configuration diagram have appreciably different stiffnesses, yet their minima are quite close together so that (a) the broadening is produced primarily from the difference in curvature (b) matrix elements are only appreciable to low-lying vibrational states and for these quantum effects are appreciable.

A comment may be added here about the F center. The Huang-Rhys parameter S is simply $A^2 \langle x^2 \rangle_0 / (\hbar \omega)^2$ and since S is given the empirical value of 22, condition (3.25) is easily satisfied. Since we may anticipate that K/B and hence $\lambda(0)$ will be of the order unity, (3.25) is a sufficient condition for the validity of the semi-classical method. We therefore expect that the F center absorption can be adequately represented by a Gaussian at low temperatures, and by (3.12) at high temperatures, except for the influence of cubic terms in the latter case.

Early measurements of F center absorption due to Mollwo³³ are shown in Figure 5. More careful measurements have been made recently by Hesketh and Schneider³⁶ in an attempt to analyze the shape of the F band. Figure 6 shows a comparison of their experimental results with a Lorentzian shape--such as had previously been assumed by Smakula³⁷ and others to be valid on the basis of dispersion theory. The agreement is poor--since the fundamental mechanism for broadening is not the usual one of dispersion theory. Figure 7 shows a Gaussian plot by Hesketh and Schneider of their data. A straight line of slope λ indicates

³⁶ R. V. Hesketh and E. E. Schneider, Phys. Rev. 95, 8372 (1954).

³⁷ A. Smakula, Z. Physik 59, 603 (1930).

a curve shape of the form $\exp \left[-(\nu - \nu_{\max})^m \right]$. Hesketh and Schneider find $m = 2$ on the high frequency side, but $m = 2.5$ on the low frequency side. The latter may be partly a result of anharmonic forces.

It has been pointed out to the author by D. L. Dexter that the customary use of Smakula's formula to determine the number of F centers in a crystal, or their oscillator strength is incorrect because of Smakula's assumption of a Lorentzian shape, so that a considerable amount of experimental data must be reevaluated. If we note that the absorption constant $\alpha(\nu)$ equals $N_c \sigma(\nu)$ where N_c is the number of centers, the integrated absorption for a line of oscillator strength f can from (2.5-2.7) be written:

$$\int \alpha(\nu) d(h\nu) = (N_c f) \frac{m}{K} \left(\frac{E_e}{E} \right)^2 \frac{2\pi^2 \hbar e^2}{m^* c} \quad (3.30)$$

where $K \approx n^2$ = square of index of refraction. Unfortunately the usual evaluation of experimental data estimates the integrated absorption, not by integration, but merely by taking a suitable produced of maximum absorption α_m and the full width at half power W . For a Lorentzian shape

$$\int \alpha(\nu) d(h\nu) = (\pi/2) \alpha_m W \approx 1.57 \alpha_m W \quad (3.31)$$

whereas for a Gaussian shape

$$\int \alpha(\nu) d(h\nu) = \frac{1}{2} (\pi/\ln 2)^{\frac{1}{2}} \alpha_m W \approx 1.07 \alpha_m W \quad (3.32)$$

Smakula's formula is equivalent to the use of (3.30) and (3.31) combined with the assumption $(E_e/E)^2 \simeq (\mathcal{M}^2 + 2)^2/9$, i.e. the assumption that the effective field E_e is equal to the Lorentz field $E + (4\pi/3) P$. On the basis of the experimental shape, (3.30) should be more nearly combined with (3.32). Furthermore, the F center electron is sufficiently diffuse that the effective field is considerably less than the Lorentzian field. A more detailed discussion of these points will be given in the Physical Review by D. L. Dexter.

4. Broadening: Relation of Many Body and One Body Viewpoints

Although the one parameter treatment discussed above is an oversimplification of the situation for a real impurity center, it is nevertheless quite feasible to use a simple configuration diagram, for the purpose of deciding whether a semi-classical treatment is permissible and to understand the observed spectrum. We shall try to explain in terms of a many body viewpoint why for most problems a one-parameter analysis is likely to yield qualitatively correct results. Our essential conclusion will be that if the modes which participate in the broadening do not have too great a frequency spread, a one-parameter viewpoint using a suitable mean frequency will yield fairly accurate results.

We shall start by assuming that the configurational energy difference ΔE is a function, possibly non-linear, of a single parameter x where the latter is a linear combination of the displacements or the normal coordinates q_j of the initial state:

$$x = N^{-\frac{1}{2}} \sum_{j=1}^N a_j q_j \quad (4.1)$$

where N is the total number of normal coordinates.

If the semi-classical approximation is valid, we proved in I that the one-parameter spectrum (3.6) and (3.7) is valid (c.f. I(5.7) and I(5.19)) providing merely that $\langle x^2 \rangle$ is given its correct rather than its one parameter value. This value from (4.1) is

$$\begin{aligned} \langle x^2 \rangle &= N^{-1} \sum_j a_j^2 \langle q_j^2 \rangle \\ \langle x^2 \rangle &= N^{-1} \sum_j a_j^2 \left(\frac{\hbar}{m\omega_j} \left[\bar{n}(\omega_j) + \frac{1}{2} \right] \right) \end{aligned} \quad (4.2)$$

The question we may ask is this: is there a harmonic oscillator with effective mass M_e and frequency ω_e such that its mean oscillation

$$\langle x^2 \rangle = \left(\hbar / M_e \omega_e \right) \left[\bar{n}(\omega_e) + \frac{1}{2} \right] \quad (4.3)$$

is a good approximation to (4.2) at all temperatures? Both formulas are linear with temperature at high temperatures and have a zero-point value at low temperatures. The best that we can do is to choose M_e and ω_e so that there is agreement with the high temperature slope and the zero point value. This leads to the choice

$$\omega_e = A_V(\omega^{-1}) / A_V(\omega^{-2}) \quad (4.4)$$

$$M_e = (M/R) A_V(\omega^2) / [A_V(\omega^{-1})]^2 \quad (4.5)$$

$$\text{where } R = \sum a_j^2 / N \quad (4.6)$$

The averaging operation A_V used in (4.4) and (4.5) is a weighted average over the modes using a_j^2 as weight:

$$A_V[f(\omega)] = \sum a_j^2 f(\omega_j) / \sum a_j^2 \quad (4.7)$$

It is clear that if the coefficients a_j that measure the extent to which modes q_j participate in the broadening emphasize a small range of frequencies, then ω_e will be somewhere within the range, and M_e will be essentially M/R . There is a certain amount of genuine arbitrariness in M_e through the choice of the normalization constant R . For example if x represents the sum of six radial displacements, then the kinetic energy would be $6 M(\dot{x}/6)^2 = M/6$ and $R = 6$. If x represents the average of the six radial displacements, then the kinetic energy is $6 M \dot{x}^2$ and $R = 1/6$. In any case, M/R is equivalent to the intuitive choice for the effective mass. The presence of dispersion among the important frequencies can only increase the effective mass since

$$A_V(\omega^2) > [A_V(\omega^{-1})]^2$$

To illustrate the above remarks, we shall consider two cases. In the first, we shall let $x = x_0$, the displacement of one atom. In this case all the a_j are equal. For the acoustic modes, with a Debye spectrum this yields

$$\omega_e = (\bar{\omega}/2) \quad (4.8)$$

$$(M_e/M) = 4/(3R) \quad (4.9)$$

where $\bar{\omega}$ is the highest acoustic frequency. If, however, we were to consider a coordinate $x = x_1 - x_{-1}$, say the difference between the displacement of a K atom on each side of the Tl center in Williams case, the weighting factor associated with a phonon of propagation constant τ would be $[1 - \cos \tau \cdot (x_1 - x_{-1})]$ which takes account of correlations in the motions of the two particles. The contributions then come largely from short wave-length acoustical and optical modes. (For long wave length modes of either type, the two K atoms move in unison). If only acoustical modes were considered, we would find $\omega_e \simeq .66 \bar{\omega}$, and $M_e \simeq 1.1 (M/R)$. This estimate assumes a Debye spectrum unperturbed by the center. A stiffness increase near the center, and the inclusion of optical modes will both tend to raise ω_e . Note that the modes q_j which are used in (3.29) should be the perturbed modes of the lattice in the presence of the center! If the stiffness change near the center is sufficiently large, a trapped molecular type mode will occur, and this one mode will make a predominant contribution to the parameter x , thus insuring the validity of the one-parameter viewpoint.

When a fully quantum mechanical calculation is necessary, it is more difficult to assess the validity of a one-parameter viewpoint, since the quantum-mechanical many-body problem has not been completely solved. Three cases have been solved however:

- (1) The energy difference ΔE is linear in the normal coordinates, and the latter all have the same frequency (Huang and Rhys²⁹).
- (2) The energy difference ΔE is linear in the normal coordinates, and the latter have a spread in frequencies (Lax¹⁸).
- (3) The energy difference contains a diagonal quadratic form

$$N \sum_j B_j q_j^2$$
in addition to linear terms (O'Rourke³⁸).

The pertinent results may be summarized as follows:

- (a) The Huang Rhys spectrum for many modes of the same frequency is identical to that which would have been obtained from a single parameter with the same frequency and a suitably chosen linear energy difference.
- (b) The Lax spectrum I(3.12) reduces to the Huang and Rhys spectrum I(9.1) if there is only a small dispersion of frequencies--so that a one-parameter description is possible.
- (c) The O'Rourke spectrum is identical in shape to the Lax spectrum but has a shift of mean energy of an amount $\langle N^{-1} \sum_j B_j q_j^2 \rangle$. This shift is exactly what one would expect from the moment formula I(4.3). The same frequency shift can be obtained, to a good approximation in a one-parameter problem by having a suitable stiffness change. In a one parameter problem however, this frequency shift will always be accompanied by a change of shape. In this case, it is not the one-parameter result which is wrong, but rather that a quadratic change in potential energy near a center $\frac{1}{2} B x^2$ becomes a quadratic form $N^{-1} \sum_j B_j q_j q_j$ containing important off-diagonal terms when expressed in terms of the normal coordinates.

³⁸ R. C. O'Rourke, Phys. Rev. 91, 265 (1953).

Pending the results of a more detailed analysis involving off-diagonal quadratic terms, it is probably safe to say that the criteria for the validity of a one parameter viewpoint will remain valid: The important modes that contribute must have a small dispersion of frequencies. If this is the case, it will be possible to choose an effective frequency and mass to fit the breadth of the spectrum over the entire temperature range. If appreciable skewness is present, however, it may be difficult to fit over an entire temperature range by choosing one parameter B , unless some restrictions are placed on the second order energy change

$$N^{-1} \sum B_{ij} q_i q_j$$

As an interesting example of the relationship between the one parameter and the many body viewpoint we shall discuss the case of impurity levels in semi-conductors.²⁰ We note that for Boron doped Silicon there are about 500 atoms within a sphere whose radius a is the first Bohr radius of the trapped electron in its 1s state. The broadening is produced by the vibration of these atoms through the electron lattice interaction. We may describe the latter by the deformation potential.

$$V(r) = E, \text{ div } \delta R \simeq i E, N^{-\frac{1}{2}} \sum_{\tau} \tau \exp(i\tau \cdot r) q(\tau) \quad (4.10)$$

so that the energy shift associated with an electron in state $\psi(r)$ is given approximately by

$$\Delta E \simeq (\psi(r), V(r) \psi(r)) = i E, N^{-\frac{1}{2}} \sum_{\tau} \tau N(\tau) q(\tau) \quad (4.11)$$

where $N(\tau) = (\psi(r), \exp(i\tau \cdot r) \psi(r)) \simeq [1 + (\frac{1}{2} a \tau)^2]^{-\frac{3}{2}}$ (4.12)

and the explicit form for $N(\tau)$ is based on a hydrogenic wave function of Bohr radius a . The normal coordinate $q(\tau)$ is associated with phonons of propagation constant τ .

To connect with a one parameter viewpoint, we simply introduce for our parameter x , the energy shift ΔE itself. The constant a_j , now written a_τ obey

$$|a_\tau|^2 = E_1^2 \tau^2 |N(\tau)|^2 \quad (4.13)$$

The effective frequency assuming a Debye spectrum can now be obtained from (4.4) and (4.11):

$$\omega_e = \frac{\int |N(\tau)|^2 \tau^4 \omega^{-1} d\tau}{\int |N(\tau)|^2 \tau^4 \omega^{-2} d\tau} = \frac{16}{3\pi} \frac{v}{a} \quad (4.14)$$

where $v = \omega/\tau$ is the velocity of sound. The integrals in (4.14) were evaluated by extending the limits to infinity since $\frac{1}{2} a \tau_{\max} \approx 7.7$.

The (squared) broadening at absolute zero may be obtained by setting $\bar{m} = 0$ in (4.2):

$$\langle (\Delta E)^2 \rangle_{T=0} = \frac{\hbar}{M v a} \frac{2}{(a \tau_{\max})^3} E_1^2 \quad (4.15)$$

The ratio of the squared broadening $\langle (\Delta E)^2 \rangle$ to its absolute zero value can from (4.2) be written:

$$R(T) = 1 + 24 \int_0^\infty x^3 (1+x^2)^{-4} [\exp(\Delta x/T) - 1]^{-1} dx \quad (4.16)$$

where $x = \frac{1}{2} a \tau$ and $\Delta = 2 \hbar v / k_0 a$. An approximate formula for $R(T)$ using the single effective frequency ω_e is simply

$$R_0(T) = 1 + 2 \bar{m}(\omega_e) = \coth(\frac{1}{2} \hbar \omega_e / k T) \quad (4.17)$$

We note that $\hbar \omega_e / k = (8/3\pi)\Delta$. A comparison of the "exact" and approximate $R(T)$ from (4.16) and (4.17) is shown in Figure 8. They both have the same zero point value and high temperature slope. Near

$$T=0 \quad R(T) \simeq 1 + 0.1 (2\pi T/\Delta)^4$$

$$\text{whereas } R_a(T) \simeq 1 + 2 \exp(-4\Delta/3\pi T)$$

The exponential decrease in $R_a(T)$ is characteristic of the Einstein approximation we have made, whereas the power law decrease in $R(T)$ is characteristic of the contributions of the low frequency phonons--as in the Debye theory of specific heats.

To compare these results with experiment, we note that the zero point line width obtained from (4.15) is of the order of 0.004 e.v. whereas the experimental width at liquid helium temperatures is about 0.001 e.v. (see figure 1). The theoretical line width may be an overestimate because of the use of the Born-Oppenheimer approximation. It may also be an overestimate because the deformation constant E_1 has been overestimated. The reason for the latter possibility is that E_1 is determined by comparing an experimental mobility with a theoretical mobility based on thermal scattering--neglecting interband transitions which are undoubtedly significant in p type silicon.

To see whether we have assumed the correct basic mechanism for broadening, namely interaction of the electron with acoustic modes, we can examine the way in which broadening changes with temperature.

An examination of (4.16) indicates that the modes of importance have an energy $k_0 \Delta$ where Δ is about 90°K in silicon. These are modes of quite low energy--they have wave-lengths whose size is of the order of the Bohr radius of the trapped hole. Does experiment bear this out? Figure 8 shows that $R(T)$ is of the order of 2 at $T = \Delta$, i.e. an appreciable broadening should occur theoretically for temperatures as low as 90°K. An examination of Figure 1 shows that a broadening of just the right order of magnitude $\sqrt{2}$ occurs between nitrogen and helium temperatures. This substantiates the importance of low energy modes in the broadening. Since our calculated absolute broadening is of the right order of magnitude, our basic picture of the phenomenon must be correct.

5. Thermal Ionization and Capture

As is undoubtedly discussed in other papers of this conference, the sensitivity of a photoconductor increases with the lifetime of the electrons in the conduction band, but its rapidity of response decreases. (Corresponding remarks can be made about holes in the valence band but will henceforth be omitted). The photoconductive lifetime is determined by a competition between the rate of thermal ionization and the rate of recombination. For example, if we are dealing with a crystal containing two types of impurity centers: N_D donors/cm³ and N_A acceptors/cm³, with $N_D > N_A$, then we will have n type photoconductivity with a lifetime

$$\frac{1}{\tau} = B \left[(K + N_A)^2 + K(N_D - N_A) \right]^{\frac{1}{2}} \quad (5.1)$$

where B is the recombination rate and $K = A/B$ is the ratio of ionization to recombination rates, or the equilibrium constant:

$$K = (2\pi m^* k_0 T / h^2)^{3/2} \exp(-E/kT) \quad (5.2)$$

where E_g is the (ground state) ionization energy of the center, assumed to have only one state,³⁹ and m^* is the effective mass. If the electron energy has several minima within the Brillouin zone, and an ellipsoidal

³⁹ The K of (5.2) must be divided by the factor

$$\left\{ 1 + \sum_{m \neq g} g_m / g_g \exp[(E_g - E_m)/kT] \right\}$$

where the states E_m are the excited states and g_m is the corresponding degeneracy factor. See Burstein, Bell, Davisson and Lax, J. Phys. Chem. 57, 849 (1953) and K. S. Shifrin, Tekhnicheskoi Zhurniel Fiski 14, 43 (1944).

energy surface with masses m_1 , m_2 and m_3 , then we must make the replacement

$$(m^*)^{3/2} \longrightarrow (\text{No. of valleys}) (m_1 m_2 m_3)^{1/2} \quad (5.3)$$

since the latter expression takes proper account of the density of states near the minimum band energy.

At high temperatures, we will have $K \gg N_A$ and

$$\frac{1}{\tau} \simeq BK = A, \quad (T \text{ large}) \quad (5.4)$$

the ionization rate, whereas at low temperatures we will have

$K \ll N_A$ and

$$\frac{1}{\tau} \simeq B N_A, \quad (T \text{ small}) \quad (5.5)$$

the recombination rate--since the number of ionized donors at low temperatures will be approximately equal to N_A the number of acceptors available to remove electrons from the donor levels. In germanium with $N_A \simeq 10^{14}$ acceptors/cm³, the temperature dividing the regions of validity between (5.4) and (5.5) is about 25°K.

As we shall see in the subsequent discussion, one of the difficulties that faces a basic calculation of ionization rates is that fairly large values must be obtained in order to agree with experiment. For example, germanium with about 10^{14} acceptors/cm³ has a photoconductive lifetime τ of less than 10^{-5} seconds even at liquid helium temperatures.⁴⁰ This implies that $B > 10^{-9}$ cm³/sec, or since $K \simeq 10^{-1}$, $A > 10^{-10}$ /sec. Perhaps a more understandable way to put this statement is to note that at 4°K, thermal velocities are of the order 3×10^6 cm/sec so that the center has an effective cross-section of the order of 3×10^{-16} cm² or larger for thermal capture.

⁴⁰ Burstein, Davissan, Bell, Turner and Lipson, Phys. Rev. 93, 65 (1954).

As a general experimental argument for high radiationless transition probabilities, we note that most electron traps do not luminesce. In particular, a careful search for F center luminescence has been made by Klick⁴¹ whose essential conclusion is that radiative transitions are never more than 3 per cent of the non-radiative transitions.

One of the first attempts to treat thermal ionization from electrons trapped in semi-conductors was made by Goodman, Lawson and Schiff.⁴² They assumed that the essential interaction as far as ionization is concerned is the interaction between the trapped electron and the vibrating core atom:

$$V_{G.L.S.} = -\frac{e^2}{K|R-R|} + \frac{e^2}{KR} \simeq \frac{e^2}{K} \frac{R}{R^3} \cdot R \quad (5.6)$$

where R is the nuclear displacement. Their unperturbed wave-functions were simple ("Hartree") products of an electronic-wave function times a vibrational wave function, and the transition is caused by $V_{G.L.S.}$ as a perturbation. We shall refer to this as the Hartree approximation.

Using only terms linear in R , only one-phonon processes are allowed in the Hartree approximation. Since the ionization energies of hydrogen-like traps in Ge or Si are less than the corresponding Debye energies, acoustic phonons are available to make a one-phonon transition possible. The Goodman-Lawson-Schiff answer, for the ionization probability turns out too small by about two orders of magnitude.

⁴¹ C. C. Klick, Phys. Rev. 94, 1541 (1954).

⁴² Goodman, Lawson and Schiff, Phys. Rev. 71, 191 (1947).

Further discussion of the G.L.S. interaction will be given later.

Goodman, Lawson, and Schiff also made an estimate of the probability for multi-phonon processes using terms of order R^m in the potential and found their contribution to be small.⁴³ Seitz⁴² in unpublished work treated the same interaction $V_{G.L.S.}$ in a Born-Oppenheimer approximation, arriving at results, according to Goodman, Lawson and Schiff of the same order as their own. An explanation for this agreement will be given later.

During the summer of 1951, in treating the broadening of impurity levels in silicon with the deformation potential interaction, I also estimated the thermal ionization probability with the same interaction using the Hartree approximation. Although the broadening came out one order of magnitude too high, with the experimental constants then available, the thermal ionization was an order of magnitude low. Because of this puzzling discrepancy, publication of this work was postponed, and both problems were reexamined. The thermal ionization problem was treated in the Born-Oppenheimer approximation and the many

⁴³ The problem of non-radiative transitions between bands had been discussed earlier by F. Moglich and R. Rompe, *Physikalische Zeitschrift* 41, 236 (1940); *Zeits. fur Phys.* 115, 707 (1940). They used a Hartree viewpoint and suggested that the many-phonon processes required here by energy conservation were obtained from terms in the electron lattice interaction of high order in the nuclear displacements. Only qualitative estimates were made for transition rates.

body sums were performed following methods used in the broadening analysis.¹⁸ But the answer did not change appreciably. The disagreement for the broadening calculation was reduced in the meantime partly by taking into account "motional narrowing" and partly by changed experimental constants due to improved mobility measurements.⁴⁴

Leurgans,⁴⁵ in his thesis, also considered the thermal ionization problem with the deformation potential and the Hartree approximation. His results confirmed the discrepancy we found. Yafet⁴⁶ reconsidered the problem in the Born-Oppenheimer approximation and found that multi-phonon contributions were negligible so that the answer Leurgans and I had obtained using the Hartree approximation would not be appreciably increased by multi-phonon contributions. An appreciable increase was found, however, when Coulomb wave-functions rather than plane waves were used for the final state. A more detailed discussion will be given later in this section.

Kubo⁴⁷ suggested that perhaps quadratic terms in the interaction energy are important--so that the vibration frequencies in the excited and ground electronic states were different. He used the Goodman, Lawson and Schiff interaction, the Born-Oppenheimer approximation and treated the central atom as a simple harmonic oscillator. He more or less arbitrarily chose the change in frequency of the harmonic oscillator

⁴⁴ M. B. Prince, Phys. Rev. 93, 1204 (1954).

⁴⁵ P. J. Leurgans, Thesis 1952 University of Illinois.

⁴⁶ Y. Yafet, Private communication.

⁴⁷ R. Kubo, Phys. Rev. 86, 929 (1952).

because of a change in electronic state to be 10 per cent. Because of the arbitrariness of Kubo's model, it is difficult to assess the applicability of his results, however, there is no question but that any significant change in vibrational frequencies will appreciably increase the rate of thermal ionization.

In addition to the case of electrons trapped at impurity levels in semi-conductors, considerable effort has been spent on radiationless transitions in F centers. From the formal point of view, the first major contribution was made by Huang and Rhys who made a many body calculation in the Born-Oppenheimer approximation assuming an interaction energy linear in the normal coordinates. The major limitation of their calculational technique--as in their treatment of broadening--is that all the modes must have one frequency. (This limitation can easily be by-passed by using techniques developed in the author's analysis of the Franck-Condon principle).

The rate for radiationless transitions from the 2p to the 1s state calculated by Huang and Rhys²⁹ was so low in comparison to radiative transitions, (10^{-19} in KBr at 30°K) that luminescence should be easily observed at most temperatures for all the alkali halides. This is definitely not the case, however.

Meyer⁴⁸ suggested that a possible explanation for the low radiationless transition rate was the neglect of quadratic terms in the energy difference between the two states. He introduced therefore, a diagonal quadratic form in addition to the Huang-Rhys interaction energy

⁴⁸ H. J. G. Meyer, Physica 20, 181 L (1954).

and recalculated the transition rate. The diagonal coefficients are somewhat arbitrary, however, and he chose them so as to agree with the observed temperature shift in the optical absorption peak. He then found a sufficiently high radiationless rate to explain why luminescence has been difficult to observe. (Radiation less/radiative $\simeq 30$ in KBr at 20°K).

In a subsequent unpublished manuscript, however, Meyer comes to entirely different conclusions:

- (1) He finds it permissible to neglect quadratic terms in the energy difference--having first estimated their size by comparison with experiment.
- (2) He finds that the ratio of radiationless to radiative transition probabilities from the excited to the ground state of the F center is now 10^{-7} in KBr at 0°K.--so that luminescence should be observable.

The difference between this result and his previous one is apparently due to different ways of determining empirically the Huang-Rhys parameter S which measures the strength of the linear terms in the interaction energy. If H is the full width at half-power, his new method of determining S is to use the relationship:

$$H^2 = 8 \ln 2 (\hbar \omega)^2 \left[S \coth \left(\frac{1}{2} \hbar \omega / kT \right) - C \right] \quad (5.7)$$

which is found to hold empirically. The formula previously used, which had a theoretical justification was identical to (5.7) with $C = 0$.

It was not clear to me why a moderate change in S would change his answer for radiationless transitions by a factor 10^8 . However, a detailed examination of his formula in the limit $T = 0^\circ\text{K}$ revealed a factor S^y where y is the number of phonons involved in the

transition--which is of the order 70 in KBr--so that a 20 per cent error in S can yield a factor 10^8 in the transition probability! In view of the sensitivity of Meyer's result, conclusions about the feasibility of observing luminescence must be regarded as provisional.

An attempt to generalize the Huang-Rhys method to the case when a distribution of frequencies are present has been made by Tewordt⁴⁹ for application to semi-conductors. Tewordt's approach, however, parallels Huang and Rhys closely, and he is consequently unable to carry out explicitly the sums over the vibrational states. He was apparently unaware that this portion of the problem had already been solved.¹⁸

Pekar⁵⁰ has written an interesting paper on the diffusion of electrons toward a trap and their eventual capture. His analysis uses classical statistics and the diffusion equation outside a somewhat arbitrary radius r_0 at which capture is supposed to take place at a rate $\beta n(r_0)$ where $n(r_0)$ is the density at r_0 . His final result is an effective capture rate B_{eff} cm³/sec given by:

$$B_{\text{eff}} = \frac{\beta \exp[-eV(r_0)/kT]}{1 + \beta (4\pi D)^{-1} \exp[-eV(r_0)/kT] \int_0^{1/r_0} \exp[eV(r)/kT] d(1/r)} \quad (5.8)$$

⁴⁹ L. Tewordt, Zeits fur Physik 137, 604 (1954).

⁵⁰ S. I. Pekar, Abh. Sow. Phys. 1, 47 (1951) translated from Z. f. exp. u. theor. Phys. 20, 267 (1950).

If the second term in the denominator is large compared to the first (capture rate large compared to diffusion rate), the process will be diffusion limited with a rate given by:

$$B_{eff} \approx B_d = 4\pi D \left[\int_0^{1/n_0} \exp[eV(r)/kT] d(1/r) \right]^{-1} \quad (5.9)$$

The diffusion constant D can be calculated from the mobility μ using the Einstein relation⁵¹

$$D = \mu k_0 T / e \quad (5.10)$$

The potential can be taken to be $eV(r) = -(e^2 / K r)$ where K is the dielectric constant. At sufficiently low temperatures that

$kT \ll e^2 / K r_0$) the integral in (5.9) becomes insensitive to its upper limit which may be set equal to infinity. Thus if $kT \ll E_g$ = the ionization energy of the center, we find that

$$B_d \approx 4\pi \mu e / K \quad (5.11)$$

The diffusion rates thus obtained are quite high. At liquid helium temperatures, using an experimental mobility of the order of 5×10^5 , we find $B_d \approx 6 \times 10^{-2}$ cm³/sec, whereas the calculated quantum capture rate is of the order of $B \approx 10^{-9}$ cm³/sec in germanium at the same temperature. Thus the diffusion is very rapid, and the limiting factor is the capture process itself.

⁵¹ For experimental verification see Transistor Teachers Summer School, Phys. Rev. 88, 1368 (1952).

⁵² E. Conwell, Proc. I. R. E. 40, 1327 (1952).

It is of some interest to note that if we define

$$B = \beta \exp[-e V(n_0)/kT] \quad (5.12)$$

to be the capture rate adjusted for the increase in density near the origin, Pekars equation can be rewritten in the form

$$\frac{1}{B_{eff}} = \frac{1}{B} + \frac{1}{B_d} \quad (5.13)$$

indicating that the total time for trapping is the sum of the diffusion time and the adjusted capture time. Since the diffusion time is, by our estimates, usually negligible, we shall be concerned primarily with the adjusted capture time.

The adjustment (5.12) is somewhat sensitive to the choice of n_0 , but the latter can be taken to be of the order of a Bohr radius so that

$B \approx \beta \exp(E_g/kT)$. Since we have assumed kT is small compared to the ionization energy E_g , an enormous increase in capture would occur, if this result were taken literally. However, the electron density cannot suffer such a marked increase near the center because of the uncertainty principle.

It is therefore necessary to take account, quantum mechanically, of the increase in density near the center. Gummel and I have done this by using Coulomb continuum wave functions instead of plane waves to describe the incoming electrons.⁵³ Roughly speaking the increase in density near the center is the Sommerfeld factor. A detailed evaluation of the matrix element for the transition yields an additional factor 2, so that the appropriate correction in the squared matrix element for the use of coulomb rather than plane waves is

⁵³ H. Gummel and M. Lax, Phys. Rev., to be submitted.

$(8\pi/y) [1 - \exp(-2\pi/y)]^{-1}$ where $y = ka$, k is the propagation constant of the incident electron, and a is the Bohr radius of the trapped state.

A rough indication of the Coulomb correction at low temperatures can be obtained by noting that the important k 's in the equilibrium distribution are of the order $(\hbar^2 k^2 / 2m^*) \simeq k_0 T$ or $ka \sim (k_0 T / E_g)^{1/2}$. Thus the correction factor is roughly $8\pi(E_g / k_0 T)^{1/2}$ which can be of the order of 200 at liquid helium temperatures (for $E_g \simeq .0125$ e.v. in germanium). At high temperatures, the Boltzmann factor puts only a weak limit on k , but the matrix element for the deformation potential interaction contains a factor $[1 - (ka)^2]^{-5}$ which means the important values of ka are smaller than say $1/2$. Even at high temperatures, then, the correction factor can be as large as 50.

To illustrate these results in more detail, we note that the total capture rate B is a Boltzmann average over the capture rates W_{ak} from a given state k :

$$B = V \int d\vec{k} P(k) W_{ak} \quad \text{cm}^3/\text{sec} \quad (5.14)$$

For simplicity, we assume spherical energy surfaces, so that the normalized distribution function is given by:

$$P(k) = (2\pi m^* k_0 T / \hbar^2)^{-3/2} \exp[-\hbar^2 k^2 / (2m^* k_0 T)] \quad (5.15)$$

The transition probabilities W_{ak} can be written in the form:

$$W_{ak} = \frac{\Omega}{2\pi M} \frac{\tau^2}{\hbar \omega} (1 + \bar{m}) D \quad (5.16)$$

$$\bar{m} = [\exp(\hbar \omega / k T) - 1]^{-1}$$

where Ω is the volume of a unit cell, M is the mass of one atom, τ is the propagation constant of a phonon, $\hbar\omega = \hbar\omega(\tau)$ is its energy, and $v = d\omega/d\tau$ is the corresponding velocity of sound. We must insert for τ and ω a value consistent with conservation of energy:

$$\hbar\omega = E_g + \hbar^2 k^2 / (2m^*) \quad (5.17)$$

If we let $\hbar\omega(\tau_0) = \hbar\omega_0 = E_g$, then for a hydrogenic impurity

(5.17) is equivalent to the conditions

$$\tau = \tau_0(1 + y^2) ; \quad \omega = \omega_0(1 + y^2) \quad (5.18)$$

For the case in which the perturbing potential is the deformation potential we have

$$D = \frac{1}{2} E_1 \tau^2 \left| \left(e^{i\tau \cdot r} \right)_{ak} \right|^2 \quad (5.19)$$

The matrix element of $\exp(i\tau \cdot r)$ between the free state k and the bound state a has been calculated exactly. Because τ is large compared to a^{-1} , the reciprocal Bohr radius, however, the resulting expression can be greatly simplified. If the free state is described by a plane wave we get

$$D_{p.w.} \simeq \frac{1}{2} E_1 \tau^2 \left(64\pi a^3 / \sqrt{y} \right) (\tau a)^{-8} \quad (5.20)$$

If the free state is described by a Coulomb wave we get

$$D_{coul.} \simeq D_{p.w.} \left\{ (8\pi/y) [1 - \exp(-2\pi/y)] \right\} \quad (5.21)$$

Thus justifying the previous remarks about the importance of the Coulomb correction.

The corresponding formulas for D using the Goodman, Lawson, Schiff interaction are:

$$D_{P.W.} = \frac{32\pi a E_g^2}{V} \frac{(y - \tan^{-1} y)^2}{y^4} \quad (5.22)$$

$$D_{Coul.} = \frac{64\pi^2 a E_g^2}{V} \frac{\exp[-(4/y)\tan^{-1} y]}{y(1+y^2)[1-\exp(-2\pi/y)]} \quad (5.23)$$

The four values of D can be inserted into (5.16) and (5.14) to obtain expressions for the total capture rate. For simplicity, we list the results for the temperature range $k_0 T \ll E_g$ -- the range of greatest interest.

$$B_{P.W.}^{deform} \simeq \frac{16 E_g^2 \Omega}{M E_g v a} \frac{1}{(\tau_0 a)^4} \quad (5.24)$$

$$B_{Coul}^{deform} \simeq \frac{256 \sqrt{\pi} E_g^2 \Omega}{M E_g v a} \frac{1}{(\tau_0 a)^4} \left(\frac{E_g}{k_0 T} \right)^{1/2} \quad (5.25)$$

$$B_{P.W.}^{G.L.S.} \simeq \frac{8(k_0 T) \Omega (\tau_0 a)^2}{3 M v a} \quad (5.26)$$

$$B_{Coul}^{G.L.S.} \simeq \frac{64 \sqrt{\pi} e^{-4} E_g \Omega (\tau_0 a)^2}{M v a} \left(\frac{E_g}{k_0 T} \right)^{1/2} \quad (5.27)$$

At liquid helium temperatures in germanium, the capture rate using the deformation potential and Coulomb waves is about 10^{-9} cm³/sec. The use of plane waves yields a result smaller by a factor of about 175. The Goodman-Lawson-Schiff interaction with plane waves gives a result smaller by a factor 5000; with Coulomb waves the result is smaller by a factor 23. Thus the primary mechanism at low temperatures seems to be the usual electron lattice interaction--and Coulomb corrections are important.

A B of 10^{-9} cm³/sec with 10^{14} compensating impurities would lead to a photoconductive life-time τ of

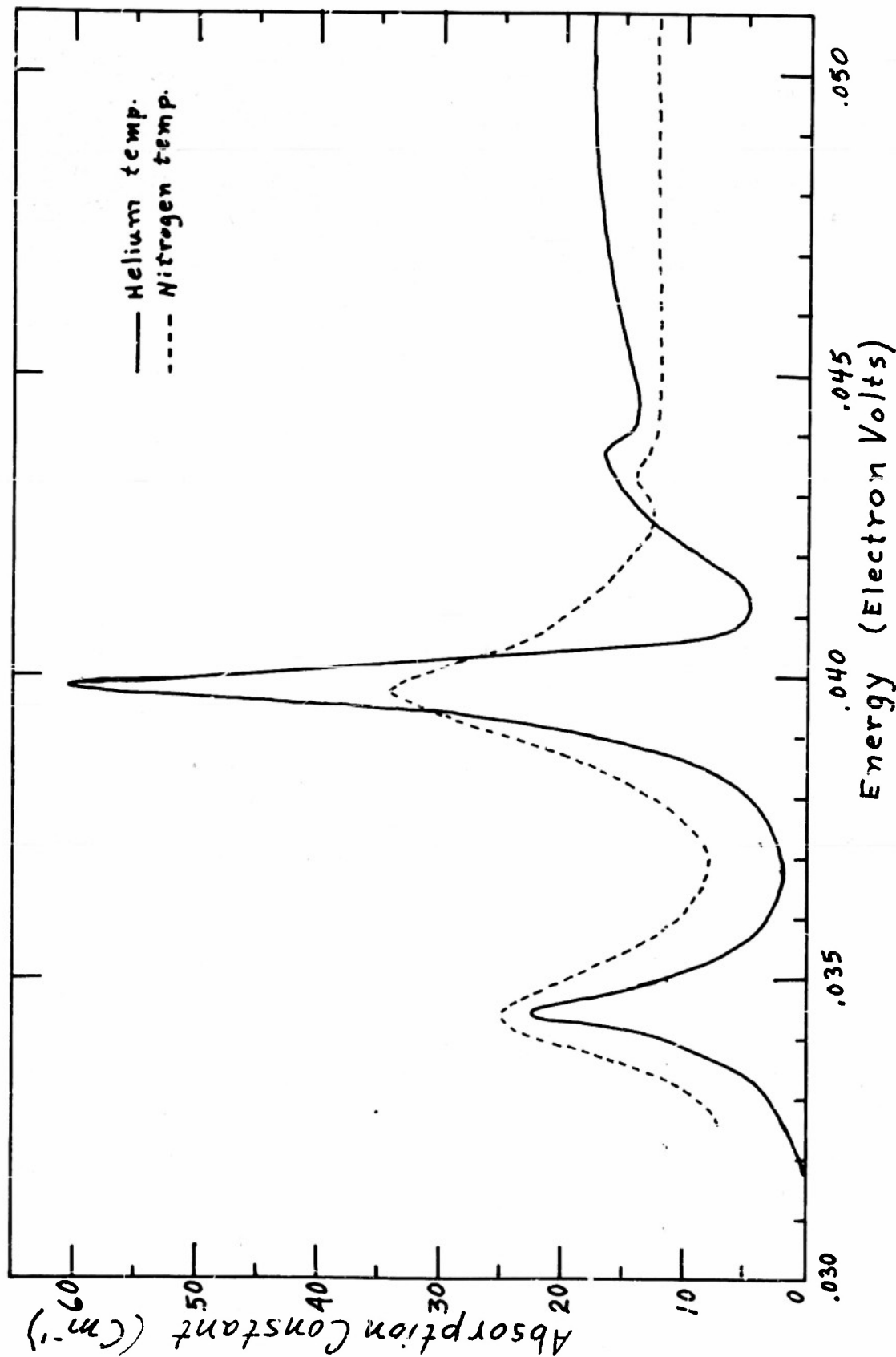
$$\frac{1}{\tau} \simeq 10^{-9} \cdot 10^{14} \simeq 10^5 / \text{sec} \quad (5.28)$$

On the other hand, Burstein et al,⁵⁴ find that for Zn doped germanium 10^{-5} sec is an upper limit for the life-time--so that the theoretical capture rate may be all right, but is possibly too small.

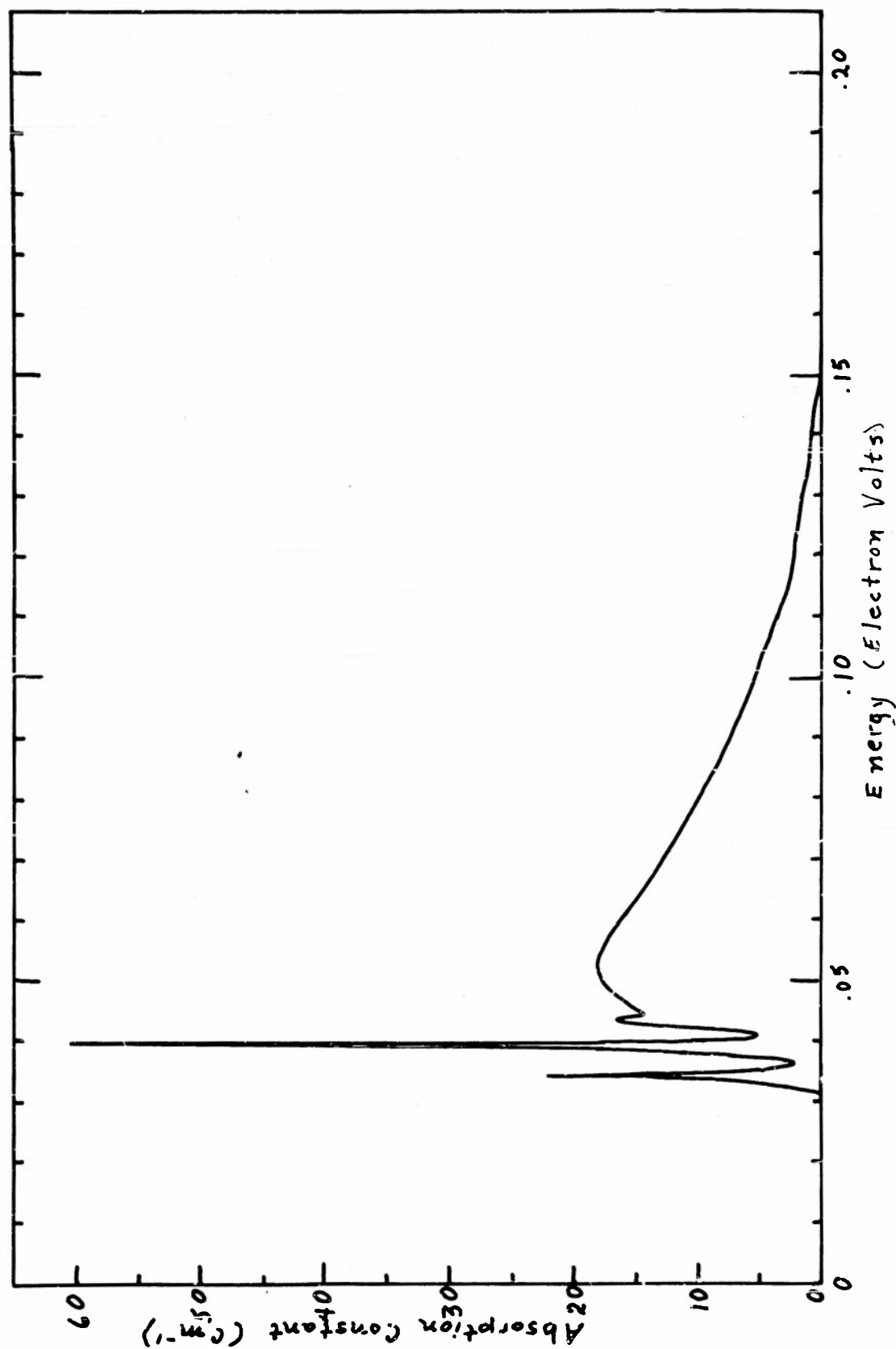
For silicon, the theoretical capture rate is 10^{-7} cm³/sec. The large increase compared to germanium is produced by a smaller value of $\tau_0 a$ because of the higher velocity of sound in silicon. Assuming the number of compensating impurities in fairly pure silicon to be of the order of 10^{15} cm³, the photoconductive life-time is given by $\tau \simeq (10^{-7} 10^{15})^{-1} \simeq 10^{-8}$ sec which is well within the experimental limit $\tau < 10^{-4}$ sec set by Burstein.⁵⁴

⁵⁴

E. Burstein, J. J. Oberly and J. W. Davisson, Phys. Rev. 89, 331 (1953).



Infrared absorption of a single crystal of silicon doped with boron (E. Burstein, E. E. Bell, and B. W. Hennis, unpublished). Further discussion of this data may be found in J. Phys. Chem. 57, 849 (1953), (Burstein, Bell, Davisson, and Lax).



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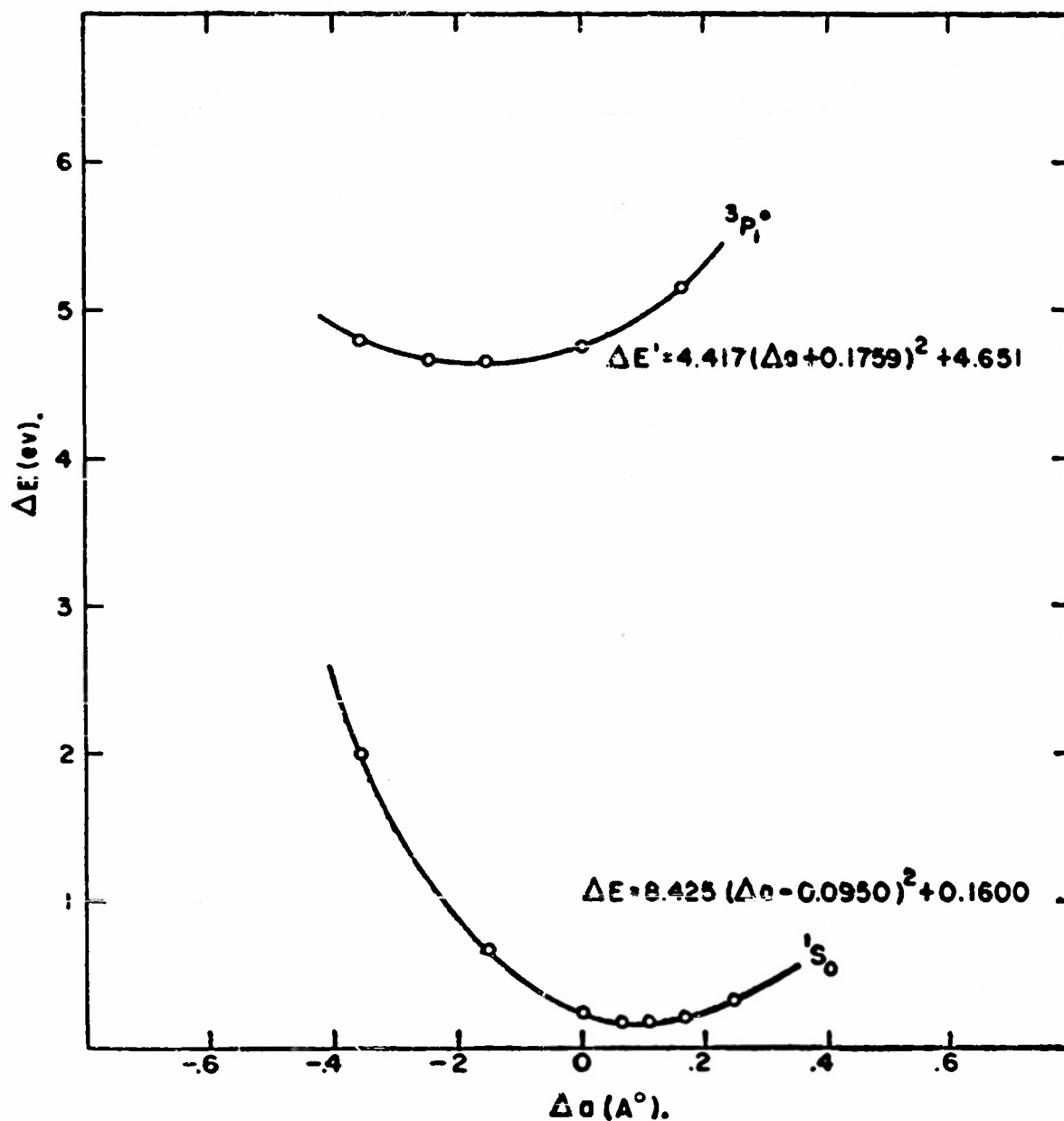


Figure 3. Configuration coordinate diagram of the activator system for KCl:Tl including the effect of angular dependence of the Tl^+ charge density and the perturbation of the states of Tl^+ by the crystal field. (F. E. Williams, J. Phys. Chem. 57, 780 (1953)).

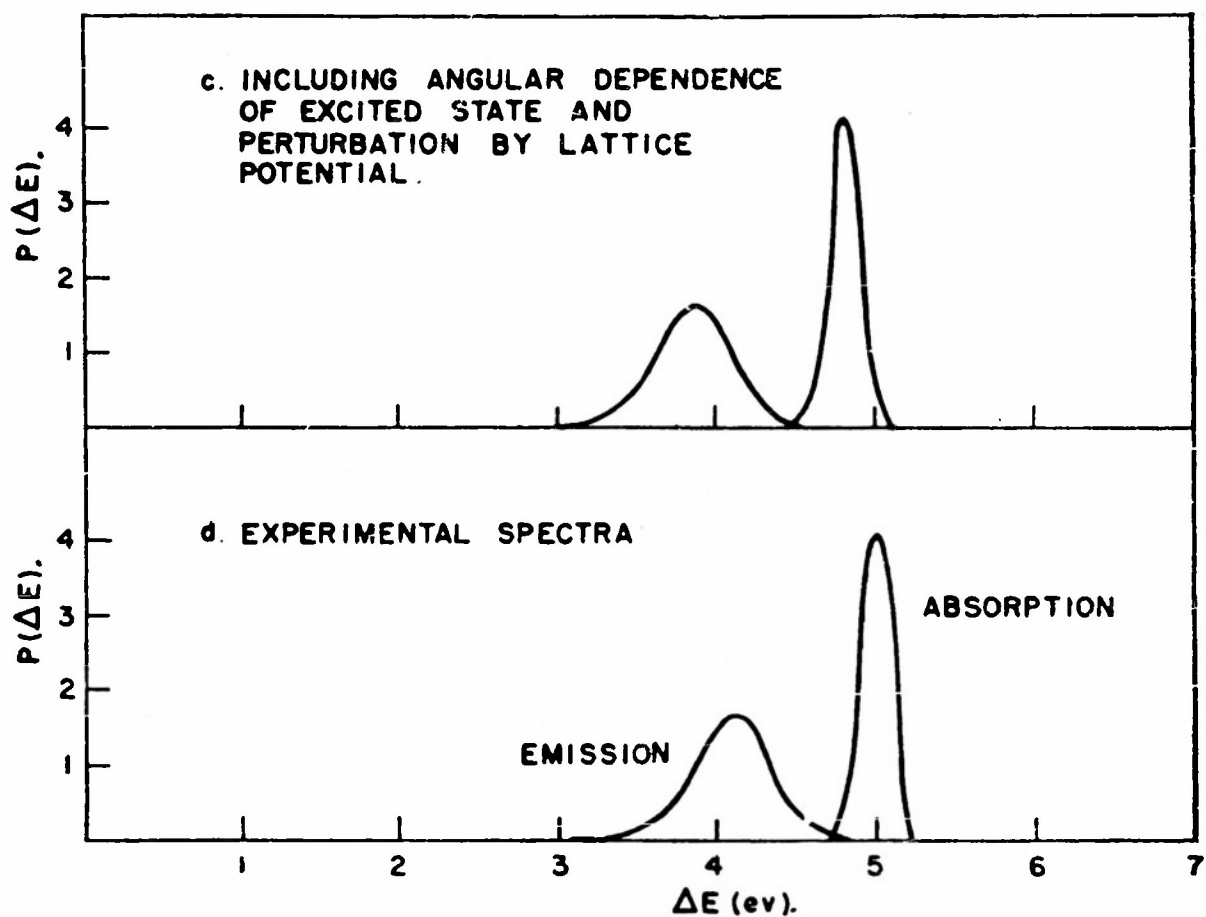


Figure 4. Theoretical and experimental absorption and emission spectra of KCl:Tl. (F. E. Williams, J. Phys. Chem. 57, 780 (1953)).

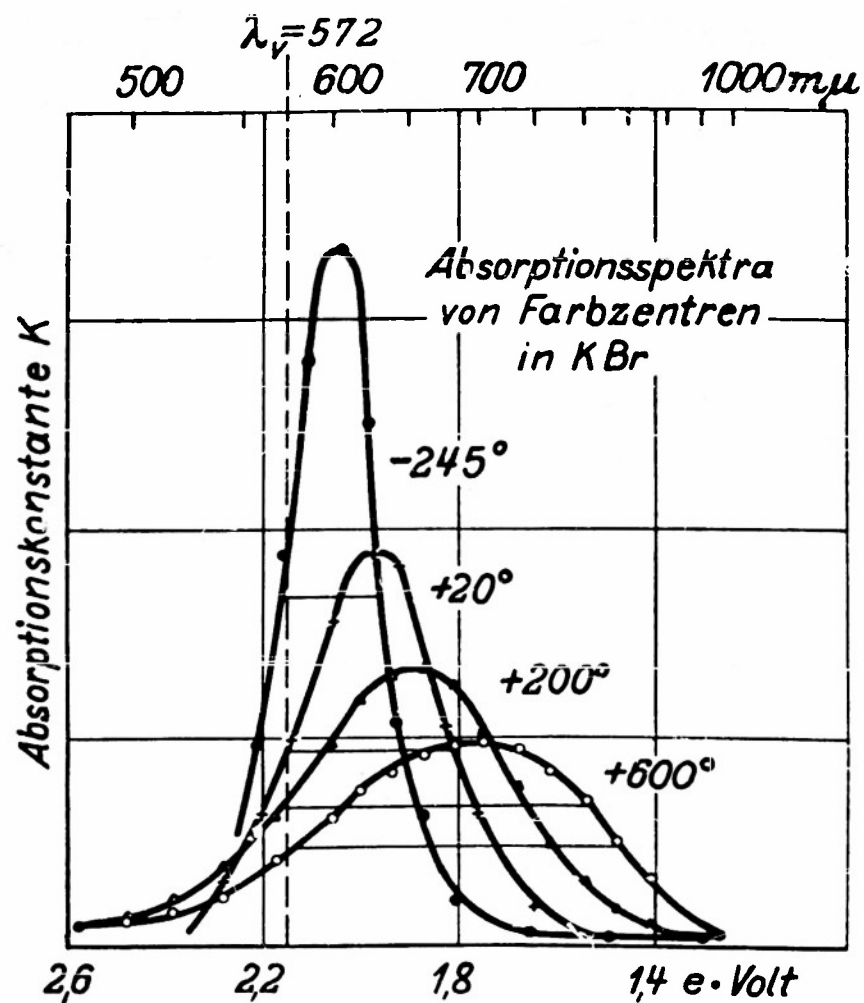


Figure 5. The influence of temperature on the absorption spectrum of color centers in KBr. (E. Mollwo, Zeits. für Physik 85, 56 (1933)).

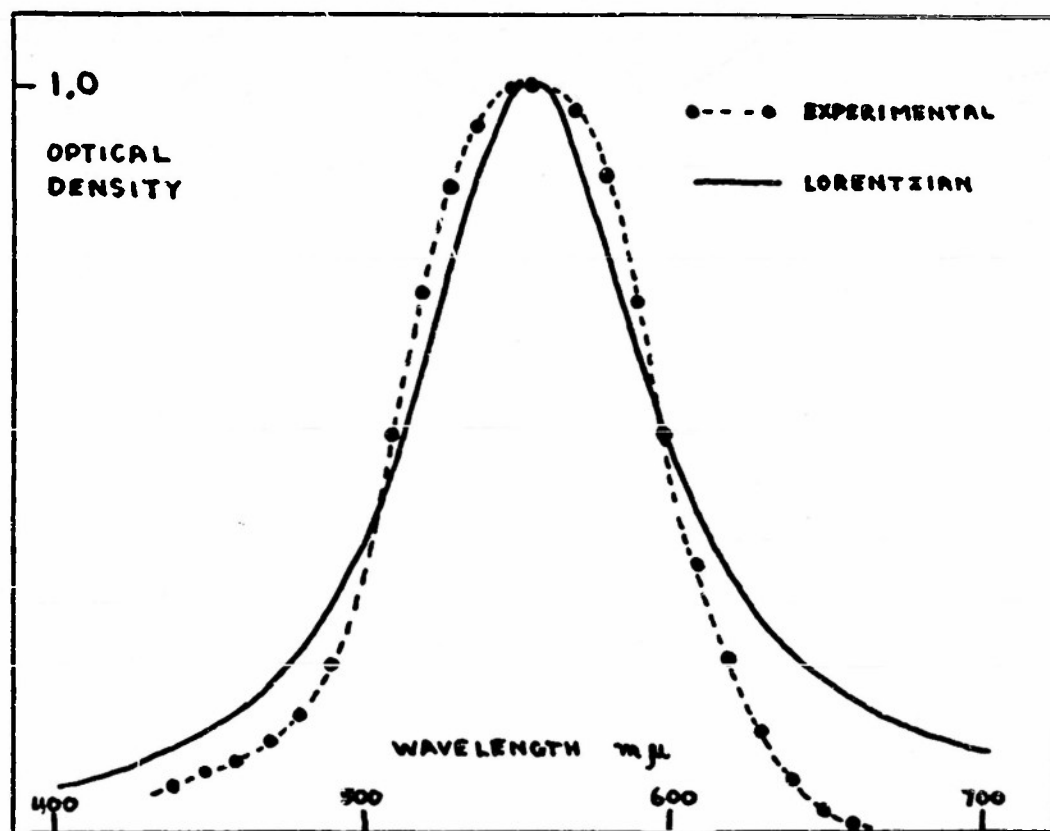


Figure 6. The F band at 290°K. (R. V. Hesketh and E. E. Schneider, Phys. Rev. 95, 837 (1954)).

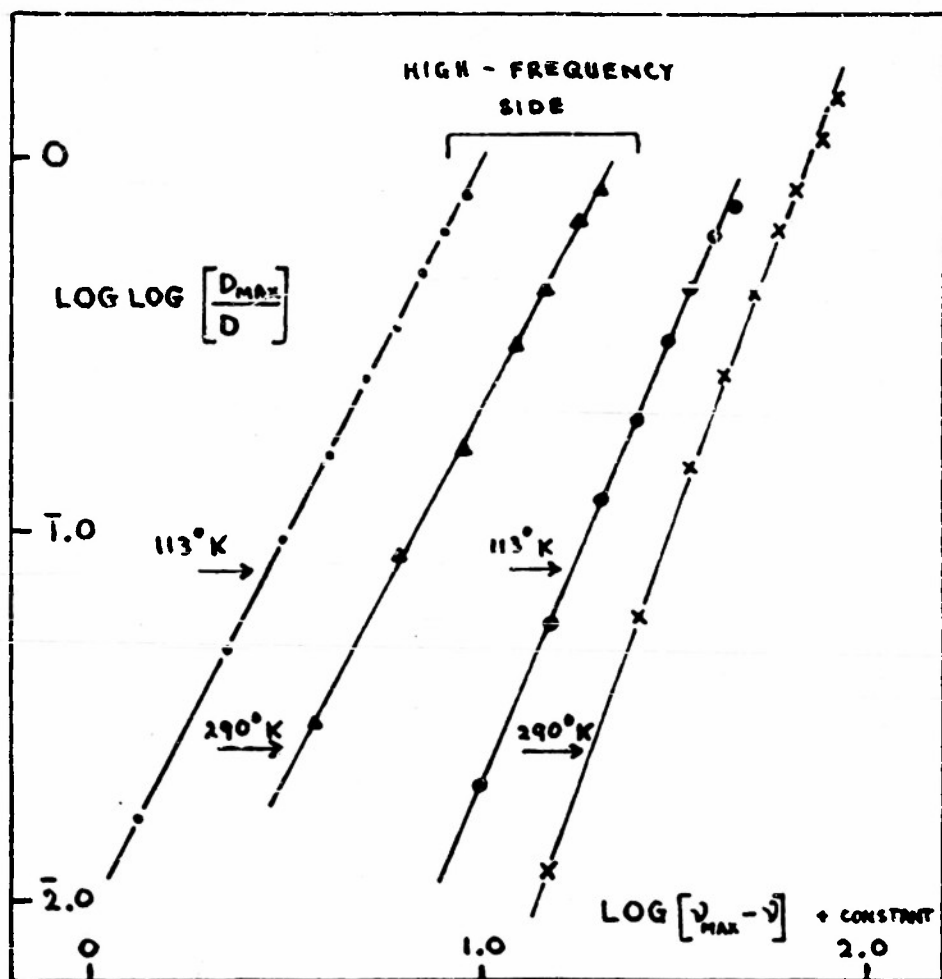
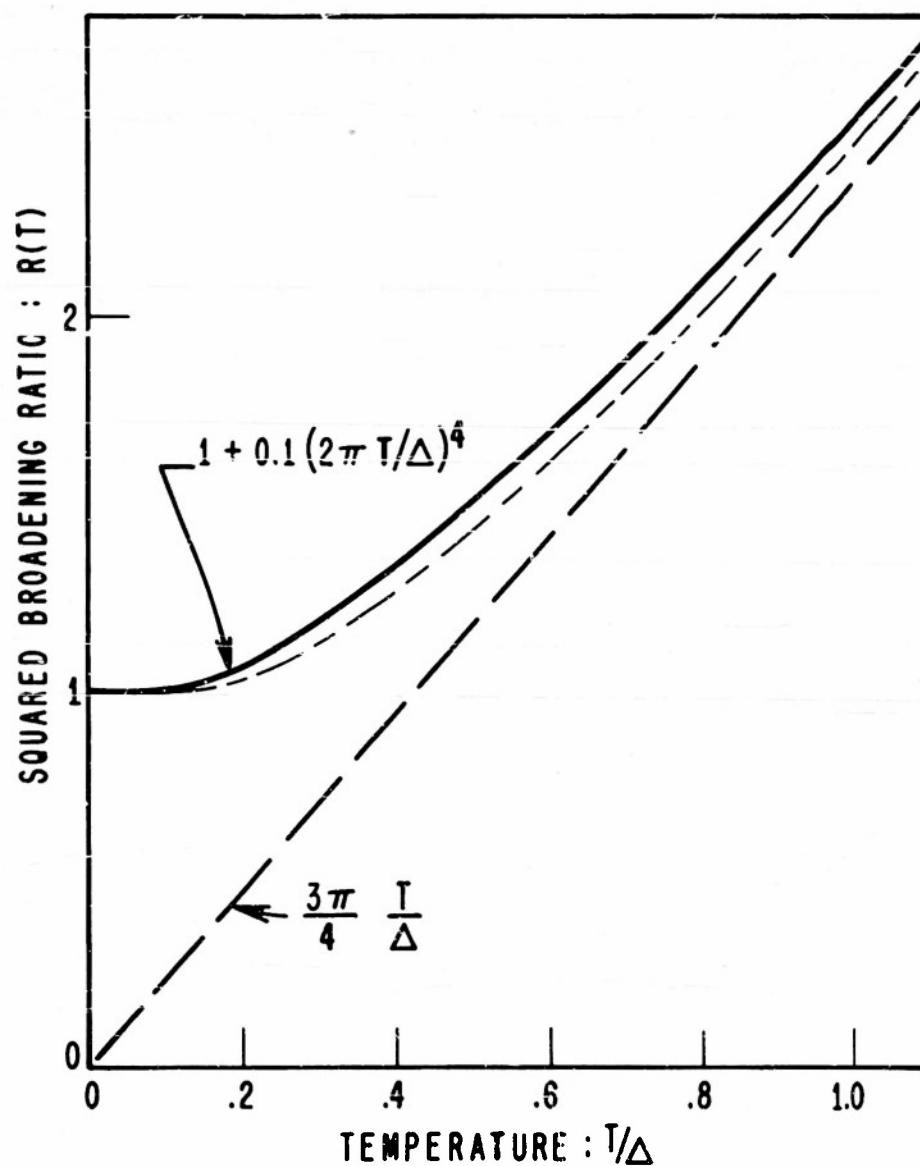


Figure 7. A Gaussian plot of the F band absorption. (R. V. Hesketh and E. E. Schneider, Phys. Rev. 95, 837 (1954)).



The theoretical ratio $R(T)$ of the squared broadening at the temperature T to its zero point value, is plotted as a function of the dimensionless variable T/Δ . The temperature $\Delta = 2\hbar v/k_0 a \approx 94^\circ \text{K}$ in silicon, where v is velocity of sound, a is the Bohr radius in the crystal, and k_0 is the Boltzman constant.

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