account of by shifting all of the calculated curves toward the lower end of the radius scale by an amount equivalent to 1.5 Mev.

From Figs. 2 and 7 it is seen that the experimental distributions are in general agreement with those calculated from the stripping process described by Serber. The experimental data are not good enough to permit us to make a choice between the transparent model and the opaque model.

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Temperature Dependence of Electron Energy Levels in Solids*

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In many crystalline insulators there is a temperature proportional displacement of the long wave-length absorption limit towards longer wave-lengths. These are crystals which have a broad, nearly structureless absorption which is caused by the transition of an electron from a full to an empty electron band. Previous attempts to explain this phenomenon have shown that the effects of thermal expansion are far too small to account for the observed shift. In this paper it is shown that there is a broadening of electron energy levels due to collisions with the thermally vibrating lattice which results in reducing the effective width of the "forbidden" energy region between occupied and conducting bands. Calculations indicate that, in polar crystals for which the observations have been made, this effect is of the proper magnitude to explain the experimental data. In non-polar crystals the effect would be very small. However, no absorption shift in non-polar crystals has been observed.

1. INTRODUCTION

(a) General Discussion of the Shift of Absorption with Temperature in Insulating Crystals

It is well known that in many crystalline insulators there is a displacement of absorption toward longer wave-lengths with increasing temperature.[1,2] This is manifested in many cases by a deepening of the color. For example, ZnI, white at room temperature, becomes yellow at higher temperatures. This is due to the fact that the absorption, which at room temperature starts about 3600A and extends far into the ultraviolet, shifts into the blue at higher temperature.

The shift toward longer wave-lengths at higher temperature applies to excitation lines as well as to the long wave absorption limit of the main absorption. However, this paper treats the latter case primarily, although, as indicated at the end

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[1] F. Möglich and R. Rompe, Zeits. f. Physik 119, 472 (1942), containing data of the shift of the absorption limit. H. Fesefeldt, *ibid.* 64, 623 (1930) the data of which probably pertains to shift of excitation lines (see Section III).

[2] There is also a much larger shift which sets in suddenly at higher temperature. Möglich and Rompe state that this is due to "multiple collisions." Naturwiss. 29, 105, Feb. 21, and 120, Feb. 28 (1941).

of Section 3, the method used here offers a line of attack for the case of excitation lines also. This paper does not treat cases in which the absorption is due to external excitation of localized groups of atoms (as in $KMnO_4$).

The following discussion, then, applies to those crystals having a very broad absorption region in which the absorption is due to the fact that an electron is lifted from a full band to an empty or conduction band. The order of magnitude of the shift (of the long wave-length absorption limit toward larger wave-length with increasing temperature) is the same for most cases, about 1A per degree at 5000A.

The shift of the absorption toward the red can be explained in two ways: as a broadening of the region of absorption—caused by a broadening of the energy levels, so that the upper limit of the full electron band and the lower limit of the excited electron band come closer to each other; or as a shift of the whole absorption region to the red. No measurements of change at the short wave-length limit have been made, so that no choice between these two interpretations can be made on the basis of direct experimental data.

By analogy with x-rays, in which it is found that the scattering of the x-rays by the thermal vibrations of the crystal lattice particles cause a reduction in the width of the region of total reflection, one would expect that the thermal scattering of electrons by the lattice particles should likewise result in a reduction of the width of the "forbidden" energy region between the full and the lowest conducting band.

Möglich, Riehl, and Rompe[3] have investigated the amount of broadening which would result from the scattering of an electron by the lattice vibrations. It can be inferred from their work that the effect so calculated is far too small to account for the facts.

Möglich and Rompe have then tried the other possibility, by explaining the phenomenon as attributable to thermal expansion. This effect, however, is also too small by a factor of at least four.

The present investigation was undertaken with the aim of a scrutiny of the assumptions made by Möglich and Rompe, to find a way out of this dilemma. Therefore, the mathematical procedures were considered more carefully than is usual in investigations of this type; they, however, were found not to be responsible for the difficulty. Instead the key was found in a fundamental difference between polar and nonpolar crystals. Möglich and Rompe's assumptions and results are valid for nonpolar crystals, while most of the observations apply to polar crystals, for which the much larger interaction between electrons and lattice vibrations leads to the correct results for the broadening of the absorption.

(b) General Discussion of the Method

The method followed in this paper is to consider an electron which by some means (for example, because of radiation in the case of absorption) has been raised from the full band to the lower levels of the upper band, leaving behind a hole in the lower band. The electron or hole collides with a lattice vibration, which throws the electron (or hole) into a different level of the same band. This transition therefore shortens the lifetime of the electron or hole in its state. This shortened lifetime is equivalent to a broadening of the energy level, analogous to the collision broadening of spectral lines.[4]

Since each level, both in the full band for the hole and in the conduction band for the excited electron, is widened, the bands made up of these levels are correspondingly widened.

In Section 3, the number of collisions are calculated for three different types of crystals—non-polar monatomic, non-polar diatomic, and polar—and the resulting shift in absorption compared with experiment.

Some of the calculations are contained in Appendices I, II, and III, while Appendix IV considers a lattice with permanently displaced atoms; this is for the purpose of seeing how much influence the mere *displacement* and how much influence the *motion* of the lattice has.

The writer wishes to express in some small measure his great indebtedness and gratitude to his teacher, Professor Karl F. Herzfeld, for suggesting the problem and the method of attack.

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[3] F. Möglich, N. Riehl, and R. Rompe, Zeits. tech. Physik 21, 6, 128 (1940).

[4] The same calculations apply to the hole as to the electron, provided a suitable mass is assigned to the hole.

2. COLLISIONS AND ENERGY BROADENING

The purpose of this section is to show the relationship between energy broadening and collisions, in a manner applicable to the collisions of an electron or hole of small kinetic energy and the thermally vibrating lattice.[5]

Call $\psi(N, \mathbf{q})$ the spatial wave function of a simple harmonic oscillator of quantum number $N(\mathbf{q})$ corresponding to a lattice vibration with wave vector $\mathbf{q}$. The energy associated with this vibration[6] will be

$$E(N, \mathbf{q}) = (N(\mathbf{q})+\tfrac{1}{2})\hbar\omega(\mathbf{q}),$$

where $\omega(\mathbf{q})$ is the circular frequency of vibration.

The wave function of an electron in a periodic field is

$$\psi(\mathbf{K}, \mathbf{r}) = e^{i(Kr)}u(K)/n^{\frac{1}{2}}, \qquad (1)$$

where $\mathbf{K}$ is the wave vector of the electron, n, the number of unit lattice cells, $u(\mathbf{K})$ a periodic function normalized in each cell, and $\mathbf{r}$ the electron position vector.

The energy of the electronic state will be approximated by that of the free electron:

$$E(\mathbf{K}) = lK^2, \quad l = \hbar^2/2m, \qquad (1')$$

where m is the effective electron mass.

The solution of the time-dependent Schrödinger equation for the complete system, lattice plus electron, is given by:

$$\Psi = \prod{}_{\mathbf{q}}\psi(N, \mathbf{q})\psi(\mathbf{K})e^{-iEt/\hbar} \qquad (2)$$

where E, the total energy $= \Sigma_{\mathbf{q}}(E(N, \mathbf{q}))+E(\mathbf{K})$ for the case in which the lattice thermal vibrations and the electron would not interact: and by

$$\Psi = a_0\psi_0 e^{-iE_0t/\hbar}+\Sigma_{j\neq 0}a_j\psi_j e^{-iE_jt/\hbar} \qquad (3)$$

for the case in which an interaction energy, W, causes transitions in the system ("collisions" between electron and lattice), bringing the electron into a different state $\mathbf{K}'$ and changing one or more $N(\mathbf{q})$. Here ψ_0 and E_0 are the spatial wave function and total energy of the complete system in its state at $t=0$ and ψ_j and E_j correspond to other states.

The coefficients, a_j, satisfy the normalization conditions

$$|a_0|^2+\textstyle\sum_{j\neq 0}|a_j|^2 = 1 \qquad (3')$$

and at $t=0$.

$$a_0 = 1 \text{ and all the other } a_j = 0. \qquad (3'')$$

Thus $\Sigma_{j\neq 0}|a_j|^2$ equals the total collision probability[7]

The perturbation matrix element is:

$$W_{j0} = \int \psi_j^* W\psi_0 d\tau \text{ (electron and lattice).} \qquad (4)$$

Let the electron wave vectors and quantum numbers of the states 0 and j, respectively, be $\mathbf{K}_0$, $N(0, \mathbf{q})$,—and $\mathbf{K}_j$, $N(j, \mathbf{q})$ where $\mathbf{q}$ is an arbitrary lattice vibration vector.

W_{j0} vanishes unless the following conditions are fulfilled: For $\mathbf{p} = (\mathbf{K}_0-\mathbf{K}_j)$ (conservation of linear momentum), the quantum number of the lattice vibration changes by one

$$N(0, \mathbf{K}_0-\mathbf{K}_j) = N(j, \mathbf{K}_0-\mathbf{K}_j) \pm 1;$$

and for all other p remains unchanged.

The coefficients in (3) satisfy the well-known differential equations

$$\frac{-\hbar}{i}\frac{\partial a_0}{\partial t} = a_0W_{00}+\Sigma_{j\neq 0}a_jW_{0j}e^{-it(E_j-E_0)/\hbar}. \qquad (5)$$

W_{00} and each W_{jj} are zero in all cases considered here.

$$\frac{-\hbar}{i}\frac{\partial a_j}{\partial t} = a_0W_{j0}e^{-it(E_0-E_j)/\hbar}$$
$$+\Sigma_{k\neq 0}a_kW_{jk}e^{-it(E_k-E_j)/\hbar}, \quad j\neq 0. \qquad (5')$$

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[5] For a classical discussion of the energy broadening resulting from collisions, see V. Weisskopf, Phys. Zeits. **34**, 1 (1933). The discussion here is an adaptation to the problem at hand of the quantum-mechanical treatment employed by Weisskopf and Wigner to determine the width of spectral lines. (See Zeits. f. Physik **63**, 54 (1939).)

[6] In a composite lattice having S particles per unit cell there will be S nodes of vibration corresponding to each wave vector $\mathbf{q}$. For a given $\mathbf{q}$ the energy associated with the sth mode of vibration will be

$$E(N, s, \mathbf{q}) = (N(s, \mathbf{q})+\tfrac{1}{2})\hbar\omega(\mathbf{q}).$$

[7] Strictly speaking, the quantity $P \equiv \Sigma_{j\neq 0}|a_j|^2$ is the total probability that at the time, t, the system is no longer in the original state, rather than the total collision probability. The latter designation does not take into account the fact that a particle which has made a transition from the original state 0 to a state j has a possibility of return to the original state or transitions to other states. However, for small times, for which $P\ll 1$, the number of transitions out of the states j will be small compared with the transitions out of the original state.

In first approximation[8] one obtains

$$P(t)\equiv\Sigma_{j\neq 0}|a_j|^2=(1/\hbar^2)\Sigma_j|W_{j0}|^2\Omega(E_j-E_0), \tag{6}$$

where

$$\Omega(z)=\sin^2(tz/2\hbar)/(z/2\hbar)^2$$

(z is used below to represent (E_j-E_0)). Approximately,

$$P=\int_{z\text{ min}}^{z\text{ max}}(L(z)/\hbar^2)\Omega(z)dz, \tag{7}$$

where $L(z)$ is obtained by first integrating (6) over the surfaces of constant z, and z max and z min represent maximum and minimum values of z, respectively.

If, now, the conditions (8) and (9) are fulfilled:

$$(z\text{ max})t/2\hbar\geqq\pi,\quad\text{and}\quad(z\text{ min})t/2\hbar\leqq\pi; \tag{8}$$

and $L(z)$ varies so slowly that, at least for the range of z given by

$$-\pi\leqq zt/2\hbar\leqq\pi, \tag{9}$$

L can be replaced by its value, $L(0)$, when $z=0$; then[9] P will be nearly time proportional (provided t is not too short), and in (7) L can be replaced by $L(0)$ and the limits may be replaced by $\pm\infty$, respectively. Thus

$$P\cong(4\pi^2/h)L(0)t. \tag{10}$$

Also,

$$P\ll 1. \tag{11}$$

Let $2\Gamma=(4\pi^2/h)L(0)$ and let A be an arbitrary real number. From (3)[10]

$$|a_0|^2=1-2\Gamma t\quad\text{or}\quad a_0\cong e^{-\Gamma t+iAt}. \tag{12}$$

From (3) one sees that A must vanish to first-order approximation, for $(-\hbar A)$ represents an energy shift which equals W_{00} to the order. Hence,

$$a_0=e^{-\Gamma t} \tag{13}$$

where Γ is half the number of collisions per second.

Although (10) is true only for small t satisfying (11), it can be shown that the expression (13) for a_0 remains correct for greater values of t. This will be done by solving the Eqs. (5′) to obtain a higher order approximation for $(\Sigma_{j\neq 0}|a_j|^2)$ valid for a wider range of t. The corresponding higher order approximation for a_0 is again (13).

In the right side of Eqs. (5′) use the approximation

$$a_0=e^{-\Gamma t}$$

and neglect all terms involving a_j $(j\neq 0)$.[11] Then

$$|a_j|^2=(|W_{j0}|^2/\hbar^2)\left[\frac{e^{-2\Gamma t}+1-2e^{-\Gamma t}\cos(zt/\hbar)}{(z^2+\Gamma^2\hbar^2)/\hbar^2}\right].$$

Again expressing $\Sigma_{j\neq 0}|a_j|^2$ as an integral analogous to (7),

$$P=\Sigma_{j\neq 0}|a_j|^2\cong\int_{z\text{ min}}^{z\text{ max}}(L(z)/\hbar^2)\times\left[\frac{e^{-2\Gamma t}+1-2e^{-\Gamma t}\cos(zt/\hbar)}{(z^2+\Gamma^2\hbar^2)/\hbar^2}\right]. \tag{14}$$

Equation (14) may be integrated under the conditions that: t is long enough so that (8) is satisfied; L is substantially independent of z in the range given by (9); and

$$|z\text{ min}|\gg\Gamma\hbar,\quad\text{and}\quad|z\text{ max}|\gg\Gamma\hbar. \tag{15}$$

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[8] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, New York, 1938), Section 96.

[9] Reference 8, Section 99.

[10] One could obtain the same value for a_0, but less simply from the differential equation (5). The normalization condition yields the same results as (5) because the fact that the normalization condition remains true for $t>0$ follows directly from the original Schrödinger equation; i.e., if $\Psi(t)$ is the solution of the Schrödinger equation at any time t,

$$\frac{\partial}{\partial t}\left(\int|\Psi|^2d\tau\right)=0.$$

[11] The neglect of all terms involving a_j in the right side of (5′), even in second approximation, is justified by the fact that from (4′) the matrix element W_{jk} must vanish for any state, k, for which both W_{k0} and W_{j0} are different from 0. Thus, if one considers a state j which does combine with state 0, the terms remaining on the right side of (5′) besides a_0 would involve coefficients a_l satisfying the conditions at $t=0$,

$$a_l=0,\quad\text{and}\quad\partial a_l/\partial t=0.$$

These coefficients would therefore be infinitesimals of the second order (or higher) and would be negligible for small t. For large t the phase factors $e^{-it(E_j-E_l)/\hbar}$ will range almost continuously from approximately (-1) to (1) (see (8)) and therefore

$$\Sigma_{l\neq 0}a_lW_{jl}e^{-it(E_j-E_l)/\hbar}$$

may be neglected in this approximation. The limits of validity for this approximation are that Γt must not become so large that $a_0(=e^{-\Gamma t})$ becomes so small as to be of the same order of magnitude as the sum of the terms remaining on the right side of (5′). However, a_0 would then be so small that the Fourier expansion (16′) would be a very good approximation. The above differs from the usual treatment in the case of spectral lines[6] in which no coefficients other than a_0 and a_j appear in the right side of the equations corresponding to (5′).

(15) replaces (8).[12]

It is then a satisfactory approximation to extend the limits in (14) to plus and minus infinity so that

$$P=(L(0)/\hbar^2)[\pi\hbar(e^{-2\Gamma t}+1)/\Gamma-\pi 2\hbar e^{-2\Gamma t}/\Gamma] \quad (16)$$

or

$$P=1-e^{-2\Gamma t}.$$

From the normalization condition one again obtains the expression (13) for a_0.

By Fourier analysis it is found that the wave function $a_0\psi_0 e^{-iE_0t/\hbar}$, where $a_0=e^{-\Gamma t}$, is mathematically equivalent to the wave packet

$$(\psi_0/2\pi)\int_{-\infty}^{+\infty}(\Gamma+2\pi i\nu)^{-1}e^{-2\pi i(E_0/h-\nu)t}d\nu. \quad (16')$$

Equation (16′) represents a distribution of energy levels so that an energy level

$$E=E_0-h\nu$$

occurs with a relative probability proportional to

$$|\Gamma+2\pi i\nu|^{-2}=(4\pi^2\nu^2+\Gamma^2)^{-1}$$
$$=(1/4\pi^2)[(E_0-E)^2/h^2+\Gamma^2/4\pi^2]^{-1}.$$

This represents a distribution of energies analogous to the distribution of absorption in a spectral line of half-width

$$(\Gamma/2\pi)=(1/4\pi)\times(\text{number of collisions per second})=\pi L(0)\equiv\Delta E. \quad (17)$$

The widening calculated above for a single level making up the conduction band will also apply to the lower edge of the conduction band, and, if the mass appropriate for a hole is used (see Eq. (1′)), to the upper edge of the full band. The absorption will therefore be widened at both ends, and the long wave-length limit shifted toward the red by the sum of the values of $(\Gamma/2\pi)$ taken for the upper edge of the full band and the lower edge of the empty band.[13]

3. DETAILED DISCUSSION OF COLLISIONS FOR INSULATING CRYSTALS

(a) Simplifying Assumptions

The following simplifying assumptions are made in the case of all types of lattices discussed herein:

(A) The lattice particles are arranged in a cubic lattice. Call a the distance between adjacent particles.

(B) The displacement of the particles due to thermal vibrations is given by the Hooke's law approximation:[14]

$$\mathbf{x}[\mathbf{r}(b,p)]=\Sigma_{s,\mathbf{q}}\, a(s,\mathbf{q})\xi(b,s,\mathbf{q})e^{i[q\cdot r(b,p)]}[(M(b))n]^{-\frac{1}{2}} \quad (19)$$

where:

$\mathbf{x}[\mathbf{r}(b,p)]$ is the vector displacement of the bth particle in the pth unit cell;

$\mathbf{q}$ is the wave vector of the vibration;

$M(b)$ is the mass of the bth particle;

n is the number of unit cells in the lattice;

$a(s,\mathbf{q})$ is the time-dependent amplitude of the sth mode of vibration having wave vector $\mathbf{q}$. The atomic normal vibration coordinates may be expressed in terms of the $a(s,\mathbf{q})$;

$\mathbf{r}(b,p)$ is the equilibrium position of the bth particle in the pth cell relative to the origin of coordinates;

$\xi(b,s,\mathbf{q})$ is a constant vector corresponding to the sth mode of vibration (of the bth particle) of wave vector $\mathbf{q}$. The ξ are normalized according to the equations:

$$\Sigma_b\xi(b,s,\mathbf{q})\cdot\xi^*(b,s',\mathbf{q})=\delta s,s'. \quad (20)$$

Also $\xi(b,s,-\mathbf{q})=\xi^*(b,s,\mathbf{q})$.

In order that the $x(b,p)$ should be real,

$$a^*(s,\mathbf{q})=a(s,-\mathbf{q}). \quad (21)$$

Call $T(E)$ the kinetic energy of lattice vibration; $V(E)$, the potential energy; $\omega(s,\mathbf{q})$, the circular frequency of the sth mode of vibration of wave vector $\mathbf{q}$. As a result of (19), (20), and (21) it can be shown that:

$$\begin{aligned}T(E)&=\tfrac{1}{2}\Sigma_{\mathbf{q},s}\,|\dot{a}(s,\mathbf{q})|^2,\\ V(E)&=\tfrac{1}{2}\Sigma_{\mathbf{q},s}\,\omega^2(s,\mathbf{q})|a(s,\mathbf{q})|^2.\end{aligned} \quad (22)$$

(C) Let $N(s,\mathbf{q})$ and $\omega(s,\mathbf{q})$ be the quantum number and circular frequency, respectively, of the sth mode of vibration with wave vector $\mathbf{q}$. It will be assumed for the sake of

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[12] Condition (15) can only be fulfilled if Γ is not too large (the temperature not too high). If (15) is fulfilled amply, then (8) is also fulfilled, since one is not interested in times for which Γt is very small; otherwise (13) and (16) are not significant. Then (9) means that

$$\left|\frac{z}{z\ \text{min}}\right|\ll 1.$$

Now it turns out that

$$L(z)=f(z+|z\ \text{min}|).$$

Therefore, if $|z|\ll|z\ \text{min}|$, L will be nearly constant in that range of z. (For the hole $L(z)=f(z+|z\ \text{max}|)$ and a similar argument applies. If the temperature is too high, Γ too large, the method of approximation used is not valid. Nevertheless the formula found will be used at higher temperatures. A similar difficulty arises in the theory of metallic conductivity. The temperature dependence of the conductivity of metals is found experimentally to obey the law derived by application of the simple perturbation method at temperatures far beyond that for which the method is strictly valid. (Cf. E. Kretschmann, Zeits. f. Physik **87**, 518 (1934); **88**, 786 (1934); R. Peierls, *ibid.* **88**, 786 (1934).)

[13] W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1944), Chapter III, Section 12.

[14] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Section 22.

simplicity that the high temperature approximation (23) may be used:[13]

$$N(s,\mathbf{q})\cong[N(s,\mathbf{q})+\tfrac{1}{2}]\cong kT/\hbar\omega(s,\mathbf{q}). \tag{23}$$

(*D*) It will be assumed that there are so few electrons in the upper band that they can be treated as a Boltzmann gas.

(*E*) In this paper one is only interested in the neighborhood of the edges of the bands and therefore deals only with electrons of small kinetic energy and consequently small $|K|$ (See Eq. (1′)). Therefore only lattice vibrations of small wave vector $|q|$ contribute significantly to collisions probabilities. For it follows from Section 2 that only collisions in which total energy is very nearly conserved, or

$$z\cong 0$$

are important. Now

$$z=lK'^2-lK^2\pm\hbar\omega(\mathbf{q}).$$

Hence from (31)[15]

$$z=2l(K\cdot q)+lq^2\pm\hbar\omega(\mathbf{q}).$$

For small $|K|$ compared with $|q|$ the first term may be neglected. Now $l=6.1\times10^{-28}$ (using $m=$ mass of free electron); $\omega(\mathbf{q})$ maximum $=2\pi\times10^{13}$. Hence for collisions of interest here, $|q|$ should not exceed 4×10^6, which is roughly only 4 percent of the maximum value, π/a, of $|q|$.

(b) Non-Polar Monatomic Crystals

The general procedure, used by Sommerfeld and Bethe[16] in computing the electron collision probability in connection with the conductivity of metals, is applicable here except as follows:

(1) Only one electron state in the upper band is assumed to be occupied . (See paragraph 3a(D).)

(2) The sound energy (see below), emitted or absorbed by an electron as a result of a collision with the lattice, can no longer be neglected in comparison with the electron energy, since electrons of very low energy are being considered instead of electrons at the top of the Fermi distribution.

The perturbation energy, W, will be computed by the "deformed lattice" method.[17]

Corresponding to the atomic vibration (19), the displacement at any point, $\mathbf{r}$, in the lattice is:[18]

$$\mathbf{x}(\mathbf{r})=\Sigma_{\mathbf{q}}a(\mathbf{q})\xi(\mathbf{q})(Mn)^{-\frac{1}{2}}e^{i(qr)}. \tag{24}$$

In this case $\xi(\mathbf{q})$ is a unit vector indicating the direction of the vibration displacements.

Let V be the atomic potential at the point r. Then:

$$W(\mathbf{r})=[x(\mathbf{r})\cdot\operatorname{grad}V]. \tag{25}$$

Let $\mathbf{K}$ be the wave vector of the initial electron state in the upper lattice.

In accordance with Eqs. (2) and (4) the matrix component of W—connecting for example the states determined (a) by the lattice-vibration quantum numbers $N(\mathbf{q})$ and the electron wave vector $\mathbf{K}$, and (b) the quantum numbers $N'(\mathbf{q})$ and electron wave vector $\mathbf{K}'$—is:

$$W(\mathbf{K}'N'(\mathbf{q}),\, KN(\mathbf{q})$$

$$=\int\Pi_{\mathbf{q}}\psi^*(N',\mathbf{q})\psi(\mathbf{K}')(x\cdot\operatorname{grad}V)\Pi_{\mathbf{q}}\psi(N,\mathbf{q})\psi\,(\mathbf{K})d\tau$$

$$=\Sigma_{\mathbf{q}'}\int\Pi_{\mathbf{q}}\psi^*(N',\mathbf{q})a(\mathbf{q}')n^{-\frac{1}{2}}\Pi_{\mathbf{q}}\psi(N,\mathbf{q})d\tau(\text{atomic})$$

$$\cdot\int\psi^*(\mathbf{K}')[\xi(\mathbf{q}')\cdot\operatorname{grad}V](M)^{-\frac{1}{2}}$$

$$\times e^{i(q'r)}\psi(\mathbf{K})d\tau(\text{electronic}). \tag{26}$$

The integration in (26) over the atomic coordinates vanishes unless for a particular wave vector $\mathbf{q}$:

$$N(\mathbf{q})=N'(\mathbf{q})-1, \tag{27}$$

or

$$N(\mathbf{q})=N'(\mathbf{q})+1; \tag{27'}$$

and for all other wave vectors, for example $\mathbf{w}$,

$$N(\mathbf{w})=N'(\mathbf{w}). \tag{28}$$

The integration over the atomic coordinates yields (29) and (29′), corresponding to (27) and (27′), respectively.

$$[(N(\mathbf{q})+1)\hbar]^{\frac{1}{2}}[2n\omega(\mathbf{q})]^{-\frac{1}{2}}, \tag{29}$$

$$[N(\mathbf{q})\hbar]^{\frac{1}{2}}[2n\omega(\mathbf{q})]^{-\frac{1}{2}}. \tag{29'}$$

Let u_0 be the speed of sound waves in the crystal. For small $|q|$, which alone are important (see paragraph 3a (*E*))

$$\omega(q)=u_0|q|. \tag{30}$$

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[15] The collisions (*Umklappprozesse*) for which $\mathbf{K}'=\mathbf{K}+\mathbf{q}+\mathbf{g}$ ($\mathbf{g}$ being a reciprocal lattice principal vector) will be neglected, since in such cases the condition for energy conservation would be for small $|K|$

$$lq^2+lg^2+2l(q\cdot g)\pm\hbar\omega(\mathbf{q})=0,$$

and this could not be satisfied even for $|q|$ maximum $(=|\tfrac{1}{2}\mathbf{g}|)$.

[16] A. Sommerfeld and H. Bethe, *Handbuch der Physik*, XXIV/2 (1933).

[17] Reference 14, p. 520.

[18] The subscripts s and b in (19) have been omitted since here there is only one atom in the unit cell.

Equations (27) and (27′) correspond, respectively, to the emission or absorption by the electron of the sound energy $\hbar\omega(q)$.

The integration in (26) over the electronic coordinates vanishes except for the longitudinal vibration of wave vector $\mathbf{q}$ for which:

$$\mathbf{K}'=\mathbf{K}+\mathbf{q}.^{18} \tag{31}$$

When (31) is satisfied, the integration over the electronic coordinates equals in absolute value:

$$|\tfrac{2}{3}qC(M)^{-\frac{1}{2}}|, \tag{32}$$

where C is the electronic interaction constant.

$$C=l(R)^{-2}, \tag{33}$$

R being the approximate atomic radius.

$$(l=\hbar^2/2m).$$

Combining (29) and (32) and using (23), (26) yields:

$$|W(\mathbf{K}'N'(\mathbf{q}),\ \mathbf{K}N(\mathbf{q})|^2 =(2C^2kT)(9u_0^2nM)^{-1}\equiv D^2. \tag{34}$$

The left side of (34) will be written as D^2 for brevity. It will be noted that D^2 is independent of $\mathbf{q}$ and $\mathbf{K}$.

Take polar coordinates about the point $\mathbf{K}$ in the inverse lattice. One obtains for the total collision probability, P:[20]

$$P=(Na^3D^2)[(2\pi)^3h^2]^{-1}\int_0^{q\ \max}\int_0^{\pi} 2\pi q^2\Big[(\sin^2[(t/2\hbar)(E(\mathbf{K}')-E(\mathbf{K})+\hbar u_0 q)]) \times([(E(\mathbf{K}')-E(K)+\hbar u_0q)/2\hbar]^{-2})+(\sin^2[(t/2\hbar)(E(K')-E(\mathbf{K})-\hbar u_0q)]) \times([(E(\mathbf{K}')-E(\mathbf{K})-\hbar u_0q)/2\hbar]^{-2})\Big]\sin\theta d\theta dq. \tag{35}$$

From (35) one obtains (see Appendix I)

$$P=(2a^3C^2kTt)(9\pi\hbar l u_0^2M)^{-1}[K+(\hbar u_0/2l)^2/K],\quad K\geqq \hbar u_0/2l, \tag{36}$$

$$P=(2a^3C^2kTt)(9\pi u_0 l^2M)^{-1},\quad K\leqq \hbar u_0/2l. \tag{37}$$

The second term in (36) is a correction which can be neglected for large K.

The transition point

$$K=\hbar u_0/2l,$$

between formulas (36) and (37), corresponds to the point where the electron speed equals the speed of the sound waves, since the momentum of the electron equals $\hbar K$.

From (37) and (33) it will be noted that for small $|K|$ the collision probability is independent both of the initial electron wave vector and of the electronic mass.

Using (37) for germanium one obtains 1.66×10^8 as the number of collisions per second per degree.[19] Assuming an equal broadening for the electron in the upper band and the hole in the lower band, it follows from (17) that there would be a shift in the absorption limits of 9×10^{-4} wave numbers per degree or 2.25×10^{-4}A per degree at 5000A, much too small to be observed optically. It is also too small to affect the formula for the number of thermally excited electrons.

A similar result of a shift too small to be observed would result from application of the formula (37) to other non-polar insulating crystals except possibly for loosely bound molecular crystals for which u_0, the speed of sound waves, might be very small. However, a temperature proportional shift has not been observed in non-polar crystals. Möglich and Rompe[1] state that there is no positive evidence of a temperature proportional shift in quartz; if a shift exists, it is smaller than that observed in polar crystals. As will be seen in the next subsection, the computed shift in composite non-polar crystals is practically the same as for monatomic crystals.

Experimental measurements[21] on the conductivity of germanium confirm formula (36) for the case of large $|K|$ where the correction factor may be neglected.

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[19] This is based upon the value of 2.78×10^5 for u_0 as computed from the Debye temperature of 290.

[20] A zone of reciprocal lattice space is here approximated by a sphere of the same volume.

[21] Lark-Horovitz, Miller, and Walerstein, Phys. Rev. **69**, 258 (1946).

(c) Diatomic Non-Polar Crystals

In a diatomic lattice there will be two modes of lattice vibration (one at high frequency and one at low frequency), associated with each vibration wave vector **q**, which may interact with the electron. The low frequency vibrations (acoustic branch) correspond to the case of the monatomic lattice just considered. In the case of the high frequency vibrations (optical branch), for small $|q|$, the two atoms in the unit cell are displaced in opposite directions, the magnitudes of the displacements being in inverse ratio to the atomic masses.[22, 23]

As in the monatomic case, the "deformed lattice" method will be used to compute the perturbation. The two atoms in each unit cell will be numbered 1 and 2, respectively. In accordance with (19), the displacements of the two atoms (having equilibrium locations $\mathbf{r}(1)$ and $\mathbf{r}(2)$) will be given by $x(1)$ and $x(2)$, respectively:

$$\begin{aligned}\mathbf{x}(1)&=\Sigma_{s,\mathbf{q}}a(s,\mathbf{q})\xi(1,s,\mathbf{q})e^{i(q\cdot r(1))}[M(1)n]^{-\frac{1}{2}},\\ \mathbf{x}(2)&=\Sigma_{s,\mathbf{q}}a(s,\mathbf{q})\xi(2,s,\mathbf{q})e^{i(q\cdot r(2))}[M(2)n]^{-\frac{1}{2}},\end{aligned} \tag{38}$$

where n is again the number of unit cells in the lattice; thus there are $2n$ atoms total. The notations L or H will be used in the future where it is necessary to distinguish between lower and upper frequencies of lattice vibration, respectively.

The volume of a unit cell is now $2a^3$. Each atom will be assigned a subcell of volume a^3; it will be assumed that the perturbation in each subcell is determined primarily by the displacement of the associated atom. Thus the perturbing potential at any point, $\mathbf{r}$, of subcell No. 1 will be

$$(x(1)\cdot\operatorname{grad}V(1))\,; \tag{39}$$

and in subcell No. 2 the perturbation will be

$$(x(2)\cdot\operatorname{grad}V(2)), \tag{40}$$

where $V(1)$ and $V(2)$ are the atomic potentials.

The perturbation matrix element, corresponding to (26) for the sth mode of vibration will be

$$\begin{aligned}W(\mathbf{K}'N'(s,\mathbf{q}),\,\mathbf{K}N(s,\mathbf{q}))=\Sigma_{\mathbf{q}'}\Bigg[\int\Pi_{\mathbf{q}}\psi^*(N'(s,\mathbf{q}))a(s,\mathbf{q}')n^{-\frac{1}{2}}\Pi_{\mathbf{q}}\psi(N(s,\mathbf{q}))d\tau(\text{atomic})\\ \times\int\Big(\psi^*(\mathbf{K}')(\xi(1,s,\mathbf{q}')\cdot\operatorname{grad}V(1))[M(1)]^{-\frac{1}{2}}e^{i(q'r)}\psi(\mathbf{K})d\tau(\text{electronic subcell No. 1})\\ +\psi^*(\mathbf{K}')(\xi(2,a,\mathbf{q}')\cdot\operatorname{grad}V(2))[M(2)]^{-\frac{1}{2}}e^{i(q'r)}\psi(\mathbf{K})d\tau(\text{electronic subcell No. 2})\Big)\Bigg].\end{aligned} \tag{41}$$

The magnitude of (41) will be denoted by $D(s)$.

From Eq. (41) it appears that the integration over the atomic coordinates will give the same result as for the monatomic case except that $N(s,\mathbf{q})$ is substituted for $N(\mathbf{q})$ and $\omega(s,\mathbf{q})$ for $\omega(\mathbf{q})$.

In order for the integration over the electronic coordinates to differ from zero it will again be necessary that

$$\mathbf{K}'=\mathbf{K}+\mathbf{q}. \tag{31}$$

For the lower frequency branch the two atoms in the unit cell vibrate in the same direction with nearly equal amplitude as long as q is small.[22] Hence from (38):

$$\xi(1,L)[M(1)]^{-\frac{1}{2}}=\xi(2,L)[M(2)]^{-\frac{1}{2}}. \tag{42}$$

Using the normalization condition (20), one obtains

$$\begin{aligned}\xi(1,L)&=[M(1)/(M(1)+M(2))]^{\frac{1}{2}}\mathbf{n},\\ \xi(2,L)&=[M(2)/(M(1)+M(2))]^{\frac{1}{2}}\mathbf{n}.\end{aligned} \tag{42'}$$

where $\mathbf{n}$ is a unit vector.

Since the electronic wave amplitude function, $u(\mathbf{K})$, (see (1)) is now normalized over the unit

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[22] L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946), p. 52.

[23] A monatomic lattice could be considered as a diatomic lattice with $M(1)=M(2)$. If one considers it as monatomic, the lattice waves of high frequency have a large $|q|$ and for that reason do not interact with the electron (see paragraph 3a (E)). If one considers now the lattice as diatomic, the high frequencies would be allocated to the upper branch and assigned a low $|q|$, so that they could—from this standpoint—interact with the electrons. But now they give again no contribution because in (47) $M(1)=M(2)$.

cell volume of $2a^3$ in lieu of a^3, it follows that

$$\left|\int \psi(\mathbf{K}')(n\cdot\text{grad}\,V)\psi(\mathbf{K})d\tau(\text{subcell})\right| = |\tfrac{1}{3}qC| \quad (43)$$

or $\frac{1}{2}$ the value in the monatomic case (see (32)). Thus

$$D(L)^2 = 2C^2kT/[9u_0^2n(M(1)+M(2))]. \quad (43')$$

Comparison with the corresponding expression (34) for the monatomic lattice yields

$$D(L)^2 = MD^2/(M(1)+M(2)). \quad (44)$$

In the limiting case of a monatomic lattice

$$M(1)\rightarrow M, \quad M(2)\rightarrow M, \quad D(L)^2\rightarrow\tfrac{1}{2}D^2.$$

However, the collision probability, $P(L)$, would be equal to P for the monatomic case since in (35) the volume of the unit cell, $2a^3$, would be substituted for a^3 (see also (47)).

The expression (37) therefore holds for the collision probability due to the lower frequency branch of lattice vibrations, except that M is replaced by $\frac{1}{2}(M(1)+M(2))$. Thus the expression is the same as for the monatomic case except that the average mass of the two atoms in the unit cell is used.

For the upper frequency branch of lattice vibrations the displacements of the two atoms in the unit cell for a particular small q satisfy the relations:

$$x(1)/x(2) = -M(2)/M(1). \quad (45)$$

Hence,

$$\begin{aligned}\xi(1,H) &= [M(2)/(M(1)+M(2))]^{\frac{1}{2}}\mathbf{n},\\ \xi(2,H) &= -[M(1)/(M(1)+M(2))]^{\frac{1}{2}}\mathbf{n}.\end{aligned} \quad (46)$$

Let ν be the highest frequency of lattice vibration,[24] corresponding to the point on the upper frequency branch for which $q=0$. To first approximation[25] the frequency may be assumed independent of q for small q.

The integration over the atomic coordinates in (41) still yields the expressions (29) (in $N(H, \mathbf{q})$ and $\omega(H, \mathbf{q})$), but it must be taken into account that the circular frequency $\omega(H, \mathbf{q})$ is no longer proportional to q but is constant.

Equation (41) may now be evaluated for this case and gives:

$$\begin{aligned}D(H)^2 = C^2kTq^2(M(2)-M(1))^2/\\ 72\pi^2\nu^2(M(1)+M(2))M(1)M(2)n.\end{aligned} \quad (47)$$

This expression vanishes for $M(2)=M(1)$ as would be expected[23] and is no longer independent of q as in the previous cases.

The sound energy emitted or absorbed by an electron during a collision is now $h\nu$, which is comparatively large. Where the electron energy is less than $h\nu$, as in this case, the probability of a collision in which the electron emits energy will be very small. Hence, in place of (35), one obtains for the total collision probability, $P(H)$ due to the upper frequency branch.

$$\begin{aligned}P(H) = (2a^3n/(2\pi)^3\hbar^2)\int_0^{q\,\max}\int_0^{\pi} 2\pi q^2 D(H)^2\\ \times(\sin^2[(t/2\hbar)(E(\mathbf{K}')-E(\mathbf{K})-h\nu)])\\ \times[(E(\mathbf{K}')-E(\mathbf{K})-h\nu)/2\hbar]^{-2}\sin\theta d\theta dq.\end{aligned} \quad (48)$$

The solution for $P(H)$ which is proportional to time is then (see Appendix II) for small $\mathbf{K}$:

$$\begin{aligned}P(H) = [a^3h^{\frac{1}{2}}kTC^2(M(2)-M(1))^2t]\\ [18l^{5/2}\nu^{\frac{1}{2}}(M(2)+M(1))\\ \times M(1)M(2)2\pi^2]^{-1}.\end{aligned} \quad (49)$$

Suppose one mass, $M(2)$, much larger than the other. Then

$$P(H) = (a^3h^{\frac{1}{2}}kTC^2t)(18l^{5/2}\nu^{\frac{1}{2}}M(1)2\pi^2)^{-1}, \quad (50)$$

which would usually be smaller by at least the factor 10^2 than the collision probability (37) for the monatomic case, since (50) equals (37) multiplied by

$$(1/8\pi)(hu_0^2/l\nu)^{\frac{1}{2}}.$$

Thus it will be seen that ordinarily the upper frequency branch of lattice vibrations would contribute very little to the electron collision probability. A similar result would be expected for crystals with a greater number of atoms per unit cell.

(d) Diatomic Polar Crystals

In a polar crystal, as pointed out by Fröhlich,[26] the scattering of electrons is due mainly to those

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[24] ν differs only slightly from the Restrahlfrequenz. See R. B. Barnes, Zeits. f. Physik **75**, 732 (1932). ν is of the order 10^{13} sec.$^{-1}$.

[25] Reference 22, Eq. (15.5).

[26] H. Fröhlich, Proc. Roy. Soc. **160**, 230 (1937); H. Fröhlich and N. F. Mott, *ibid.* **171**, 496 (1939). The

thermal vibrations, in which positive and negative ions move in opposite directions, so that, because of the long range of electric forces, many atoms cooperate, producing a polarization field. This field has a much greater perturbing effect on an electron than the effect of the local distortion of the lattice field which is alone present in non-polar crystals.

The displacements $\mathbf{x}(1)$ and $\mathbf{x}(2)$ of the two ions in a particular cell will be given by (38). The polarization per unit volume due to these displacements is then:

$$e(\mathbf{x}(1)-\mathbf{x}(2))/2a^3. \tag{51}$$

Hence, since only small q are important, only the lattice vibrations of the upper frequency branch, in which the ions move in opposite directions, will produce an appreciable polarization field.

Using (46), the polarization per unit volume becomes[27]

$$\Sigma_{\mathbf{q}} ea(s, \mathbf{q})e^{i(qr)}/(2a^3(nM)^{\frac{1}{2}}). \tag{52}$$

Here M is the reduced mass

$$(1/M=1/M(1)+1/M(2)).$$

The periodic perturbation potential energy,[28] W, is derived from (52) by use of Poisson's equation. It is found that W vanishes except for longitudinal vibrations where

$$W=[-4\pi ie^2/(2a^3(nM)^{\frac{1}{2}})] \times[\Sigma_{\mathbf{q}}(a(s, \mathbf{q})/q)e^{i(qr)}]. \tag{53}$$

Since only longitudinal vibrations result in a polarization potential, it will be necessary to use the longitudinal vibration frequency (denoted by $\nu(l)$) rather than the transverse frequency (denoted by $\nu(t)$) which is observed in the infrared. As shown by Fröhlich,

$$\nu(l)^2=\nu(t)^2+e^2/2\pi Ma^3. \tag{54}$$

The matrix components of the perturbation, W, may now be computed:

$$W(\mathbf{K}'N'(s, \mathbf{q}), \mathbf{K}N(s, \mathbf{q}))=\Sigma_{\mathbf{q}'}\int \Pi_{\mathbf{q}}\psi(N'(s, \mathbf{q}))a(s, \mathbf{q}')(n)^{-\frac{1}{2}}\Pi_{\mathbf{q}}\psi(N(s, \mathbf{q}))d\tau(\text{ionic})$$
$$\times\int\psi(\mathbf{K}')(-4\pi ie^2/2a^3M^{\frac{1}{2}}q')e^{i(q'r)}\psi(\mathbf{K})d\tau(\text{electronic}). \tag{55}$$

The magnitude of (55) will be denoted by D.

The expressions (29) (in $N(s, q)$ and $\omega(s, q)$) are valid for the integration over the ionic coordinates. Hence, using (23) and (31),

$$D^2=e^4kT/(2a^6q^2nM\nu(l)^2). \tag{56}$$

For low energy electrons only those collisions in which the electron absorbs sound energy need be considered (because in the upper vibration frequency branch the phonon energy is large). Hence the expression (48) applies for the total collisions probability, $P(H)$, here also, except that (56) is substituted for $D(H)$ in (48). It is then found (see Appendix III) that for small K

$$P(H)=e^4kTt/(a^3Mh^{3/2}\nu(l)^{5/2}(\hbar^2/2m)^{\frac{1}{2}}). \tag{57}$$

The displacement of the absorption edge in energy units is then obtained by substituting from (57) into (17)

$$\Delta E=e^4kT/(4\pi a^3Mh^{\frac{1}{2}}\nu(l)^{5/2}(\hbar^2/2m)^{\frac{1}{2}}), \tag{58}$$

plus a corresponding displacement due to the collisions of the hole in the lower band.

The expression (58) will now be compared with experimental results.

It should be noted that, as pointed out by Möglich and Rompe,[1] very few quantitative measurements have been made of the displace-

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treatment in the present paper differs from that of Fröhlich in that here the collisions per unit time are computed in order to determine the energy broadening from (17). On the other hand Fröhlich, because he was interested in conductivity, computed the time required for an electron velocity component in a particular direction to be reduced to zero. Hence, instead of simply summing the collision probabilities for the various lattice vibration vectors as is done here, Fröhlich first weighted each collision probability by a suitable factor taking into account the change in the electron velocity component.

[27] It will be noted that $(n)^{\frac{1}{2}}$ is used here, whereas in Fröhlich's similar expression $(2n)^{\frac{1}{2}}$ appears, since as may be seen from (19), the number of unit cells, and not the number of ions, enters into the normal coordinate solution for the ionic displacements.

[28] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. **171**, 496 (1939) show that the effect of screening is negligible for electrons having small $|K|$.

ment with temperature of the long wave absorption limit. These authors state that for many substances the displacement is of the magnitude of 1A per degree at 5000A but give quantitative data only for ZnS and CdS. For CdS the value of the Restrahlfrequenz was not available to the writer.

For ZnS the Restrahlfrequenz is 10^{13} sec.$^{-1}$. The longitudinal frequency is then 1.22×10^{13} sec.$^{-1}$. (58) gives an energy broadening of 7.85×10^{-16} erg per degree due to electron collisions. (The effective mass of an electron in the upper band has been assumed equal to the mass of a free electron.)

The experimental results for ZnS are 8.43×10^{-16} erg per degree shift from 77° to 290° and 12.9×10^{-16} erg per degree from 290° to 478°.

In view of the approximation (23), it seems more appropriate to compare (58) with the higher temperature results. It will be seen that (58) agrees with the high temperature results provided one assumes that the effective mass of the hole in the lower band is approximately one-fourth the mass of a free electron. This is in agreement with the viewpoint of Mott and Gurney[29] that the effective mass of a positive hole in a broad lower band, such as exists in sulfides, is much smaller than the mass of a free electron.

The statement of Möglich and Rompe, that the temperature displacement of the absorption limit is of the same order of magnitude for many substances, may be understood from (58).

Let U_1'' be a constant equal to the approximate restoring force per unit displacement of a lattice particle. Then[30]

$$\nu(l)^2=(1/4\pi^2)(2U_1''/M). \tag{59}$$

Thus, in (58) one may replace $(M\nu(l)^2)$ by $(1/2\pi^2)U_1''$; $(U_1''a^3)$ should be roughly a constant for ionic crystals according to the Madelung theory.[31] Therefore the only variable in (58) between different substances would be $\nu(l)$ in the denominator. Since the wave-length of the Restrahlfrequenz lies between 20μ and 150μ for most substances, it will be seen that the variation in (58) should not exceed a factor of 3 or 4 in most cases. However, the effective mass of the hole introduces an additional variable in (58) as noted below.

In addition to the results given by Möglich and Rompe, Fesefeldt[1] has reported some measurements of the displacement with temperature of the absorption peaks of KI and RbBr. Although, as Mott and Gurney[32] point out, these peaks are probably excitation levels rather than the absorption limits, it is interesting to compare these results with the broadening predicted by (58).

Substance	Shift in ergs/degree (from Fesefeldt)	$\nu(l)$*	$\Delta E/T$ from (58) (in ergs/degree)
KI	19.1×10^{-16} (at 23°) to 15.2×10^{-16} (at 493°)	5.05×10^{12}	23×10^{-16}
RbBr	12×10^{-16} (87° to 493°)	4.49×10^{12}	24.7×10^{-16}

* The actual maximum transverse frequency, as given by Barnes, reference 24, has been used in computing $\nu(l)$.

Thus it will be seen that the broadening computed due to the collisions of either the electron or the hole is already greater than that observed.[33] The results may be understood on the basis that here one is dealing with excitation lines. If the exciton is considered as a positive hole coupled to an electron, the collisions of the pair may be expected in many cases to be of the same order of magnitude as given by (58), but somewhat less since the effects of the polarization perturbation field on the hole and electron would tend to cancel, depending upon their separation.

APPENDIX I. DERIVATION OF EQS. (36) AND (37)

In the first integral of (35) it is desired to replace the variable θ by Z where $Z=E(\mathbf{K}')-E(\mathbf{K})+\hbar u_0 q$.

Utilizing (1′) and (31) one obtains:

$$Z=lq^2+2lKq\cos\theta+\hbar u_0 q, \tag{60}$$

so that

$$-\sin\theta d\theta=dZ/2lKq. \tag{61}$$

Similarly, in the second integral of (35) substitute:

$$z=lq^2+2lKq\cos\theta-\hbar u_0 q. \tag{62}$$

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[29] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1940), and Chapter V, No. 5, p. 76.

[30] Reference 22, p. 54.

[31] Reference 14, Eq. (4), p. 77.

[32] Reference 29, Chapter IV, Sections 6 and 7.

[33] For the narrow filled bands of the halides the effective mass of the hole should be equal to or greater than the mass of a free electron.

The results of these substitutions are:

$$P=(na^3D^2)[2\hbar^2(2\pi)^2lK]^{-1}\left[\int_0^{q\,\max}\int_{Z-}^{Z+}q(\sin^2tZ/2\hbar)(Z/2\hbar)^{-2}dZdq+\int_0^{q\,\max}\int_{z-}^{z+}q(\sin^2tz/2\hbar)(z/2\hbar)^{-2}dzdq\right],\quad(63)$$

where $Z+=lq^2+2lKq+\hbar u_0q$ and $Z-=lq^2-2lKq+\hbar u_0q$ and similarly for the z limits. If now one interchanges the order of integration, the limits of the variables are:

Case No. 1: Assume that

$$K\geqq\hbar u_0/2l.\quad(64)$$

It is then found from (61) that

$$Z\text{ minimum}=-l(K-\hbar u_0/2l)^2\quad(65)$$

and that the limits of q in the first integral of (63) are:

Range of Z	Upper limit of q	Lower limit of q
Z min to 0	$(K-\hbar u_0/2l)+[(\hbar u_0/2l-K)^2+Z/l]^{\frac{1}{2}}$	$(K-\hbar u_0/2l)-[(\hbar u_0/2l-K)^2+Z/l]^{\frac{1}{2}}$
0 to Z max	$(K-\hbar u_0/2l)+[(\hbar u_0/2l-K)^2+Z/l]^{\frac{1}{2}}$	$-(K+\hbar u_0/2l)+[(\hbar u_0/2l+K)^2+Z/l]^{\frac{1}{2}}$

Similar expressions apply to z minimum and the limits of q in the second integral of (63) except that the sign of $(\hbar u_0/2l)$ is changed.

Z max and z max are so large that they can be replaced by infinity.

Case No. 2:

$$K\leqq\hbar u_0/2l.\quad(66)$$

This differs from the previous case by the fact that

$$Z\text{ minimum}=0$$

and the limits of q from z minimum to $z=0$ in the second integral of (63) are as follows:

Range of z	Upper limit of q	Lower limit of q
z minimum to $z=-l(\hbar u_0/2l-K)^2$	$(K+\hbar u_0/2l)+[(K+\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}$	$(K+\hbar u_0/2l)-[(K+\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}$
$z=-l(\hbar u_0/2l-K)^2$ to $z=0$	$-(K-\hbar u_0/2l)-[(K-\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}$	$(K+\hbar u_0/2l)-[(K+\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}$
	$(K+\hbar u_0/2l)+[(K+\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}$	$-(K-\hbar u_0/2l)+[(K-\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}$

Performing the integration in (63) over q, one then obtains a result analogous to (7):

$$P=[na^3D^2/(2(2\pi)^2lK)]\left[\int_{-l(K-\hbar u_0/2l)^2}^{Z\,\max}(2/\hbar^2)\times(K-\hbar u_0/2l)[(K-\hbar u_0/2l)^2+Z/l]^{\frac{1}{2}}(\sin^2(tZ/2\hbar))\times(Z/2\hbar)^{-2}dZ+\int_{-l(K+\hbar u_0/2l)^2}^{z\,\max}(2/\hbar^2)(K+\hbar u_0/2l)\times[(K+\hbar u_0/2l)^2+z/l]^{\frac{1}{2}}(\sin^2(tz/2\hbar))(z/2\hbar)^{-2}dz\right].\quad(67)$$

The evaluation of (67) in accordance with (10) and use of (34) then yields (36) and (37).

APPENDIX II. DERIVATION OF EQ. (49)

In (48) replace the variable θ by z where $z=E(\mathbf{K}')-E(\mathbf{K})-h\nu$

$$z=lq^2+2lKq\cos\theta-h\nu.\quad(68)$$

Using (47), one then obtains, after changing the order of integration:

$$P(H)=[a^3C^2kT(M(2)-M(1))^2]\times[18(2\pi)^4\hbar^2\nu^2K(M(1)+M(2))M(1)M(2)]^{-1}\times\int_{z\,\min}^{z\,\max}\int q^3(\sin^2(tz/2\hbar))(z/2\hbar)^{-2}dqdz,\quad(69)$$

z max may be replaced by infinity. From (68),

$$z\min=-(lK^2+h\nu).\quad(70)$$

The limits of q are:

Range of z	Upper limit of q	Lower limit of q	
z min to $(-h\nu)$	$K+[K^2+(h\nu+z)/l]^{\frac{1}{2}}$	$K-[K^2+(h\nu+z)/l]^{\frac{1}{2}}$	(71)
$(-h\nu)$ to z max	$K+[K^2+(h\nu+z)/l]^{\frac{1}{2}}$	$-K+[K^2+(h\nu+z)/l]^{\frac{1}{2}}$	

Integrating with respect to q in (69),

$$P(H)=[a^3C^2kT(M(2)-M(1))^2]\times[18(2\pi)^4\nu^2l(M(1)+M(2))M(1)M(2)]^{-1}\times\int_{-(lK^2+h\nu)}^{z\,\max}dz[(K^2+(h\nu+z)/l)^{\frac{3}{2}}+K^2(K^2+(h\nu+z)/l)^{\frac{1}{2}}(\sin^2(tz/2\hbar))(z/2\hbar)^{-2}].\quad(72)$$

Evaluation of (72) in accordance with (10) leads to a quadratic expression in K. For small values of K (lK^2, the kinetic energy of the electron, small compared to $h\nu$, the energy of the phonon) one retains only the important term which gives (49).

APPENDIX III. DERIVATION OF EQ. (58)

One again uses (48) with D^2 from (56) in place of $D(H)^2$. Proceeding again as in appendix 2 one obtains

$$P(H)=e^4kT(2a^3Mh^2\nu(l)^2lK)^{-1}\int_{z\,\min}^{z\,\max}\int(1/q)\times(\sin^2(tz/2\hbar))(z/2\hbar)^{-2}dqdz\quad(73)$$

z min and the limits of q are given by (70) and (71), respectively.

$$P(H)=e^4kT(2a^3Mh^2\nu(l)^2lK)^{-1}\times\int_{z\,\min}^{z\,\max}\log([K+(K^2+(h\nu(l)+z)/l)^{\frac{1}{2}}]\times[K-(K^2+(h\nu(l)+z)/l)^{\frac{1}{2}}]^{-1})\times(tz/2\hbar)/(z/2\hbar)^2dz.\quad(74)$$

The pole in the integrand when $z=-h\nu(l)$ is due to the fact that the substitution (68) is not valid at the point $q=0$.

One readily finds that the integration in (73) over a small region around the point $q=0$ tends towards 0 as the volume of the region is reduced.

Equation (74) may then be evaluated in accordance with (10):

$$P(H)=e^4kT(2a^3Mh\nu(l)^2l)^{-1}[(1/K)\log[(K+[(K^2+h\nu(l))/l]^{\frac{1}{2}})\times(-K+[(K^2+h\nu(l))/l]^{\frac{1}{2}})^{-1}]]t.$$

As $K \rightarrow 0$ the quantity in the brackets approaches $2[l/(h\nu(l))]^{\frac{1}{2}}$ and the derivative with respect to K of the quantity in brackets$\rightarrow 0$.

Thus for sufficiently small K one obtains (57).

APPENDIX IV. COLLISIONS IN A SLIGHTLY PERTURBED NON-VIBRATING LATTICE

In the calculations of collision probabilities the treatments given in this paper have taken into account the motion of the lattice particles. It is also of interest to consider a procedure, similar to that usually used in computing the thermal scattering of x-rays, in which the lattice particles are considered "frozen" in a particular displacement and the deviations from periodicity cause the electron collisions. A non-polar monatomic lattice will be considered in this manner.

It will be noticed that in this case the collisions are elastic, i.e., there is no transfer of energy between the electrons and the lattice.

The perturbation energy, W, will again be given by

$$W = (x(r) \cdot \mathrm{grad}\, V) \tag{25}$$

where $\mathbf{x}(r)$ is given by (24).

If the electron wave vector changes from $\mathbf{K}$ to $\mathbf{K}'$ as a result of a collision, the matrix element of W will be:

$$W(\mathbf{K}', \mathbf{K}) = \int \psi(\mathbf{K}')^*(x(r) \cdot \mathrm{grad}\, V)\psi(\mathbf{K})d\tau(\text{electronic}). \tag{75}$$

Hence, the condition in Eq. (31), $\mathbf{K}' = \mathbf{K} + \mathbf{q}$ still holds, so that from (32)

$$|W(\mathbf{K}', \mathbf{K})|^2 = (|a(q)|^2 + q^2C^2)/9Mn, \tag{76}$$

where $|a(q)|^2$ is the square of the amplitude of the coefficient in the q term in the Fourier analysis of the deviation from an ideal lattice.

Therefore, the average collision probability, P, is given by

$$P = \Sigma_{K'} |W(\mathbf{K}', \mathbf{K})|^2 \sin^2[t(E(\mathbf{K}') - E(\mathbf{K}))/2\hbar] \times [(E(\mathbf{K}') - E(\mathbf{K}))/2\hbar]^{-2}. \tag{77}$$

It will be noted that the value of P is determined primarily by the transition probability to states for which the electronic energy is nearly conserved, i.e.,

$$E(\mathbf{K}') = E(\mathbf{K}),$$

while in the vibrating lattice the important states were those for which $E(\mathbf{K}') = E(\mathbf{K}) \pm h\nu$. The difference is of importance only when the initial electronic energy is of comparable magnitude or smaller than the phonon $h\nu$.

Equation (77) will be approximated by an integration over the electron wave vector space. Take coordinates about the origin. The only variable in the integration is then $\mathbf{K}'$, for from (1′):

$$E(\mathbf{K}') - E(\mathbf{K}) = l(K')^2 - lK^2.$$

Let $z = E(\mathbf{K}') - E(\mathbf{K})$

$$P = \int_{-lK^2}^{z\,\max} [(4C^2|a(q)|^2)/9Mn](1/\hbar^2)(na^3)(2\pi)^{-3} \times (4\pi/2l)(z/l + K^2)^{\frac{1}{2}} \sin^2(tz/2\hbar)/(z/2\hbar)^{-2}dz. \tag{78}$$

The solution for P which is proportional to time is[34]

$$P = (2a^3C^2kTKt)/(9\pi\hbar l u_0^2 M) \tag{79}$$

which is identical except for a correction term with Eq. (36) for the case of large K when the motion of the lattice particles are taken into account. This agreement was to be expected since, when the electron energies are large, the electrons are moving rapidly with respect to the lattice so that the motion of the lattice particles may be neglected to first approximation.

However, (79) is different from (37) when K is very small since according to (37) the collision probability is then independent of K. This is also to be expected since for small electron energy the collision probability depends upon the number of states for which the increase in electron energy equals the energy absorbed from the lattice so that energy is nearly conserved.

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[34] In order to compare the collisions in this case with those for a vibrating lattice, one can choose $|a(q)|^2$ equal to the average square of the displacement in thermal motion at high temperatures. Then from (22)

$$[|a(q)|^2] = kT/(u_0^2q^2).$$