

Line Broadening of an Impurity Spectrum in Silicon*†

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Adapting an idea proposed by Fermi to explain the shifts of the high-series lines in the alkali spectra under perturbation by foreign gases, the present paper develops a theory of the broadening of impurity levels in semiconductors. In its principal assumptions it follows the work of Lax and Burstein, but it is simpler and leads perhaps to somewhat better agreement with their own experimental data. While in the problem of the alkalis a large valence orbit is disturbed by the random motion of foreign gas molecules, the same effects result in the present instance from collisions between a hole and the phonons. In detail, the broadening arises from two mechanisms: the scattering of the bound hole by the acoustic motion of the crystal atoms and the fluctuation in polarization energy of the atoms lying between the approximately hydrogen-like orbits of the hole. The former effect is dominant and accounts reasonably well for the experimental results. The calculation is applied to boron-doped silicon and yields a total zero-point broadening of 1.6×10^{-3} electron volts; this is to be compared with an experimental value of about 1×10^{-3} ev and the result of 3×10^{-3} ev obtained by Lax and Burstein. Some question remains about the temperature dependence of the effect.

INFRARED absorption lines of a single crystal of silicon doped with boron have been measured by Burstein, Bell, Davisson, and Lax.¹ The interesting qualitative interpretation of the spectrum involves the assumption that the lines arise from transitions between approximately hydrogenic orbits of very large radii, pursued by a hole bound to an impurity center. The lines are broadened because of the perturbations to which these large "atoms" are exposed, and the widths have been determined by the above-named authors.

A theory of the broadening was given recently by Lax and Burstein,² who calculate the intensity within a line by methods adapted from the spectra of polyatomic molecules. The elaborate nature of their careful work, with its need for various approximations, makes an assessment of the accuracy of the results obtained somewhat difficult; hence it is hard to see the cause for the discrepancy (by about a factor 3) between their theory and the experiments. It seems desirable, therefore, to try here a much simpler theoretical approach to the broadening problem in order to illustrate the physical processes involved and, perchance, to get a better quantitative understanding.

The situation under study has many features in common with an older problem in spectroscopy, the shifts and broadening of the high-series lines in the spectra of the alkalis resulting from impacts of foreign gases.³ Here, too, the orbits of the valence electron embrace a great number of perturbers, and the line structure arises from the random motion of the foreign gas atoms inside and along the orbits of the radiating electron. Fermi⁴ suggested a very beautiful explanation

of the effects observed. He attributed them to two causes: the collision of the valence electron with atoms along its path and the polarization of the perturbers inside the electron orbit by the core of the radiating atom. To be sure, his theory aimed only at an explanation of the line shifts, but its extension to widths is an easy problem.

The difference between the impurity problem and the optics of the high-series members of the alkalis arises from the fact that in the former the perturber motion is organized into a phonon spectrum, whereas in the latter it is random. This changes the details of Fermi's theory but not its essence. In the sequel, then, we compute the effect on the line width expected from the following mechanisms: 1. The encounter of the boron hole with silicon atoms or, more properly stated, the scattering of the hole by the acoustic motion of the silicon atoms; 2. The fluctuations in the polarization of the orbit-enclosed silicon atoms. The first of these will be shown to be the important effect and to account reasonably well for the observed line widths. Our theory holds of course equally for electrons bound to atoms in group V and for holes bound to group III impurity atoms.

The physical assumptions to be made are those of Lax and Burstein: The levels will be taken to be "hydrogenic," and the hole will be described as having an effective mass of 0.45 times the mass of the electron. The ground state orbit, from which absorption takes place, has a radius of 13.5 Å. For an appraisal of these idealizations the reader may turn to the paper quoted. The speed of the hole in its ground state orbit is 1.9×10^7 cm/sec, a value of the same magnitude as the speed of a hole near the top of the valence band. Thus, as far as collision effects are concerned, the hole will be amenable to treatment by conduction theory; in particular it will have a mean free path given by a slight extension of considerations familiar from the problem of mobility. The hole will collide with phonons and we shall show that at low temperatures the mean free path is inversely proportional to the speed of the hole (Ramsauer effect),

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¹ Burstein, Bell, Davisson, and Lax, *J. Phys. Chem.* **57**, 849 (1953).

² M. Lax and E. Burstein, *Phys. Rev.* **100**, 592 (1955).

³ E. Amaldi and E. Segrè, *Nuovo cimento* **11**, 145 (1934).

⁴ E. Fermi, *Nuovo cimento* **11**, 157 (1934).

while at high temperatures it is constant. For these reasons the hole makes fewer collisions in its various upper states than in its ground state, and we have a situation, somewhat anomalous in atomic spectra and reminiscent of meson processes, of a ground state with shorter life time than the upper states. The line broadening is therefore accounted for almost wholly by a study of the ground state alone, and different $1s-np$ transitions produce approximately the same widths. This has already been noted by Lax and Burstein and is in accord with experiment.

EFFECT OF PHONON IMPACTS

All the foregoing facts suggest that the broadening be treated on the basis of Lorentz' simple theory, according to which the (full) width at half-maximum is given by

$$\Delta\nu = 1/\pi\tau, \quad (1)$$

where τ is the mean life of a phase-coherent atomic state between collisions. It is of course not necessary for an impact to destroy the atomic state in the sense of raising the hole to a higher bound state in order that the radiative act be effectively terminated. As Weisskopf and others have shown, a phase change of sufficient magnitude, accompanied by an insignificant energy change, counts as a Lorentz impact. If the Lorentz theory is accurate, the line ought to have dispersion shape, but this is hard to establish from the experimental data. It must also be true for the validity of this approach that the mean free path exceed by a sufficient margin the length of the orbit pursued by the hole, as will in fact turn out to be the case.

There remains, then, only the task of computing τ , or the mean free path $\nu\tau$. In doing this we assume that any effects on collision frequency arising from the curvature of the path of the bound hole may be neglected since the orbits are large. Hence, the hole may be treated as moving with the indicated speed, but in the valence band, with the important difference, however, that the bound hole remains in the region near one impurity atom, making collisions only with phonons. On the other hand, a normal hole in the valence band would wander through the crystal, being scattered predominantly by impurity centers at the low temperatures for which line measurements are possible. We must therefore extend the theory of lattice-scattering mobility, which is observable only at high temperatures, down into the region of low temperatures where it is ordinarily inapplicable. This would introduce little uncertainty into our results if an adequate theory of lattice-scattering mobility were available which took account of interband scattering between the two bands degenerate at $k=0$ and gave agreement in its temperature dependence with experiment. At present no such theory is available. Thus we use here the well-known mobility theory of Seitz⁵ and of Bardeen and Shockley,⁶

in which the valence band is assumed to be a single nondegenerate band with spherical energy surfaces centered about $k=0$.

Using the deformation potential introduced by the last-named authors, we write for the perturbing potential to which the hole is subjected

$$H' = A \nabla \cdot \mathbf{R}(\mathbf{r}) = \frac{Ai}{\sqrt{M}} \sum_{\mu, \sigma} a_{\mu}(\sigma) \sigma \cdot \xi_{\mu}(\sigma) \exp(i\sigma \cdot \mathbf{r}), \quad (2)$$

an expression in which $\mathbf{R}(\mathbf{r})$ is the displacement vector, evaluated at the coordinate \mathbf{r} of the hole; A is a constant to be adjusted by comparison with the measured mobility, M is the mass of the crystal, $\xi_{\mu}(\sigma)$ is a unit vector pointing in the direction of the displacement resulting from the μ th vibrational mode with wave number σ . The form of Eq. (2) presupposes that the two atoms in a primitive cell of the Si crystal vibrate in unison and can be replaced by a single mass twice that of a Si atom, an assumption also made by our predecessors.

The states of the system are represented by the products

$$\psi(\mathbf{k}_j, \mathbf{r}) e^{i\mathbf{k}_j \cdot \mathbf{r}} U_j,$$

in which $\psi e^{i\mathbf{k}_j \cdot \mathbf{r}}$ is a Bloch function describing the state of the hole, while U_j is a product of harmonic oscillator functions of the amplitudes a_{μ} and, through them, of σ ; the quantum numbers of U_j are integers $n_{\mu}(\sigma)$ which specify the number of phonons of wave vector σ and mode μ that are present.

The probability of a transition from an initial state (1) to a final state (2) in time t equals

$$W_{21}(t) = 4 |H'_{21}|^2 \frac{\sin^2(\omega_{21}t/2)}{\hbar^2 \omega_{21}^2}. \quad (3)$$

Following Seitz,⁷ we define the complex amplitudes, a , in terms of the real ones, α , by the relation

$$a_{\mu}(\sigma) = 2^{-1/2} [\alpha_{\mu}(\sigma) + i\alpha_{\mu}(-\sigma)]; \quad a_{\mu}^*(\sigma) = a_{\mu}(-\sigma). \quad (4)$$

The α 's have matrix elements which are given by the usual formulas

$$(n+1|\alpha|n) = \left(\frac{\hbar n+1}{\omega} \right)^{1/2}, \quad (5)$$

in which n and ω are of course functions of μ and σ .

The linearity of H' implies that the perturbation induces only single phonon transitions, hence the system frequency ω_{21} appearing in (3) is related to the phonon frequency ω by

$$E_2 - E_1 = \hbar\omega_{21} = \epsilon_2 - \epsilon_1 \pm \hbar\omega_{\mu}(\sigma).$$

The ϵ 's are the hole energies whose difference corresponds to the energy acquired or lost when the hole suffers a collision. In truth, they are not related parabolically to the hole wave numbers \mathbf{k} . This is our least

⁵ F. Seitz, Phys. Rev. 73, 549 (1948); Seitz's $C = \frac{3}{2}A$.

⁶ J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).

⁷ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

defensible approximation, ably discussed by Lax and Burstein who employ it in a similar way but add a binding energy for the hole. Accepting these simplifications, one may write

$$\epsilon_j = \epsilon_0 + (\hbar^2 k_j^2 / 2m)$$

m being the mass of the hole.

If τ is greater than $\hbar/(\epsilon_2 - \epsilon_1)$, then, as indicated by Seitz,⁵ $\sin(\omega_{21}t/2)/\omega_{21}$ may be replaced by a δ function, and

$$W_{21}(t) = (2\pi t/\hbar) |H_{21}'|^2 \delta(E_2 - E_1). \quad (6)$$

In our case this condition is satisfied. The difference $\epsilon_2 - \epsilon_1$ equals the energy of a typical phonon involved in the scattering process and is about 3 millivolts; $2\hbar/\tau$, on the other hand, is the line width, which is about 1 millivolt, and τ exceeds $\hbar/(\epsilon_2 - \epsilon_1)$ by approximately a factor 5.

The evaluation of H_{21}' makes use of the following considerations. Of the three modes of vibration designated by μ , one is nearly longitudinal and two are nearly transverse. The latter make no contribution to H' , the former yield $|\sigma \cdot \xi| = \sigma$. The summation over μ in Eq. (2) thus disappears, and there remains only the calculation of a_{21} and of $\int \psi^*(\mathbf{k}_2, \mathbf{r}) \exp[-i(\mathbf{k}_2 - \mathbf{k}_1 - \sigma) \cdot \mathbf{r}] \psi(\mathbf{k}_1, \mathbf{r}) d\mathbf{r}$ as factors of H_{21}' . The former proceeds via (4) and (5), the latter yields $\delta(\mathbf{k}_2 - \mathbf{k}_1, \sigma)$ because $\psi(\mathbf{k}_2, \mathbf{r})$ and $\psi(\mathbf{k}_1, \mathbf{r})$ are nearly equal and normalized to 1.

The amplitude $a(\sigma)$ has nonvanishing matrix elements for the following transitions:

$$(1) \quad \begin{cases} n(\sigma) \rightarrow n(\sigma) + 1 \\ n(-\sigma) \rightarrow n(-\sigma) + 1 \end{cases} \quad (2) \quad \begin{cases} n(\sigma) \rightarrow n(\sigma) - 1 \\ n(-\sigma) \rightarrow n(-\sigma) - 1 \end{cases}$$

In thermal equilibrium $n(\sigma) = n(-\sigma)$, and one need distinguish only between the cases of gain and loss of a phonon, i.e., between sets (1) and (2).

$$\text{In case (1), } |a_{21}|^2 = [n(\sigma) + 1] \hbar / 2\omega(\sigma);$$

$$\text{in case (2), } |a_{21}|^2 = n(\sigma) \hbar / 2\omega(\sigma).$$

The range of the polar angle θ in σ space is different for cases (1) and (2) as will be seen. For most problems this has an insignificant effect. However, for the low temperatures dealt with in this study, the effect is important and categories (1) and (2) must be treated separately.

Collecting results, we find

$$|H_{21}'|^2 = \frac{A^2 \sigma^2 \hbar}{2M\omega(\sigma)} \begin{cases} n(\sigma) + 1 \\ n(\sigma) \end{cases} \quad (7)$$

for the two cases in question. This must be substituted into (6) and a summation over all σ has to be carried out, subject, however, to conservation of energy [Eq. (6)] and of momentum [see the factor $\delta(\mathbf{k}_2 - \mathbf{k}_1, \sigma)$].

The velocity of propagation of longitudinal waves varies with direction from a maximum in the (111) direction to a minimum in the (100) direction. As pointed out by Bardeen and Shockley,⁶ the variation is

not large (about 10%). Thus smaller error is introduced by making the isotropic approximation $\omega(\sigma) = \sigma c_l$, where c_l is the average velocity of the longitudinal waves. Following Lax and Burstein, we choose the velocity in the (100) direction as representative. This apparently low value allows for the fact that the waves are not purely transverse and longitudinal. The slower, nearly transverse waves do contribute somewhat to the scattering. By later using a value for A determined from experimental mobilities, however, we actually include the effects of the nearly transverse waves.

The number of transitions per second involving phonon wave number σ within a volume element $\sigma^2 d\sigma \sin\theta d\theta d\varphi$ of σ space is

$$W(t) = \frac{D(\sigma)}{t} \sigma^2 d\sigma \sin\theta d\theta d\varphi,$$

where $D(\sigma)$, the density of phonon states, is simply $(2\pi)^{-3}$ times the volume V of the crystal. The frequency of transitions $dP(\theta)$ along θ is found by integrating this expression over φ and σ and then adding the results for cases (1) and (2). Thus

$$dP(\theta) = dP_1(\theta) + dP_2(\theta)$$

and

$$dP_1(\theta) = \frac{(2\pi)^{-1} A^2}{2\rho} \int_{\sigma} \frac{n(\sigma) + 1}{\omega(\sigma)} \delta(E_2 - E_1) \sigma^4 d\sigma \sin\theta d\theta. \quad (8)$$

Here ρ is the crystal density. The integration over σ is to be carried out subject to

$$k_2^2 = k_1^2 + \sigma^2 + 2\sigma k_1 \cos\theta$$

and

$$E_2 - E_1 = \frac{\hbar^2}{2m} (k_2^2 - k_1^2) + \hbar\omega(\sigma).$$

On combining these and substituting $\omega(\sigma) = \sigma c_l$, we find

$$\sigma = -(2mc_l/\hbar) - 2k_1 \cos\theta \quad (9)$$

and furthermore,

$$d\sigma = \frac{2m}{\hbar^2 \sigma} d(E_2 - E_1) \quad \text{at} \quad E_2 = E_1.$$

One then finds

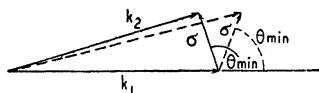
$$dP_1(\theta) = \frac{A^2 m}{2\pi \hbar^2 \rho c_l} [n(\sigma) + 1] \sigma^2 \sin\theta d\theta, \quad (10)$$

where σ is a function of θ through Eq. (9).

To obtain P_1 , we integrate (10) over θ . The upper limit of θ is clearly π ; the lower limit corresponds to $\sigma = 0$ which, by (9), is given by

$$\cos\theta_{\min} = -mc_l/\hbar k_1 = -c_l/v,$$

if v is the speed of the hole. Numerically, $\cos\theta_{\min} = -0.0436$, indicating that $\theta_{\min} > \frac{1}{2}\pi$. Figure 1 illus-

FIG. 1. Behavior of θ as $\sigma \rightarrow 0$.

trates this situation. Now replace $n(\sigma)$ in (10) by its thermal average value,

$$\{\exp[\hbar\omega(\sigma)/\kappa T] - 1\}^{-1} = [\exp(\hbar\sigma c_l/\kappa T) - 1]^{-1} \\ = \{\exp[-(B \cos\theta + C)/T] - 1\}^{-1},$$

using the abbreviations

$$B = 2\hbar k_1 c_l / \kappa = 93.5^\circ \text{K}, \quad C = 2mc_l^2 / \kappa = 4.1^\circ \text{K},$$

and put finally $x = -(B \cos\theta + C)/T$. We then have

$$P_1 = \int_{\theta_{\min}}^{\pi} dP_1(\theta) = \frac{2A^2 m k_1^2}{\pi \hbar^2 \rho c_l} \left(\frac{T}{B}\right)^3 \\ \times \int_0^{(B-C)/T} [(e^x - 1)^{-1} + 1] x^2 dx.$$

The calculation of P_2 likewise proceeds from Eq. (8). But in this case the equation for energy conservation reads

$$E_2 - E_1 = \frac{\hbar^2}{2m} (k_2^2 - k_1^2) - \hbar\omega(\sigma) = 0.$$

Equation (9) becomes

$$\sigma = (2mc_l/\hbar) - 2k_1 \cos\theta,$$

and (10) lacks the 1 in brackets. In this case, $\cos\theta_{\min} = +c_l/v$, $\theta_{\min} < \pi/2$ as indicated by the dashed arc in Fig. 1. Thus

$$P_2 = \frac{2A^2 m k_1^2}{\pi \hbar^2 \rho c_l} \left(\frac{T}{B}\right)^3 \int_0^{(B+C)/T} (e^x - 1)^{-1} x^2 dx.$$

Our result for the collision frequency is

$$\frac{1}{\tau} = P_1 + P_2 = \frac{4A^2 m k_1^2}{\pi \hbar^2 \rho c_l} \left(\frac{T}{B}\right)^3 \\ \times \left\{ \int_0^{(B-C)/T} [(e^x - 1)^{-1} + \frac{1}{2}] x^2 dx \right. \\ \left. + \frac{1}{2} \int_{(B-C)/T}^{(B+C)/T} (e^x - 1)^{-1} x^2 dx \right\}. \quad (11)$$

This expression will be evaluated for low and high temperatures.

Case A: $T \rightarrow 0$.—All limits of integration in (11) are large numbers, and the only term in the curly brace that remains appreciable is

$$\int_0^{(B-C)/T} \frac{x^2}{2} dx.$$

Hence

$$\frac{1}{\tau} = \frac{2A^2 m k_1^2}{3\pi \hbar^2 \rho c_l} \left(\frac{B-C}{B}\right)^3. \quad (12)$$

Case B: $T \rightarrow \infty$.—In this case, the integrand in (11) can be expanded as follows:

$$\int_0^{(B-C)/T} x dx + \frac{1}{2} \int_{(B-C)/T}^{(B+C)/T} x dx = \frac{B^2 + C^2}{2T^2},$$

and

$$\frac{1}{\tau} = \frac{2A^2 m k_1^2}{\pi \hbar^2 \rho c_l} \frac{T}{B} \left(\frac{B^2 + C^2}{B^2}\right) = \frac{A^2 m k_1 \kappa T}{\pi \hbar^3 \rho c_l^2} \left(\frac{B^2 + C^2}{B^2}\right). \quad (13)$$

Except for the factor $1 + (C^2/B^2)$, which is quite insignificant, this result leads to Seitz's mobility formula⁵

$$\mu = \left(\frac{8\pi}{9}\right)^{\frac{1}{2}} \frac{e \hbar^4 \rho c_l^2}{A^2 (\kappa T)^{\frac{3}{2}} m^{5/2}}.$$

The constant A can therefore be taken from the empirical value of the mobility, as was done by Lax and Burstein. The constants used in evaluating (12) and (13), taken from the latter authors, are as follows:

$$A = 15 \text{ ev}, \quad m = 4.1 \times 10^{-28} \text{ g}, \\ c_l = 0.83 \times 10^6 \text{ cm/sec}, \quad k_1 = mv/\hbar = 7.37 \times 10^6 \text{ cm}^{-1}, \\ \rho = 2.33 \text{ g/cm}^3, \quad v = 1.9 \times 10^7 \text{ cm/sec}.$$

From these values one computes a mean free path, $\nu\tau$, of 1.7×10^{-5} cm at $T=0$. The length of the hole's orbit is 8.5×10^{-7} cm; at low temperatures, then, the hole makes about 20 revolutions before the orbit is destroyed.

The Lorentz line width, from Eq. (1), becomes 1.46×10^{-3} ev at low temperatures in accordance with (12). This is to be compared with the experimental value of about 10^{-3} ev.² Lax and Burstein obtained a theoretical result of 3×10^{-3} ev.

At high temperatures, our Eq. (13) leads to

$$\hbar\Delta\nu = 0.0536 T \times 10^{-3} \text{ ev}.$$

While this seems to be in rough agreement with the published data, the rise with T may be too rapid. Lax and Burstein find proportionality with $T^{\frac{1}{2}}$, a result which is conditioned by their use of a statistical theory of broadening. The exact theoretical dependence on T is influenced by the structure of the energy band which has been idealized in both treatments.

The region between low and high temperatures can be studied only by carrying out the integrations in (11) numerically. This has been done, and the findings are plotted in Fig. 2.

A word should be said about the approximation of the bound state by plane-wave functions since this does not seem justified on *a priori* grounds. It is easy, however, to expand the bound state in terms of Bloch orbitals and to perform an appropriate average of the collision

frequency over the Bloch states which correspond to the bound orbital. When this computation is made and the valence band is again assumed to be nondegenerate and to possess spherical energy surfaces, we obtain

$$\begin{aligned} h\Delta\nu|_{T \rightarrow 0} &= 1.49 \times 10^{-3} \text{ ev}, \\ h\Delta\nu|_{T \rightarrow \infty} &= 0.0455T \times 10^{-3} \text{ ev}. \end{aligned}$$

The difference between this zero-point result and the one obtained earlier in this section is not significant; the slower rise with temperature obtained here gives slightly better agreement with experiment.

II. POLARIZATION EFFECT

We now investigate the contribution to the width of the impurity levels coming from the second mechanism, the thermal fluctuation in the energy of polarization of the silicon atoms lying between the orbits involved in the transition of the hole. We call this the polarization effect. Clearly, since the effect now under study is characteristic of a bound charge (the former having concerned the motion of a free particle) it is not included in the foregoing treatment. Nor have we been able to convince ourselves that it is contained in the treatment of Lax and Burstein, which corresponds to Sec. I.

A rigorous treatment of the effects of a polarizable medium is admittedly difficult, and the following considerations are crude. They are designed to test orders of magnitude rather than provide a quantitative answer.

It is assumed that when the silicon atoms occupy their equilibrium positions, the charge of the hole is distributed uniformly over the surface of a sphere of radius equal to the orbital radius and with its center at the impurity core. The core is regarded as stationary. This assumption may be shown to have small effect on the result.⁸ On the basis of these assumptions, the

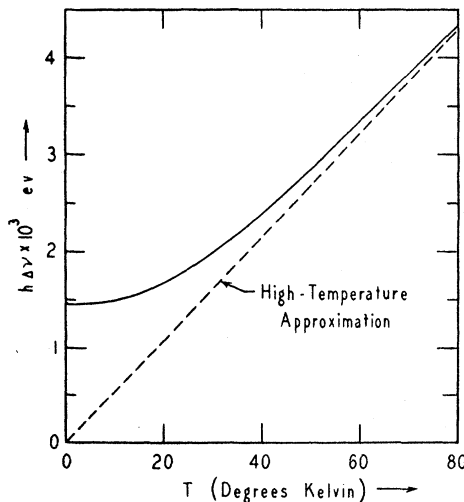


FIG. 2. Line width as a function of temperature.

⁸ Compare dissertation by Douglas Sampson (unpublished).

electric field is $-(e/Dr^3)\mathbf{r}$ within the sphere and zero outside.⁹

We turn now to the distribution function for the polarization energy. \mathbf{r}_j is the position of the j th atom with respect to the impurity center, \mathbf{r}_{j0} is its equilibrium position, and \mathbf{R}_j its displacement from equilibrium. θ_j is now the angle between \mathbf{R}_j and \mathbf{r}_{j0} .

If all of the silicon atoms in the crystal are acted upon by a harmonic force of stiffness K , the force on the j th atom is given by

$$\mathbf{F}_j = -K(\mathbf{r}_j - \mathbf{r}_{j0}) = -K\mathbf{R}_j. \quad (14)$$

When a Boltzmann distribution is assumed, the probability that the j th atom have a displacement R_j is

$$\begin{aligned} P(R_j)d\mathbf{R}_j &= (2\pi\langle R_{jx}^2 \rangle)^{-3/2} \\ &\times \exp\left(\frac{-R_j^2}{2\langle R_{jx}^2 \rangle}\right) R_j^2 dR_j \sin\theta_j d\theta_j d\varphi_j. \end{aligned} \quad (15)$$

The mean square displacement has the value

$$\langle R_j^2 \rangle = 3\langle R_{jx}^2 \rangle = 3kT/K. \quad (16)$$

Since K is the same for all atoms, we drop the subscript j in Eq. (16).

The polarization energy is

$$X = -\sum_i \frac{b}{r_j^4}, \quad (17)$$

and the probability that X be between $X - \frac{1}{2}dX$ and $X + \frac{1}{2}dX$ is given by

$$P(X)dX = \int \cdots (n) \cdots \int P(R_1)d\mathbf{R}_1 \cdots P(R_n)d\mathbf{R}_n, \quad (18)$$

provided the integration over volume elements $d\mathbf{R}_j$ is over a region such that

$$X - \frac{1}{2}dX < -\sum_i \frac{b}{r_j^4} < X + \frac{1}{2}dX. \quad (19)$$

With the use of a Dirichlet factor¹⁰ Eq. (18) becomes

$$\begin{aligned} P(X)dX &= \frac{dX}{2\pi} \int_{-\infty}^{\infty} d\lambda \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \cdots n \cdots \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \\ &\times \exp\left[i\lambda\left(X + \sum_i \frac{b}{r_j^4}\right)\right] P(R_1)d\mathbf{R}_1 \cdots P(R_n)d\mathbf{R}_n. \end{aligned} \quad (20)$$

⁹ Although the thermal vibrations of the Si atoms lying completely within the orbit of the hole produce slight variations in the electric field acting on the hole and corresponding fluctuations in the mean position of the hole, this does not change the total energy of the system, the hole plus the Si atoms inside its orbit. However, the energy which must be absorbed from without in order to produce a transition of the hole to a higher state does depend on the position of the silicon atoms between the two orbits. If we assume that the silicon atoms remain stationary during the time of an electronic transition (Franck-Condon principle, statistical theory of broadening), the distribution of the absorption energy about its mean value is given directly by the distribution function for the fluctuation in polarization energy of the Si atoms between the electronic orbits involved in the transition.

¹⁰ This procedure follows H. Margenau, Phys. Rev. 43, 129 (1933).

We assume that $R_j \ll r_{j0}$ so that

$$r_j^2 = r_{j0}^2 + 2r_{j0}R_j \cos\theta_j$$

and

$$\frac{1}{r_j^4} = \frac{1}{r_{j0}^4} \left(1 - \frac{4R_j}{r_{j0}} \cos\theta_j \right).$$

If we substitute this into Eq. (20), each of the integrations over the $d\mathbf{R}_j$ contributes $\exp(-8b^2\langle R_x^2 \rangle \lambda^2 / r_{j0}^{10})$, and

$$P(X) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp \left[-8b^2 \langle R_x^2 \rangle \sum_i \frac{1}{r_{j0}^{10}} \lambda^2 + i \left(X + \sum_i \frac{b}{r_{j0}^4} \right) \lambda \right] d\lambda. \quad (21)$$

The integration over λ yields

$$P(X) = \left(32\pi b^2 \langle R_x^2 \rangle \sum_i \frac{1}{r_{j0}^{10}} \right)^{-\frac{1}{2}} \times \exp \left[- \frac{\left(X + b \sum_i \frac{1}{r_{j0}^4} \right)^2}{32b^2 \langle R_x^2 \rangle \sum_i \frac{1}{r_{j0}^{10}}} \right]. \quad (22)$$

This is a Gaussian distribution, centered at $X_0 = -b \sum_j (1/r_{j0}^4)$, i.e., at the polarization energy when the atoms are in their equilibrium positions. The full width, defined by $P(X_0 \pm \frac{1}{2}\Delta X) = \frac{1}{2}P(X_0)$, is

$$\Delta X = 2(\log 2)^{\frac{1}{2}} (32b^2 \langle R_x^2 \rangle \sum_j r_{j0}^{-10})^{\frac{1}{2}} = 9.42b (\langle R_x^2 \rangle \sum_j r_{j0}^{-10})^{\frac{1}{2}}. \quad (23)$$

Numerical values for the various quantities needed in the sequel are, in addition to those already introduced in Sec. I:

- d (distance between nearest neighbors) = 2.35×10^{-8} cm,
- N (number of silicon atoms per unit volume) = 5×10^{22} cm $^{-3}$,
- M_s (mass of a silicon atom) = 4.65×10^{-23} gram,
- D (dielectric constant) = 11.5,
- θ_D (Debye temperature) = 658° .

Because the orbits are large in comparison with the interatomic spacings, the first orbit contains approximately 500 and the second 3×10^4 silicon atoms. Thus we are able to sum over j by the approximation

$$\sum_j \rightarrow \int_{an_1^2}^{an_2^2} 4\pi N r^2 dr$$

and obtain

$$\sum_j r_{j0}^{-10} = (4\pi N/7) [(an_1^2)^{-7} - (an_2^2)^{-7}]. \quad (24)$$

In these expressions, n_1 and n_2 are the principal quantum

numbers for the initial and final state of the hole, respectively. The second term is always negligible in comparison with the first; hence the widths for all transitions between ground state and higher states are equal, in connection with this effect as well as in collision broadening. Furthermore, by Eq. (17), the polarization energy

$$X_0 = -b \sum_j r_{j0}^{-4} = -4\pi N b [(an_1^2)^{-1} - (an_2^2)^{-1}]. \quad (25)$$

On the other hand, the energy required to bring a dielectric into a region of volume V is given by the relation¹¹

$$X = -\frac{1}{8\pi} \int_V \mathcal{E}_0^2 \left(1 - \frac{1}{D} \right) dV,$$

where \mathcal{E}_0 is the electric field before the dielectric is introduced. For our case,

$$X = -\frac{1}{8\pi} \int_{an_1^2}^{an_2^2} \frac{e^2}{r^4} \left(\frac{D-1}{D} \right) 4\pi r^2 dr = -\left(\frac{D-1}{D} \right) \frac{e^2}{2a} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right). \quad (26)$$

Equating this to the average polarization energy given by Eq. (25), we obtain

$$b = \left(\frac{D-1}{D} \right) \frac{e^2}{8\pi N} = 1.05 \times 10^{-31} \text{ ev cm}^4. \quad (27)$$

Substituting the result for $\sum_j r_{j0}^{-10}$, Eq. (24), into Eq. (23), results in

$$\Delta X = 12.6b (\langle R_x^2 \rangle N / a^7)^{\frac{1}{2}},$$

since $n_1 = 1$ for the ground state. This leads to

$$\Delta X = 32.5 \times 10^4 \langle R_x^2 \rangle^{\frac{1}{2}} \text{ ev-cm}^{-1}. \quad (28)$$

Actually one is justified in using classical distribution functions for the harmonic oscillators only when the frequency, $\omega = (K/M_s)^{\frac{1}{2}}$, satisfies the relation $\hbar\omega \ll \kappa T$. But the quantum distribution is also Gaussian¹² and differs from the classical one only by containing $\langle R_x^2 \rangle = (\hbar/M_s\omega)(\bar{n} + \frac{1}{2})$ in place of $\kappa T/K$, \bar{n} being $[\exp(\hbar\omega/\kappa T) - 1]^{-1}$. To summarize

$$\text{if } T \rightarrow 0, \quad \langle R_x^2 \rangle = \hbar/2M_s\omega, \quad (29)$$

$$\text{if } T \rightarrow \infty, \quad \langle R_x^2 \rangle = \kappa T/M_s\omega^2. \quad (30)$$

The Einstein theory for specific heats is based on a similar model, treating all the atoms of the solid as harmonic oscillators of the same frequency. Thus we might expect that the Einstein frequency obtained from specific heat data for silicon would give the best choice for ω .

¹¹ See C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, New York, 1952).

¹² M. Born, Repts. Progr. Phys. 9, 294 (1942-3), Appendix I.

Now our statistical approach is valid only when the frequency of the hole (ω_h) is considerably greater than the frequency of the atomic vibrations. But the Einstein frequency for silicon is about $7 \times 10^{13} \text{ sec}^{-1}$, while the hole frequency is

$$\omega_h = \hbar / ma^2 = 1.4 \times 10^{14} \text{ sec}^{-1}. \quad (31)$$

Thus the criterion for the validity of our approach is poorly satisfied if the Einstein frequency is the correct value to use.

In reference 8, a more accurate treatment is carried out, the atomic displacements \mathbf{R}_j being expressed as a summation over the normal modes of vibration. It is found that $P(R_j)$ is again given by Eq. (15). In detail,

$$\begin{aligned} \langle R_{jx}^2 \rangle &= \langle R_x^2 \rangle = \frac{1}{3N} \sum_{\sigma, \mu} \frac{\langle \alpha_\mu(\sigma)^2 \rangle}{M_s}, \\ \langle \alpha_\mu(\sigma)^2 \rangle &= \frac{\hbar}{\omega_\mu(\sigma)} \left\{ \left[\exp\left(\frac{\hbar \omega_\mu(\sigma)}{\kappa T}\right) - 1 \right]^{-1} + \frac{1}{2} \right\}. \end{aligned} \quad (32)$$

This equation is exactly true only for cubic lattices. In other cases the thermal mean square values for the three cartesian components of \mathbf{R}_j are not necessarily equal. The \mathbf{R}_j for different atoms and hence the probabilities $P(R_j)$ are not independent. Consequently the correct integral form for $P(X)$ has in place of the product of N three-dimensional Gaussian distribution functions, $P(R_j)$ of Eq. (20), a single $3N$ -dimensional Gaussian involving cross terms between all components of the \mathbf{R}_j . The coefficients of these cross terms contain summations over the normal modes of vibration and are small except when (a) the frequency of oscillation is low and (b) the cross terms involve coordinates of atoms lying close together. The exact expression for $P(X)$ cannot be integrated. Here we neglect the cross terms, thus restoring the independence of the $P(R_j)$. $P(X)$ then reduces to Eq. (20), and the width is again given by Eq. (28) with the $\langle R_x^2 \rangle$ expressed by Eq. (32).

In order to evaluate $\langle R_x^2 \rangle$, we use the Debye approximation

$$\frac{1}{3N} \sum_{\sigma, \mu} \rightarrow 3\omega_{\max}^{-3} \int_0^{\omega_{\max}} \omega^2 d\omega.$$

Equation (32) then becomes¹³

$$\langle R_x^2 \rangle = \frac{3\hbar^2 T^2}{M_s \kappa \theta_D^3} \int_0^{\theta_D/T} [(e^x - 1)^{-1} + \frac{1}{2}] x dx. \quad (33)$$

In this expression, θ_D is the Debye temperature and $x = \hbar \omega / \kappa T$. For $T \gg \theta_D$, this approaches the value

$$\langle R_x^2 \rangle = 3\hbar^2 T / M_s \kappa \theta_D^2. \quad (34)$$

¹³ This result agrees with and is indeed obtainable from the theories of P. Debye [Ann. Physik 43, 49 (1914)] and I. Waller [Uppsala dissertation, 1925 (unpublished)]. For the explicit expression for $\langle R^2 \rangle$ based on their theories, see K. Lonsdale, Acta Cryst. 1, 142 (1948).

Hence, from (28),

$$\Delta X = 1.13 \times 10^{-5} T^{\frac{1}{2}} \text{ ev.}$$

In general the integral in Eq. (33) may be written as a series

$$\int_0^{\theta_D/T} (e^x - 1)^{-1} x dx = \frac{\pi^2}{6} - \sum_{n=1}^{\infty} e^{-n\theta_D/T} \left[\frac{\theta_D/T}{n} + \frac{1}{n^2} \right].$$

For the present range of interest ($T = 0$ to 80°K), the series involving the exponential factor is negligible in comparison with $\frac{1}{6}\pi^2$ and Eq. (33) becomes

$$\langle R_x^2 \rangle_{T < \theta_D} = \frac{3\hbar^2 T^2}{M_s \kappa \theta_D^3} \left[\frac{\pi^2}{6} + \frac{(\theta_D/T)^2}{4} \right].$$

Substitution of this expression into Eq. (28) yields

$$\Delta X = 32.5 \times 10^4 \left(\frac{3\hbar^2 T^2}{M_s \kappa \theta_D^3} \left[\frac{\pi^2}{6} + \frac{(\theta_D/T)^2}{4} \right] \right)^{\frac{1}{2}}. \quad (35)$$

As $T \rightarrow 0$, $\frac{1}{6}\pi^2$ may be neglected and

$$\langle R_x^2 \rangle_{T \rightarrow 0} = 3\hbar^2 / 4 M_s \kappa \theta_D = 3\hbar / 4 M_s \omega_{\max}.$$

On comparing this with the quantum mechanical value for $\langle R_x^2 \rangle$ in a single-frequency model [see Eq. (29)], one obtains an effective frequency $\omega_{\text{eff}} = \frac{2}{3}\omega_{\max} = 5.74 \times 10^{13} \text{ sec}^{-1}$. For very high temperatures, $T \gg \theta_D$, according to Eqs. (30) and (34), $\omega_{\text{eff}} = (1/\sqrt{3})\omega_{\max} = 4.96 \times 10^{13} \text{ sec}^{-1}$. Since these values do not differ greatly, a single-frequency model should work quite well.

With the numerical values given above, we find

$$\Delta X|_{T \rightarrow 0} = 32.5 \times 10^4 \left(\frac{3\hbar^2}{4 M_s \kappa \theta_D} \right)^{\frac{1}{2}} = 0.145 \times 10^{-3} \text{ ev.} \quad (36)$$

When $T = 80^\circ\text{K}$, Eq. (35) leads to

$$\Delta X|_{T=80^\circ} = 0.151 \times 10^{-3} \text{ ev.}$$

Thus the polarization width is small and almost constant over the range of temperatures here considered. When added to the collision effect it brings the total zero-point broadening to $1.6 \times 10^{-3} \text{ ev.}$

Since the ratio $\omega_h / \omega_{\text{eff}} \cong 2.4$, our approach for polarization broadening is not wholly adequate. The hole will not be sensitive to the exact motion of the silicon atoms, but will rather see them more nearly in their average positions. The conclusion is that the polarization effect, while given correctly as to order of magnitude by the foregoing treatment, may be less important than Eq. (36) indicates; it is probably not negligible when improved experimental data are at hand, but is smaller than the collision effect by at least a factor 10. Its dependence on temperature, in particular the proportionality to $T^{\frac{1}{2}}$ at high temperatures, must not be taken as accurate; for the validity of our statistical theory depends critically on $\omega_h / \omega_{\text{eff}}$, being good only when that ratio is large.