Equations (42) and (43) may both be shown to satisfy (11) and (23); they may also be derived directly from physical considerations.

The second approach lies in the use of the "extra" boundary condition (28c) or (40c). In Eq. (35), for instance, if we consider the region in the E_0-t plane determined by $\beta t<E_0<2\beta t$, then not more than one of the two factors g in the integral can differ from 0 for any v. We thus have a homogeneous, linear equation, which may be solved by using the Green's function F. We may then use this solution to study the region $2\beta t<E_0<3\beta t$, obtaining an inhomogeneous equation involving the previous solution, and so forth. The boundary condition (28b) must be introduced by letting $E_0\rightarrow 0$ and $t\rightarrow 0$ with $E_0/\beta t$ between 1 and 2, or 2 and 3, etc. Successive applications of this method are quite cumbersome, and of course an infinite series is needed for a complete solution.

It may be, however, that a numerical integration procedure can be started satisfactorily with this approach.

Finally, it should be remarked that Friedman[3] has developed variational-iterational methods for F which, however, we have been unable to apply to the nonlinear equations for G.

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Temperature Dependence of the Energy Gap in Semiconductors*

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The problem treated is the effect of lattice vibrations in producing a shift of the energy levels which results in a temperature dependent variation of the energy gap in semiconductors. Calculations for silicon and germanium give results of the same order of magnitude as the observed temperature dependent shift of the absorption band edge. The effect of lattice vibrations on the energy gap has been treated previously on the basis of broadening rather than shifting of the energy levels. The effect was found to be negligible for nonpolar crystals, whereas according to our treatment it should be much larger. For polar crystals our result turns out to be essentially the same as was given by the previous treatment.

I. INTRODUCTION

Recent measurements on germanium and silicon show that the long wavelength limit of the optical absorption band shifts toward shorter wavelength with decreasing temperature.[1] The steeply rising edge of the absorption band shifts without changing its shape. The position of the band edge corresponds approximately to the width of the forbidden energy gap determined from resistivity and Hall coefficient measurements. The shift thus indicates a variation of the energy gap with temperature. An alternative explanation is that the absorption edge should actually be at a higher energy, the close agreement with the energy gap being due to deviations in the crystal from perfect periodicity which allow the violation of selection rules for optical transitions. The shift in absorption could then be attributed to the change in the degree of deviation from periodicity due to the temperature variation of the lattice vibrations.[2] However, this does not seem to be the explanation for our case, since the band edge is very sharp and shifts without changing shape. Moreover, for a given temperature samples differing in resistivity by several orders of magnitude, thus having different concentrations of impurity and different degrees of deviation from periodicity, show no appreciable difference in the position and the shape of the absorption edge. Thus, temperature variation of the energy gap is the more likely explanation. Temperature variation of the photoelectric threshold for germanium and silicon *p–n* junctions have also been observed.[3] Furthermore, analysis of the temperature variation of carrier concentrations determined by Hall and resistivity measurements also indicate such a dependence of the energy gap in these materials.[4]

The shift of absorption limit with temperature has been known for polar crystal insulators. Möglich and Rompe[5] pointed out the effect of lattice expansion on the energy gap and made rough estimations showing that it could account for only a small part of the observed temperature shift, although their work cannot be regarded as quantitative. Recently, Höhler measured the shift of absorption edge in CdS with pressure. Using his result, Seiwert[6] found that thermal expansion

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[1] M. Becker and H. Y. Fan, Phys. Rev. **76**, 1531 (1949); H. Y. Fan, Phys. Rev. **78**, 808 (1950); H. Y. Fan and M. Becker, report at Conference of Semiconducting Materials, July, 1950, to be published soon; unpublished work of H. B. Briggs, see reference 9.

[2] The author is indebted to Professor F. Seitz for raising this point in a private discussion.

[3] Unpublished work by F. S. Goucher and H. B. Briggs, see reference 9.

[4] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949); V. Johnson and H. Y. Fan, Phys. Rev. **79**, 899 (1950).

[5] F. Möglich and R. Rompe, Z. tech. Physik **119**, 472 (1942).

[6] R. Seiwert, Ann. Physik **6**, 241 (1949).

effect accounts for only one-sixth of the observed temperature shift.

Möglich, Riehl, and Rompe[7] have also considered the effect of lattice vibrations as a cause for broadening the energy levels and thereby changing the energy gap. This approach was followed later by Radkowsky,[8] who showed that the effect is large for polar crystals, the result agreeing quite well with experimental data. For nonpolar crystals, of which germanium was chosen for consideration, the effect was found to be negligible.

Bardeen and Shockley[9] have recently treated the effect of lattice expansion on the energy gap for nonpolar crystals. We shall reexamine the effect of lattice vibrations, all evidence indicating that thermal expansion cannot fully account for the observed shift of absorption edge in silicon and germanium. Rather than treat the lattice vibrations as producing a broadening of the energy levels, we consider them as causing a shift of the energy levels. A crystal with vibrating lattice not only has an additional vibrational energy of the ions, but also has a different electron-lattice interaction energy as compared with a stationary lattice. Two states of different electron distributions in a vibrating crystal will not, therefore, necessarily differ by the same amount of energy as the corresponding states in the stationary lattice, since the difference in electron-lattice interaction energy for the two states may not be the same in both cases. The energy gap is the difference in the energy of the crystal when an electron is excited from the top of the valence band up to the bottom of the conduction band. Our problem is to determine the change in the electron-lattice interaction energy of the crystal which accompanies such excitation. This change depends upon the lattice vibrations and therefore on the temperature.

The difference between our approach and the energy level broadening concept will be clear from the following discussion. The vibrating crystal in the absence of external perturbations has stationary states corresponding to various energy levels as does a vibrating molecule. As in the treatment of molecular absorption, we consider an external perturbation to produce transitions between various energy levels of the vibrating crystal. If we have only solutions for the lattice fixed, then the problem is to obtain the energy levels of the vibrating crystal by approximation methods. On the other hand, if it is specifically given that the vibrating crystal is not in one of its stationary states but is in a state which would be stationary had the lattice been fixed, then the state of the crystal will change with time. Under such conditions the crystal can be regarded as having approximately the energy computed for the fixed lattice, with an uncertainty proportional to the rate of transition of the state to other states. This is the basis of the energy level broadening treatment. Since we have no reason to deal with such nonstationary states, our approach seems to be more reasonable.

We wish to mention still another way of treating the effect of lattice vibrations on absorption, used by Muto[10] for metals. This method is based on the idea of simultaneous photon absorption and the absorption or emission of a lattice vibrational quantum. As in the energy level broadening treatment, it also starts with the crystal in a state which would be stationary if the lattice were fixed; but it deals with the change of this state due to the simultaneous actions of the lattice vibrations and the radiation field, instead of considering first the effect of lattice vibrations separately. In the case of semiconductors this treatment will give a small absorption extending beyond the direct absorption limit by a frequency range corresponding to the maximum energy of a phonon, unless simultaneous absorption of several phonons is considered. According to the point of view of dealing with stationary states of the vibrating crystal, such an effect is analogous to a change of the vibrational state of a molecule which accompanies an electron transition and should be treated along the same line. In the treatment given below this effect is not taken into account.

The results of the following treatment show that the lattice vibrations give a much larger temperature dependence of the energy gap in nonpolar crystals than that obtained by Radkowsky. The effect is comparable with the effect of thermal expansion and should help to explain the observed shift of absorption edge for silicon and germanium. These results have been discussed previously without the details of the treatment.[11] In the case of polar crystals our results turn out to be essentially the same as those obtained by Radkowsky.

II. ELECTRON-LATTICE INTERACTION ENERGY

The change in electron-lattice interaction energy due to a lattice distortion is to the first approximation proportional to the displacement of the ions. The vibrations of the ions can be analyzed into normal modes, and the change in the interaction energy for an electron can usually be written in the following form:

$$\Delta U=\sum_{\mathbf{q}}[a(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r})+a^*(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{r})]f(\mathbf{q}), \quad (1)$$

where $\mathbf{r}$ represents the coordinates of the electron and $a(\mathbf{q})$ is the time dependent amplitude of the normal mode having wave-number vector $\mathbf{q}$. Although there is more than one mode having the same $\mathbf{q}$, we will be interested in only one of them. For nonpolar crystals $f(\mathbf{q})$ is a periodic function of $\mathbf{r}$ with the periodicity of the lattice. For polar crystals it is independent of $\mathbf{r}$. The Bloch wave function for electrons in a periodic lattice

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[7] Möglich, Riehl, and Rompe, Z. tech. Physik **21**, 6, 128 (1940).

[8] A. Radkowsky, Phys. Rev. **73**, 749 (1948).

[9] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[10] T. Muto, Sci. Papers Inst. Phys. Chem. Research **27**, 179 (1935).

[11] The second and third works mentioned in reference 1. *Note added in proof:*—A similar treatment has since been reported by T. Muto and S. Oyama independently, Prog. Theor. Phys. **5**, 833 (1950).

ψ can be characterized by a reduced wave number vector $\mathbf{k}$ and an index σ indicating the energy band to which the wave function belongs. The wave function of the ions χ is a product of harmonic oscillator wave functions, one for each normal mode. It can be specified by a set of quantum numbers n for the various modes. It is well known that with such ΔU, ψ, and χ the matrix components of ΔU in the representation of $\psi\chi$ vanish except when

$$\mathbf{k}'=\mathbf{k}\pm\mathbf{q},\text{ and } n'=n \text{ except } n_q'=n_q\mp 1. \tag{2}$$

Thus, the nonvanishing elements are

$$[\psi(\mathbf{k}\pm\mathbf{q};\sigma)\chi(n_q\mp 1)|\Delta U|\psi(\mathbf{k},\sigma)\chi(n_q)]. \tag{3}$$

It is understood that the two ψ's have the same spin.

Treating ΔU as a perturbation, the interaction energy is zero in the first order of approximation, since the diagonal elements of ΔU vanish. In the second-order approximation the interaction energy for the whole crystal is[12]

$$\Delta E=\sum_{\mathbf{k},\sigma}\sum_{\mathbf{q},\sigma'}\frac{|[\psi(\mathbf{k}\pm\mathbf{q},\sigma')\chi(n_q\mp 1)|\Delta U|\psi(\mathbf{k},\sigma)\chi(n_q)]|^2}{\epsilon(\mathbf{k},\sigma)-[\epsilon(\mathbf{k}\pm\mathbf{q},\sigma')\mp\hbar\omega_q]}, \tag{4}$$

where ϵ is the electron energy in the undistorted lattice and ω_q is the angular frequency of the normal mode $\mathbf{q}$. The summation over $\mathbf{k}$ and σ (spin) covers all the occupied states, whereas the summation over $\mathbf{q}$ and σ' is limited by the requirement that $(\mathbf{k}\pm\mathbf{q},\sigma')$ must be an unoccupied state. This limitation is imposed by the Pauli principle. If we apply the perturbation theory to the crystal as a whole, using $\sum_i \Delta U_i$ summed over all the electrons as the perturbation, and assume the electronic part of the crystal wave function to be a determinant of single electron wave functions, then we get just Eq. (4), with the limitation in summation following from the antisymmetrical nature of the crystal wave function. However, the validity of the perturbation method when applied to the crystal as a whole is questionable. Equation (4) is to be preferably regarded as approximating the interaction energy of the crystal by summing the interaction energy of individual electrons.

In Eq. (4) the difference between two ϵ's in the denominator is large if σ' is different from σ, that is, if the two states belong to different energy bands. We shall therefore take only σ' identical with σ. We shall see later that in the usual approximation the matrix elements of ΔU are independent of $\mathbf{k}$. Thus, we can write

$$\Delta E=\sum_{\mathbf{k},\sigma}\sum_{\mathbf{q}}\frac{|\Delta U(\sigma,\pm\mathbf{q})|^2}{\epsilon(\mathbf{k},\sigma)-\epsilon(\mathbf{k}\pm\mathbf{q},\sigma)\pm\hbar\omega_q}. \tag{5}$$

When an electron is shifted from a state near the top of the valence band $(\mathbf{k}_t, v)$ to a state near the bottom of the conduction band $(\mathbf{k}_b, c)$, the change in the interaction energy is

$$\begin{aligned}\Delta E_G=&\sum_{\mathbf{q}}\frac{|\Delta U(c,\pm\mathbf{q})|^2}{\epsilon(\mathbf{k}_b,c)-\epsilon(\mathbf{k}\pm\mathbf{q},c)\pm\hbar\omega_q}\\&-\sum_{\mathbf{k}}\frac{|\Delta U(c,\pm\mathbf{q})|^2}{\epsilon(\mathbf{k},c)-\epsilon(\mathbf{k}\pm\mathbf{q}=k_b,c)\pm\hbar\omega_q}\\&-\sum_{\mathbf{q}}\frac{|\Delta U(v,\pm q)|^2}{\epsilon(\mathbf{k}_t,v)-\epsilon(\mathbf{k}_t\pm\mathbf{q},v)\pm\hbar\omega_q}\\&+\sum_{\mathbf{k}}\frac{|\Delta U(v,\pm\mathbf{q})|^2}{\epsilon(\mathbf{k},v)-\epsilon(\mathbf{k}\pm\mathbf{q}=\mathbf{k}_t,v)\pm\hbar\omega_q}.\end{aligned} \tag{6}$$

The first two terms are due to the introduction of an extra electron into the state $(\mathbf{k}_b, c)$, and the last two terms are due to the removal of an electron from the state $(\mathbf{k}_t, v)$. In a semiconductor only a few of the states in the conduction band are occupied, and we can let $\mathbf{q}$ take all values in the first summation. For the same reason there are few terms in the second summation over the occupied $\mathbf{k}$, which can therefore be neglected. The valence band on the other hand is practically filled. The third summation, connecting $(\mathbf{k}_t, v)$ with the unoccupied states, will thus have few terms and will therefore be negligible, whereas in the fourth summation $\mathbf{k}$ can take practically all possible values.

For the lattice undistorted by the vibrations the change in crystal energy due to shifting an electron from state $(\mathbf{k}_t, v)$ to state $(\mathbf{k}_b, c)$ is

$$E_{G0}=\epsilon(\mathbf{k}_b,c)-\epsilon(\mathbf{k}_t,v). \tag{7}$$

The energy gap in a vibrating lattice is thus

$$\begin{aligned}E_G&=E_{G0}+\Delta E_G\\&=\epsilon(\mathbf{k}_b,c)-\epsilon(\mathbf{k}_t,v)+\sum_{\mathbf{q}}\frac{|\Delta U(c,\pm\mathbf{q})|^2}{\epsilon(\mathbf{k}_b)-\epsilon(\mathbf{k}_b\pm\mathbf{q})\pm\hbar\omega_q}\\&\qquad+\sum_{q}\frac{|\Delta U(v,\pm q)|^2}{\epsilon(\mathbf{k}_t\mp q)-\epsilon(\mathbf{k}_t)\pm\hbar\omega_q}.\end{aligned} \tag{8}$$

The last term on the right is the last term in Eq. (6), where the summation over $\mathbf{k}$ has been changed to the summation over $\mathbf{q}$ which can take all possible values. The first and third terms correspond to the energy required to introduce an electron into state $(\mathbf{k}_b, c)$. The second and fourth terms give the energy required to remove an electron or to introduce a hole into the state $(\mathbf{k}_t, v)$. Thermal expansion affects the energy gap through E_{G0}, which depends on the equilibrium distance between the ions. We are concerned with the temperature dependence of the last two terms.

Equation (8) applies only when the two states, the energy difference of which defines the energy gap, have lifetimes long compared with the periods of lattice vibrations. In optical absorption the lifetime of the

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[12] H. Fröhlich, Phys. Rev. 79, 845 (1950).

excited state is of the order 10^{-8} sec. Actually, the lifetime of the states may be shorter than this, since the crystal is also perturbed by the thermal radiation. However, the maximum frequency of the acoustic vibrations is of the order 10^{13} sec^{-1}. It should be possible to take into account the effect of most of the vibrational modes by Eq. (8). Acoustic vibrations of very long wavelengths with periods longer than the lifetimes should not be included in Eq. (8). The proper way to calculate the effect of these is to determine the energy levels for each instantaneous pattern of the lattice distorted by these slow vibrations. This should result in a broadening of the absorption band edge. The effect being limited to very long waves should be negligible. It is unnecessary to determine accurately the low frequency limit for the applicability of Eq. (8). In the result obtained for nonpolar crystals, Eq. (22), cutting off at any frequency makes a negligible difference so long as the frequency is much lower than the maximum. The question does not arise in the case of polar crystals, since there only the optical modes are of consequence.

III. NONPOLAR CRYSTALS

There are various assumptions used in estimating the electron-lattice interaction potential for nonpolar crystals. The frequently used deformable-atom idea of Bloch assumes that the electronic potential in a vibrating crystal is

$$V(\mathbf{r}+\mathbf{R})=V_0(\mathbf{r}), \tag{9}$$

where $V_0(\mathbf{r})$ is the potential at point $\mathbf{r}$ if the lattice is at rest and $\mathbf{R}$ is the "displacement" of the point r due to the vibrations. The displacement of the αth ion in the pth unit cell can be written[13]

$$\mathbf{R}_{\alpha,\,p}=(M_\alpha N)^{-\frac{1}{2}}\textstyle\sum_{\mathbf{q},t}[a(\mathbf{q},t)\boldsymbol{\xi}(\mathbf{q},t)\exp(i\mathbf{q}\cdot\mathbf{r}_{\alpha p})+a^*(\mathbf{q},t)\boldsymbol{\xi}^*(\mathbf{q},t)\exp(-i\mathbf{q}\cdot\mathbf{r}_{\alpha p})], \tag{10}$$

where M_α is the mass of the ion, N is the total number of unit cells in the lattice, $a(\mathbf{q},t)$ is the time-dependent amplitude of the tth normal mode having wave number vector $\mathbf{q}$, and $\boldsymbol{\xi}$ is the polarization vector normalized according to

$$\textstyle\sum_\alpha \xi_\alpha(\mathbf{q},t)\xi_\alpha^*(\mathbf{q},t')=\delta_{t,t'}, \tag{11}$$

$\boldsymbol{\xi}$ is real if the waves are plane polarized. In the case of one atom per unit cell, there is just one α and we have a single expression for the displacement of all the ions. We can then take $\mathbf{R}$ to be given by Eq. (10) with the variable $\mathbf{r}$ in place of the ion coordinates

$$\mathbf{R}(\mathbf{r})=(MN)^{-\frac{1}{2}}\textstyle\sum_{\mathbf{q},t}\mathbf{i}(\mathbf{q},t)[a(\mathbf{q},t)\exp(i\mathbf{q}\cdot\mathbf{r})+a^*(\mathbf{q},t)\exp(-i\mathbf{q}\cdot\mathbf{r})], \tag{12}$$

where $\mathbf{i}$ is a unit vector, since according to Eq. (11) $\boldsymbol{\xi}$ is a unit vector when there is only one α. For every $\mathbf{q}$ there are in this case three modes ($t=1, 2, 3$), one longitudinal and two transverse vibrations. The matrix elements (3) of

$$\Delta U=V(\mathbf{r})-V_0(\mathbf{r})=-\mathbf{R}\cdot\operatorname{grad}V_0 \tag{13}$$

are well known in the theory of conductivity. Only the displacement due to longitudinal vibrations gives nonvanishing matrix elements. These are given by[14]

$$[\psi(\mathbf{k}\pm\mathbf{q},\sigma)\chi(n_q\mp1)\,|\,\Delta U\,|\,\psi(\mathbf{k},\sigma)\chi(n_q)]=\mp(MN)^{-\frac{1}{2}}\frac{2i}{3}qC_\sigma\left(\frac{\hbar}{2\omega_q}\right)^{\frac{1}{2}}\begin{cases}(n_q)^{\frac{1}{2}}\\(n_q+1)^{\frac{1}{2}}\end{cases}, \tag{14}$$

where C_σ is an interaction parameter independent of $\mathbf{k}$. In the theory of metallic conduction only electrons in one energy band have to be considered. Since we have to deal with both valence and conduction bands, we have to use two different C's, one for each band σ.

When there are two atoms per unit cell, the displacements of which are given by different expressions the question arises what expression to take for $\mathbf{R}(\mathbf{r})$. If we limit the values of $\mathbf{q}$ to the first Brillouin zone, then there will be six modes for each $\mathbf{q}$; three of which, having relatively low frequencies, form the acoustic branch, the other three constitute the optical branch. In the acoustic vibrations of long wavelength (small $\mathbf{q}$) the two atoms in a unit cell move approximately in the same directions with equal amplitudes. For such modes[15]

$$\boldsymbol{\xi}_1(\mathbf{q},t)/M_1^{\frac{1}{2}}=\boldsymbol{\xi}_2(\mathbf{q},t)M_2^{\frac{1}{2}}. \tag{15}$$

In view of the normalization condition we have

$$\begin{aligned}\boldsymbol{\xi}_1(\mathbf{q},t)&=\mathbf{i}(\mathbf{q},t)(M_1/M_1+M_2)^{\frac{1}{2}},\\ \boldsymbol{\xi}_2(\mathbf{q},t)&=\mathbf{i}(\mathbf{q},t)(M_2/M_1+M_2)^{\frac{1}{2}}.\end{aligned} \tag{16}$$

The displacements of all ions caused by such a mode of vibration are given then by one expression

$$[(M_1+M_2)N]^{-\frac{1}{2}}\mathbf{i}(\mathbf{q},t)[a(\mathbf{q},t)\exp(i\mathbf{q}\cdot\mathbf{r}_{\alpha p})+a^*(\mathbf{q},t)\exp(-i\mathbf{q}\cdot\mathbf{r}_{\alpha p})],$$

and we can again take the displacement of any point $\mathbf{r}$ to be given by this expression with $\mathbf{r}$ replacing $\mathbf{r}_{\alpha p}$. We shall assume that $R(r)$ due to all the acoustic modes is given by Eq. (12) with (M_1+M_2) replacing M. Thus, for germanium and silicon we use twice the atomic mass for M. For these substances the optical modes do not seem to play a significant part in determining the electron scattering in conduction problems. It might be inferred that the interaction with these modes is small compared with that with acoustic modes.[16] We shall not consider the effect of these modes.

To use Eq. (8) we have to know the difference between any energy level $(\mathbf{k}, c)$ of the conduction band and the bottom level $(\mathbf{k}_b, c)$ of the band, and the difference

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[13] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940). His Eq. (23), p. 131, omits the second term on the right-hand side of Eq. (12). For the case of one atom per unit cell see reference 14, p. 503.

[14] A. Sommerfeld and H. Bethe, *Handbuch der Physik* 24/2 (1933).

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

[16] F. Seitz, Phys. Rev. **73**, 549 (1948).

TABLE I. Temperature coefficient of the energy gap in silicon and germanium.

	$\lvert C_c\rvert$ ev	$\lvert C_v\rvert$ ev	β degree^{-1}	$\partial E_G/\partial T$ (10^{-4} ev/°K) (24)	(23)	(23+24)	$\partial E_G/\partial T$ (10^{-4} ev/°K) experimental
Si	9.75[a]	16.9[a]	10×10^{-6} [b]	-1.78	-1.8[c]	-3.58	-3 to -5[d]
Ge	2.55[a]	3.6[a]	23×10^{-6} [b]	-0.95	-0.11[c]	-1.06	~-4[d]

[a] Value given by Bardeen and Shockley (reference 9).
[b] Slightly different values were used by Bardeen and Shockley: 9×10^{-6} for Si and 19×10^{-6} for Ge.
[c] The values given in the first work of reference 11 were in error by a factor 2.
[d] Absorption measurements by M. Becker. These measurements are being repeated with greater accuracy.

between any energy level ($\mathbf{k}$, v) and the top level ($\mathbf{k}_t$, v) of the valence band. We shall assume that in both cases the difference is equal in magnitude to

$$\hbar^2|\Delta\mathbf{k}|^2/2m^*, \tag{17}$$

where m^* is the absolute value of the effective mass. The summations in Eq. (8) will as usual be replaced by integrations

$$\textstyle\sum_q=[N\Omega/(2\pi)^3]\int_0^{q_{\max}}\int_0^{\pi}\int_0^{2\pi} q^2\sin\theta dqd\theta d\varphi, \tag{18}$$

where Ω is the volume of the unit cell and $q_{\max}/2\pi$ is the radius of a sphere with volume equal to a unit cell in the reciprocal lattice

$$q_{\max}=2\pi\Omega^{-\frac{1}{3}}(3/4\pi)^{\frac{1}{3}}. \tag{19}$$

Substituting Eqs. (14), (17), and (18) into Eq. (8) we get with

$$\Delta E_G=-\frac{1}{(2\pi)^3}\frac{4}{9}\frac{\hbar\Omega}{2Mu}$$
$$\times\left[\frac{2m_c^*}{\hbar^2}C_c^2\int\int\int\left(\frac{n_q}{q-K_c}+\frac{n_q+1}{q+K_c}\right)q^2\sin\theta dqd\theta d\varphi\right.$$
$$\left.+\frac{2m_v^*}{\hbar^2}C_v^2\int\int\int\left(\frac{n_q}{q-K_v}+\frac{n_q+1}{q+K_v}\right)q^2\sin\theta dqd\theta d\varphi\right], \tag{20}$$

where the subscripts c and v refer to the conduction and valence bands, respectively, u is the sound velocity in the crystal, and $K=2m^*/\hbar^2$. If the temperature is high enough so that $kT>(\hbar\omega_q)_{\max}$ we can use the approximation,

$$n_q=1/[\exp(\hbar\omega_q/kT)-1]\sim kT/\hbar\omega_q. \tag{21}$$

The first term in each integrand has a denominator that goes through zero at $q=K$. Taking the principal value for the integrals of these, we get

$$\Delta E_G=-\frac{1}{(2\pi)^3}\frac{4}{9}\frac{\Omega}{\hbar Mu}(m_c^*C_c^2+m_v^*C_v^2)$$
$$\times\left(\frac{kT}{\hbar u}8\pi q_{\max}+2\pi q_{\max}\right). \tag{22}$$

In this equation we have neglected K compared with $q_{\max}$, since K is of the order 10^6 cm^{-1}, whereas $q_{\max}$ is of the order 10^8 cm^{-1}. In view of Eq. (19) we get

$$\partial\Delta E_G/\partial T=-(8/9\pi)(3/4\pi)^{\frac{1}{3}}(k\Omega^{\frac{2}{3}}/\hbar^2Mu^2)$$
$$\times(m_c^*C_c^2+m_v^*C_v^2). \tag{23}$$

To check this equation with the experimentally observed temperature dependence of E_G, the variation of E_{G0} with temperature has to be taken into account. According to Bardeen and Shockley[2]

$$|\partial E_{G0}/\partial\Delta|=\tfrac{2}{3}(|C_c|\pm|C_v|),$$

where Δ is the dilation of the lattice. They conclude on the basis of experimental evidence that for germanium and silicon $\partial E_{G0}/\partial\Delta$ is negative and that on the right hand side the positive sign should be taken. Thus,

$$\partial E_{G0}/\partial T=-\tfrac{2}{3}(|C_c|+|C_v|)\beta, \tag{24}$$

β being the volume coefficient of expansion. The parameters C_c and C_v can be estimated from the mobilities of conduction electrons and holes, using the well-known equation of mobility due to lattice scattering[17]

$$\mu=3(\pi/2)^{1/2}e\hbar^4Mu^2/\Omega(kT)^{3/2}m^{*5/2}C^2. \tag{25}$$

Although the mobilities have been accurately measured, the effective masses have not been reliably determined. The smaller the effective masses the larger will be both Eqs. (23) and (24). Table I gives the results of numerical calculations for silicon and germanium using the free electron mass for the effective masses.[11] Fair agreement with the experimental data is obtained for silicon. For germanium the calculated value is too small; however, if the effective masses were about one-third of the free electron mass, good agreement would have been obtained.[18] Only experimental data of the optical measurements are given in the table. There are other measurements giving information on $\partial E_G/\partial T$ as we have mentioned at the beginning. A detailed discussion of these results has been presented elsewhere.[11]

Strictly speaking, each effective mass in Eq. (23)

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[17] NDRC Report 14-585, Purdue University, 1945 (unpublished).

[18] Recently, J. H. Taylor reported measurements on the pressure dependence of the resistance of germanium, Phys. Rev. **80**, 919 (1950). Attributing the effect entirely to a variation of the energy gap, it was found that the results agree with Eq. (24) if free electron mass are used for the effective masses. The interpretation of the effect could, however, be more complicated. The author is indebted to Professor P. H. Miller, Jr. for seeing the manuscript before publication.

should be a suitable average for the band with which it is associated and will not be the same as the effective mass in Eq. (25) which applies near the band edge. In fact our assumption (17) is a good approximation only near the band edges. However, the order of magnitude of the result should not depend on the form of Eq. (17), and the brief discussion shows that the lattice vibration effect is not negligible and that its order of magnitude is compatible with experimental results. According to Radkowsky's treatment this effect would be about 10^3 times smaller.

IV. POLAR CRYSTALS

In polar crystals strong electron-lattice interaction results from the polarization of the lattice which is produced mainly by the longitudinal optical modes. The polarization in a unit cell is

$$e^*(\mathbf{R}_1-\mathbf{R}_2), \tag{26}$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ are the displacements of the positive and negative ions, respectively, and e^* is the effective charge of the ions, which differs from the true charge by the effect of the polarization of the ions as a result of their displacements. For optical modes of small $\mathbf{q}$[15]

$$\mathbf{R}_1/\mathbf{R}_2=-M_2/M_1. \tag{27}$$

The normalization condition (11) gives in conjunction with Eq. (27)

$$\begin{aligned}\xi_1(\mathbf{q})&=\mathbf{i}(\mathbf{q})(M_2/M_1+M_2)^{\frac{1}{2}},\\ \xi_2(\mathbf{q})&=-\mathbf{i}(\mathbf{q})(M_1/M_1+M_2)^{\frac{1}{2}}.\end{aligned} \tag{28}$$

Thus, for small q the polarization of a cell with center at $\mathbf{r}_p$ is, according to Eqs. (10) and (26),

$$e^*(MN)^{-\frac{1}{2}}\mathbf{i}(\mathbf{q})[a(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}_p)+a^*(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{r}_p)],$$

where $M=M_1M_2/(M_1+M_2)$ is the reduced mass. Assuming that the optical modes give a combined polarization (per unit volume) wave

$$\frac{e^*}{2a^3}\frac{1}{(MN)^{\frac{1}{2}}}\sum\nolimits_{\mathbf{q}}\mathbf{i}(\mathbf{q})[a(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}) +a^*(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{r})], \tag{29}$$

where a is the interionic distance, Fröhlich[19] has shown that the matrix elements of the interaction potential are given by

$$\frac{1}{(MN)^{\frac{1}{2}}}\frac{2\pi ee^*}{a^3q}\left(\frac{\hbar}{2\omega_q}\right)^{\frac{1}{2}}\begin{cases}(n_q)^{\frac{1}{2}}\\ (n_q+1)^{\frac{1}{2}}\end{cases}. \tag{30}$$

The frequencies of the longitudinal optical modes are approximately constant and are related to the ω_t of the transverse optical modes (Reststrahl frequency) by[20]

$$\omega^2=\omega_t^2(\epsilon_s/\epsilon_0), \tag{31}$$

where ϵ_s is the static dielectric constant and ϵ_0 is the contribution to the dielectric constant from the polarizability of the ions, i.e. the dielectric constant at frequencies too high for ion displacements to follow. The frequency ω_t itself is related to ϵ_s and ϵ_0 by

$$\omega_t^2=2\pi e^{*2}\epsilon_0/Ma^3(\epsilon_s-\epsilon_0), \tag{32}$$

from which the effective charge e^* can be determined. In view of Eqs. (31) and (32) the matrix elements of interaction potential (30) can also be written

$$\frac{4\pi e}{V^{\frac{1}{2}}}\frac{1}{q}\left[\frac{\hbar\omega}{8\pi}\left(\frac{1}{\epsilon_c}-\frac{1}{\epsilon_0}\right)\right]^{\frac{1}{2}}\begin{cases}(n_q)^{\frac{1}{2}}\\ (n_q+1)^{\frac{1}{2}}\end{cases}, \tag{33}$$

where $V=2Na^3$ is the volume of the crystal. This is the same expression derived by Fröhlich, Pelzer, and Zienau.[21]

Using Eq. (30) we get from Eq. (8)

$$\begin{aligned}\Delta E_G=&-\frac{(2\pi ee^*)^2}{a^6}\frac{\hbar}{2MN\omega}\frac{2Na^3}{(2\pi)^3}\\ &\times\left[\frac{2m_c^*}{\hbar^2}\int\int\int\left(\frac{n_q}{q^2-J_c^2}+\frac{n_q+1}{q^2+J_c^2}\right)\sin\theta dqd\theta d\varphi\right.\\ &\left.+\frac{2m_v^2}{\hbar^2}\int\int\int\left(\frac{n_q}{q^2-J_v^2}+\frac{n_q+1}{q^2+J_v^2}\right)\sin\theta dqd\theta d\varphi\right],\end{aligned} \tag{34}$$

where $J^2=2m^*\hbar\omega/\hbar^2$. Since ω is approximately constant, n_q is independent of $\mathbf{q}$ according to Eq. (21). Taking principal values for the integrals of the first term in each integrand, we get

$$\Delta E_G=-\frac{\pi(ee^*)^2\hbar^{\frac{1}{2}}}{a^3M\omega^{\frac{3}{2}}}\left[\left(\frac{2m_c^*}{\hbar^2}\right)^{\frac{1}{2}}+\left(\frac{2m_v^*}{\hbar^2}\right)^{\frac{1}{2}}\right](n+1), \tag{35}$$

where we have neglected J compared with $q_{\max}$, since $\hbar^2q_{\max}^2/2m^*$ is of the order of several electron-volts, whereas $\hbar\omega$ is of the order 10^{-1} to 10^{-2} ev. This equation gives the same dependence of ΔE_G on n (or temperature) as obtained by Radkowsky. Because of this coincidence we can refer to his discussion of the result, which shows that it is in general agreement with the experimental data on the shift of absorption edge in polar crystals.

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