direct transitions to the ground state of Fe^{56} of the 2.66-Mev and/or the 2.98-Mev levels. (The uncertainty of ±0.2 Mev does not permit a decision as to whether solely the 2.66-Mev level or the 2.98-Mev level or some combination of the two is involved.) These direct transitions are indicated by the dotted line in Fig. 2. By taking the ratio of the data in column 6 for $Na+D_2O$ and $Mn+D_2O$ one gets (neglecting a small energy correction) an estimate of the frequency of occurrence of the direct transitions to the ground state. The number of such transitions is 0.011 per disintegration. Compared to the probabilities for the transition to the 0.845 level, the low probability of 0.011 would indicate that the transition to the ground state is of a higher electric or magnetic multipolarity than the transitions to the 0.84-Mev level.

It is the experience of the authors that the photo-neutron techniques can be extended to measurements of γ-rays that are emitted with a probability as low as 0.0001 per disintegration.

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On the Mobility of Electrons in Pure Non-Polar Insulators

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It is pointed out that Peierls' condition for the validity of time-dependent perturbation theory in the determination of the mobility μ of electrons in crystals can be transformed to the form

$$\mu > 30 \text{ cm}^2/\text{volt-sec. (at room temperature)}$$

in the case in which the electrons are distributed classically. Since the recent investigations of the mobility of electrons in diamond, silicon, and germanium indicate that the mobility in these materials is at least several times greater than the foregoing limit, it would appear that perturbation methods may be used to discuss the mobility in these materials and possibly in other non-polar insulating materials, such as sulfur.

An expression is derived for the collision frequency for conduction electrons having velocity v as a result of collissions with the acoustical modes of oscillation. It is pointed out that these modes will be the only ones of interest in diamond at room temperature because the characteristic temperature is in the vicinity of 1800°K. The collision time τ is found to satisfy the equation

$$1/\tau = (4/9\pi)(C^2 k_0 T/\hbar^3 c^2 n_0)(m^{*2}/M)k, \qquad \text{(A)}$$

where C is a constant, having the dimensions of energy. that measures the interaction between the lattice and the electron, k_0 is Boltzmann's constant, T is the absolute temperature, c is the acoustical velocity, n_0 is the density of atoms, m^* is the effective electron mass, M is the mass of the atoms in the crystal, and k is the wave number vector of the electron. Since the mean free path is proportional to k, it follows that the mean free path is independent of velocity in the approximation in which (A) is valid. The conditions for validity of the equation, all of which are normally well satisfied in diamond at room temperature, are: (1) The temperature be sufficiently low that the principal inelastic collisions involve only one lattice vibrational quantum; (2) only the acoustical modes of vibration be excited; (3) the temperature of the electrons be sufficiently high that their mean energy be large compared with m^*c^2, in which c is the acoustical velocity; (4) the electrostatic field be sufficiently low that only linear terms are important. The second of these conditions is usually not satisfied in materials such as silicon, germanium, or sulfur near room temperature, although it will be satisfied at lower temperatures. The temperature m^*c^2/k_0 is near 10°K for diamond, but is much less than this for most other materials, so that (A) should be applicable for determining the mobility of conduction electrons in a large number of pure non-polar insulators at low temperatures not too close to 1°K.

In the case of diamond, the mobility at room temperature is found to have the value

$$\mu = (1.46/C^2)10^5 \text{ cm}^2/\text{volt-sec.}$$

if m^* is taken as the free electron mass. This leads to a mobility of about 156 cm²/volt-sec. if C is assumed to have a value of 30.6 ev obtained from the relation $C(\text{ev}) = 1.7 \cdot 10^{-2}\Theta$ that seems to be obeyed for the electrons in the simpler metals. In a range of temperature in which only acoustical modes of vibration are excited the relative mobilities of two different substances μ_a and μ_b should satisfy the relation

$$\mu_a/\mu_b=(\Theta_a/\Theta_b)^2(n_a/n_b)^{\frac{1}{3}}(C_b/C_a)^2(M_a/M_b),$$

in which the subscripts refer to the two different substances, Θ is the characteristic temperature, n is the atomic density, C is the interaction constant appearing in (A), and M is the atomic mass. Since C and Θ are probably roughly proportional to one another, this relationship suggests that the mobilities of various insulators should have similar values in a range of temperature where only the acoustical modes cause excitation.

The influence of non-acoustical modes in non-polar materials are discussed. It is pointed out that two interesting cases can occur and the case of diamond is discussed and clarified with use of group theory. It is found that the scattering from non-acoustical modes contributes to the collision frequency to about the same degree as the non-acoustical modes when the crystal temperature is not too far below the characteristic temperature.

The implications of the foregoing work for the problem of crystal counters is discussed. It is pointed out that the mobility is probably sufficiently large at room temperature in any of the non-polar crystalline insulators that they would make satisfactory counters if mobility were the only determining factor. It is shown that the concentration of trapping centers in a give specimen is probably the greatest limitation on the use of the material for purposes of a counter.

I. INTRODUCTION*

THE development of crystalline microwave rectifiers[1] and crystal counters[2] during recent years has given stimulus to the study of the mobilities of conduction electrons in non-metallic materials, particularly non-polar insulators and semi-conductors such as diamond, silicon, and germanium. Ionic materials[3] had been subject to a great deal of experimental and theoretical investigation prior to the war by a large number of investigators, both in this country and in Europe, because of the wide interest in the colored alkali halides, photo-conducting luminescent crystals, such as zinc sulfide, and rectifier materials such as cuprous oxide.

Fröhlich and Mott[4] have shown that when the temperature of a polar crystal is near or above the characteristic temperature, the mobility of conduction electrons that are at equilibrium with the lattice is determined primarily by the optical branch of the vibrational spectrum, the greatest electron-lattice interaction being that involving the polarization waves of long wave-length. As the crystal is cooled to a temperature well below the characteristic temperature, the conduction electrons can no longer interact with the optical modes of vibration having long wave-length, if they remain in temperature equilibrium, and the mobility increases. In the range of temperature just below the characteristic temperature in which the collisions involving the optical branch still determine the collision time τ of the conduction electrons, this quantity depends upon temperature through the equation

$$1/\tau=(1/\tau_0)\exp(-h\nu_0/kT) \qquad (1)$$

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* A large fraction of this manuscript was prepared while the writer was guest lecturer at the Berkeley campus of the University of California during the summer of 1947. He is indebted to the Department of Physics for a very pleasant and stimulating period of work.

[1] The study of crystalline microwave rectifiers was sponsored in this country during the war by Division 14 of NDRC. Particular emphasis was placed on silicon and germanium to which controlled amounts of additional agents were added to obtain desired electrical properties. No comprehensive survey of the fundamental aspects of this research has apparently appeared as yet in print in the standard journals, although such surveys have been presented at meetings of the American Physical Society (see paper by V. Johnson and K. Lark-Horovitz, Phys. Rev. **72**, 153 (1947)). The institutions and laboratories which contributed to this work are as follows: Radiation Laboratory of the Massachusetts Institute of Technology, Randal Morgan Laboratory of the University of Pennsylvania, Department of Physics of Purdue University, The Bell Laboratories, Westinghouse Research Laboratories, Sylvania Electric Corporation, RCA Laboratories. The following references have bearing on the study of these rectifiers: V. Johnson and K. Lark-Horovitz, Phys. Rev. **71**, 374 (1947); **71**, 709 (1947); E. Conwell and V. F. Weisskopf, Phys. Rev. **69**, 258 (1946); G. L. Pearson and W. Shockley, Phys. Rev. **71**, 142 (1947); B. Goodman, A. W. Lawson, and L. I. Schiff, Phys. Rev. **71**, 191 (1947); I. Estermann, A. Foner, and J. A. Randall, Phys. Rev. **71**, 484 (1947).

[2] P. J. Van Heerden, *The Crystal Detector* (Thesis. Utrecht, 1945); D. E. Wooldridge, A. J. Ahearn, and J. A, Burton, Phys. Rev. **71**, 913 (1947); R. Hofstadter, J. C. D. Milton, and S. L. Ridgway, Phys. Rev. **72**, 977 (1947); The writer desires to express appreciation to the group at the Bell Laboratories, Professor Hofstadter, Dr. Wouters of the Radiation Laboratory of the University of California, and Commander P. S. Johnson of the Bureau of Ships for very informative discussions of the properties of crystal counters.

[3] This work is surveyed in several books and review articles. See, for example, N. F. Mott and Gurney, *Electrical Processes in Ionic Crystals* (Oxford University Press, New York, 1940); F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1941), Rev. Mod. Phys. **18**, 384 (1946).

[4] H. Fröhlich, Proc. Roy. Soc. **160**, 230 (1937); **188**, 521 (1947); H. Fröhlich and N. F. Mott, Proc. Roy. Soc. **171**, 496 (1939).

in which τ_0 is practically independent of temperature and ν_0 is the frequency associated with the longest polarization wave in the optical branch. At sufficiently low temperatures, however, the collisions involving the optical branch become unimportant and the collisions involving acoustical modes determine the collision frequency. In particular, the selection rules involving conservation of energy and momentum show that only acoustical waves of fairly long wave-length are involved in these collisions.

The pure non-polar insulating crystals differ from the polar crystals in the sense that the optical modes of vibration of highest frequency are not of the polar type because the atoms are electrically neutral. In the case of diamond, for example, which possesses two atoms per unit cell and has a lattice structure similar to that of Sphalerite (ZnS), the mode of highest frequency is that in which the two atoms in a given cell move in opposite directions at the same time and in which corresponding atoms in different cells derived by pure translation from the first cell move in phase with atoms in the first cell. The crystal does not become polarized during this motion because the carbon atoms in diamond are uncharged. The crystal would become polarized for the corresponding mode of vibration in Sphalerite, however, because the zinc and sulfur atoms have a divalent change. Since polarization is absent, the interaction between the electron and lattice vibrations may be expected to be smaller in the non-polar than in the polar insulators when the temperature is near the characteristic temperature. Moreover, it may be expected that the influence of the optical modes in non-polar materials will not necessarily obliterate the influence of the acoustical modes when the former are excited.

The purpose of the present paper is to discuss the electron mobility in the non-polar insulators, using diamond, silicon, and germanium as prototypes since the values of the mobilities of these materials seem to be known, at least in order of magnitude, at room temperature. A group of investigators at the Bell Telephone Laboratories[5] has demonstrated that electrons liberated in diamond can possess a long mean free path. The experiments carried out to date indicate, in fact, that the mobility at room temperature probably is 100 cm²/volt-sec. or larger. Similarly, the work[6] of the Bell Laboratories, of Estermann and of Lark-Horowitz on combined measurements of conductivity and the Hall effect shows that the mobility of free electrons in pure silicon and germanium at room temperature is about 300 and 1300 cm² per volt-sec., respectively. In this work, use is made of the relation

$$R\sigma = 3\pi\mu/8c,$$

in which R is the Hall constant, σ the electrical conductivity, c the ratio of electromagnetic to electrostatic unit of charge, and μ is the mobility (see Eqs. (39) and (42) below). Since the characteristic temperature of diamond is in the vicinity of 1800°K, it follows that the optical modes are scarcely excited at temperatures near room temperature and below, so that the collision time is determined primarily by interaction with the acoustical modes of vibration. This simplification cannot be expected to hold in other non-polar insulators, such as silicon, germanium, or sulfur, for which the characteristic temperatures are much nearer to room temperature.

The following discussion will have only minor bearing on the mobility of electrons in the non-polar semi-conductors such as silicon and germanium in the form in which they are ordinarily employed as rectifiers, for in such cases the materials usually are intentionally contaminated with impurity agents which have a substantial influence on the mobility. The results do have bearing, however, on the mobility in pure specimens.

II. DISCUSSION OF PERTURBATION THEORY

In accordance with conventional procedure, we shall consider an electron having a wave number vector **k** that is moving through a crystal lattice whose normal modes of vibration are

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[5] D. E. Wooldridge, A. J. Ahearn, and J. A. Burton, Phys. Rev. **71**, 913 (1947). This work has not actually yielded quantitative values of the mobility to date.

[6] This work is unpublished for the most part (see reference 1). The writer is grateful to the various investigators for the opportunity of discussing their results. Dr. G. L. Pearson and his associates at the Bell Laboratories have found that the mobility in silicon can be expressed in the form $AT^{-\frac{3}{2}}$ at sufficiently high temperatures. A is $5.0 \cdot 10^5$ (cm²-deg$^{\frac{3}{2}}$/volt-cm), respectively, for silicon conducting by means of holes and electrons (p-type and n-type).

traveling waves having wave number vectors $\boldsymbol{\sigma}$ extending through as many Brillouin zones as there are atoms in the unit cell of the lattice. Three polarization waves are associated with each value of σ. We shall designate the circular frequencies associated with σ by $\omega_i(\sigma)(i=1, 2, 3)$. In the most highly symmetric crystals the three modes of vibration may be separated into two transverse and one longitudinal mode, as for an isotropic medium. The modes of vibration having frequency near zero satisfy the relation

$$\omega_i(\sigma)=c_i\sigma, \tag{2}$$

in which c_i is the constant acoustical velocity for long waves having the appropriate polarization and σ is the absolute value of the wave number vector.

The electron under consideration will possess an energy of the order of magnitude of k_0T, where k_0 is Boltzmann's constant and T is the absolute temperature. As a result it will lie near the bottom of the conduction band. For this reason, the relation between the energy ϵ and wave number k can be expressed in the manner

$$\epsilon(k)=\hbar^2k^2/2m^*, \tag{3}$$

in which $\hbar$ is Planck's constant divided by 2π, k is the absolute value of $\mathbf{k}$, and m^* is the effective electron mass which may differ from the true electron mass by a factor substantially different from unity.

As long as the lattice is treated as if completely rigid and perfect the electrons will not be deflected; however, transitions actually will take place even if the lattice contains no impurities, vacancies, or interstitial atoms because of inelastic encounters between the electrons and the lattice vibrations. According to conventional time-dependent perturbation theory, the probability that a transition will take place in time t between two states of the total system having energy E_1 and E_2, respectively, is

$$P_{12}(t)=(1/\hbar^2)\,|V_{12}|^2t^2(\sin^2x/x^2). \tag{4}$$

Here V_{12} is the matrix component of the potential representing the interaction between the electron and the lattice waves and

$$x=(E_1-E_2)t/2\hbar. \tag{5}$$

If the average time τ in which an electron changes its state from energy ϵ_1 to ϵ_2 is sufficiently long that the condition

$$\tau(\epsilon_1-\epsilon_2)/\hbar>1 \tag{6}$$

is satisfied, the function $\sin^2x/x^2$ can be replaced by a delta function for values of the argument of practical interest. Thus P_{12} can be written

$$P_{12}(t)=(2\pi t/\hbar)\,|V_{12}|^2\delta(E_1-E_2) \tag{7}$$

when (6) is satisfied.

Peierls[7] has shown that the results of perturbation theory can be used in the determination of the statistical distribution function at temperature T in the presence of an electric field even when the delta function approximation (7) is not completely valid provided the following two conditions are satisfied:

(a) The matrix components of the interaction potential connecting an initial state and those states to which transitions are possible do not vary too greatly over the range of states to which transitions are allowed.

(b) The statistical distribution function does not vary too widely over the range of energy in which (4) takes its principal value when t is of the order of magnitude of the collision time. The distribution function usually involves energy E and temperature through a factor E/k_0T and changes its value appreciably. Therefore, when E changes by an amount k_0T, in electrons of interest for conduction the second condition takes the form,

$$\tau k_0T/\hbar>1. \tag{8}$$

The condition (8) can be placed in a very convenient form if the mobility can be expressed simply in terms of the collision time. This can be done, for example, when the distribution function has the Maxwell-Boltzmann form, as is true for semi-conductors in which the electron density is not too high. In this case

$$\mu\cong e/m\tau, \tag{9}$$

where e and m are the electronic charge and mass. Hence, (8) may be written

$$\mu>e\hbar/mk_0T, \tag{10}$$

which is about 30 cm^2/volt-sec. when T is

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[7] R. Peierls, Zeits. f. Physik **88**, 786 (1934).

300°K. Van Vleck[8] has shown that this condition is too stringent in metals. In this case the parameter T appearing in (9) is the average collision time for one of the electrons at the top of the Fermi distribution, which is smaller than the average collision time for all conduction electrons by a factor of the order k_0T/ϵ_0, where ϵ_0 is the kinetic energy of an electron at the top of the Fermi distribution which is about 100 times larger than k_0T.

III. SELECTION RULES GOVERNING TRANSITIONS

As long as the amplitude of oscillation of the lattice vibrations is sufficiently small—a condition that is well satisfied at temperatures of normal interest—the potential representing the interaction between the conduction electrons and the lattice vibrations depends linearly upon the amplitude of the normal modes. In this case the first order transitions described by perturbation theory are those in which only one quantum of vibrational energy is emitted or absorbed in each step. Under the conditions in which the delta-function approximation (7) can be used, we may expect the following equation to be valid:

$$\epsilon(\mathbf{k}')=\epsilon(\mathbf{k})\pm\hbar\omega_i(\sigma), \tag{11}$$

in which $\mathbf{k}'$ is the wave number vector of the electron after the transition, $\mathbf{k}$ that before, and $\omega_i(\sigma)$ is the frequency of the mode of vibration having wave number σ that has gained or lost one quantum of energy. The positive sign is valid in the case in which vibrational energy is lost, whereas the negative sign is valid in the opposite case.

In the case in which the electron interacts with only one mode of vibration at a time, the condition of conservation of wave number is expressible in the form

$$\mathbf{k}'=\mathbf{k}+\boldsymbol{\sigma}+\mathbf{K}, \tag{12}$$

$$\cos\theta=-|\boldsymbol{\sigma}+\mathbf{K}|/2k\pm m\omega_i(\boldsymbol{\sigma})/\hbar k|\boldsymbol{\sigma}+\mathbf{K}|, \tag{13}$$

in which the plus sign corresponds to the case in which the scattered electron gains one quantum of energy and the negative sign corresponds to the reverse case. We shall consider separately the two cases in which $\mathbf{K}=0$ and $\mathbf{K}\neq 0$.

(1) $\mathbf{K}=0$.—In this case we are only interested in values of $\boldsymbol{\sigma}$ near the origin of wave number space since k is very near the origin. Hence, the approximation (3) is valid and Eq. (13) may be written

$$\cos\theta=-\sigma/2k\pm m^*c_i/\hbar k. \tag{14}$$

The ratio $m^*c_i/\hbar k$ may also be written $(m^*c_i^2/2\epsilon(k))^{\frac{1}{2}}$. The quantity $m^*c_i^2$ corresponds to an energy of the order of 0.001 ev or less for the acoustical velocities met with in all solids. Thus $m^*c_i^2/k_0$ corresponds to a temperature of 10°K for the case of diamond and usually is much smaller for other materials. It follows that the absolute value of the second term on the right-hand side of (14) is less than unity as long as the temperature of motion of the electron is not too close to absolute zero. When $\epsilon(k)$ becomes less than $m^*c_i^2/2$ for all values of i, θ becomes imaginary for all values of σ in Eq. (14) if the negative sign prevails before the second term on the right-hand side. Thus, the electron cannot lose energy in collisions for which $\mathbf{K}=0$ if its energy becomes sufficiently small. Such electrons are equivalent to the "cold neutrons" which have a very long mean free path for scattering in crystalline substances. The "cold electron" can still be scattered by collisions for $\mathbf{K}=0$ in which it gains energy, provided the lattice vibrations having energy $2m^*c_i^2$ are appreciably excited. It is evident that at very low energies $(T<m^*c_i^2/k_0)$ the electrons will have difficulty coming to temperature equilibrium[8] with the lattice through inelastic collisions with the perfect lattice for which $K=0$.

When the electron temperature is near room temperature, the electron will be able to exchange energy with modes of vibration for which $\sigma<2k\pm 2m^*c_i/\hbar\cong 2k$. Equation (14) cannot be satisfied for larger values of σ with real values of θ. Now the energy $\hbar c_i\sigma\cong 2\hbar c_ik$ of the lattice quanta associated with the uppermost value of σ is equal to $\epsilon(k)(8m^*c_i^2/\epsilon)^{\frac{1}{2}}$, which is generally much smaller than $\epsilon(k)$. It follows that if the electron and the lattice are at the same temperature, not too close to the absolute zero, the distribution of energy among the lattice vibrational quanta with which the electron can interact (when $\mathbf{K}=0$) is classical since $\hbar c_i\sigma/kT$ will be small compared with unity for these lattice

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[8] J. H. Van Vleck, Revista de la Universidad Nacional de Tecuman, 1, 81 (1940).

vibrations. This fact was apparently first pointed out by Fröhlich.[9]

(2) $\mathbf{K}\neq 0$.—It follows from Eq. (13) that $\boldsymbol{\sigma}$ must be comparable to $\mathbf{K}$, for if $\boldsymbol{\sigma}$ is very small, of the same order of magnitude as $\mathbf{k}$ or less, the absolute value of the first term on the right of (13) is very large compared with unity and the corresponding value of the second term is unity or less for reasonable values of $\mathbf{k}$. These values of $\boldsymbol{\sigma}$ are just those which would lie near the origin of wave number space if the "reduced" zone scheme is employed in which all permissible values of $\boldsymbol{\sigma}$ are taken in the first zone. Since $\omega_t(\boldsymbol{\sigma})$ has zero gradient near $\boldsymbol{\sigma}=0$ for branches other than the three acoustical branches, it follows that the corresponding values of $\omega_t(\boldsymbol{\sigma})$ can be taken to be constant in the range of $\boldsymbol{\sigma}$ that is of interest to us.

A straightforward analysis of Eq. (13) shows that the electron can always be scattered by collisions involving the umklapp process in transitions in which it gains vibrational energy; however, transitions in which the electron loses energy are permitted only when the energy of the electron is larger than the energy of the uppermost vibrational quanta. In general, ϵ must be larger than $k\Theta$ where Θ is the characteristic temperature of the lattice. It follows that transitions involving the umklapp process will not occur if the electron and lattice are at equilibrium at a temperature well below the characteristic temperature, for collisions in which the electron gains energy will be prevented by the fact that the lattice waves which can produce the transitions are not excited, whereas collisions in which the electron loses energy are prevented by the fact that Eq. (13) cannot be satisfied with real values of θ. This probably is the situation in diamond at room temperature for the available data on specific heat and inelastic constants indicate that Θ is about 1800°K. On the other hand, umklapp processes will play a role at room temperature in materials such as silicon, germanium, and sulfur, for which $\Theta\sim 300°\mathrm{K}$.

IV. THE INTERACTION POTENTIAL

To begin with, we shall consider the case in which umklapp processes can be neglected. In lieu of more exact information we shall determine the interaction potential between electrons and lattice vibrations on the assumption that the deformable atom hypothesis first introduced by Bloch[10] for the case of metals is valid. According to this assumption, the electronic potential V_d in the displaced lattice is related to the potential V_n in the normal lattice by the equation

$$V_d(\mathbf{r}+\mathbf{R})=V_n(\mathbf{r}). \tag{15}$$

Here $\mathbf{r}$ is the coordinate of the electron in the undeformed lattice and

$$\mathbf{R}(\mathbf{r})=\frac{1}{(N)^{\frac{1}{2}}}\sum_{\sigma,t}\frac{a_t(\boldsymbol{\sigma})}{M}\xi_t(\boldsymbol{\sigma})\exp(i\boldsymbol{\sigma}\cdot\mathbf{r}), \tag{16}$$

in which N is the number of unit cells in the specimen of crystal under consideration, $a_t(\boldsymbol{\sigma})$ is the complex amplitude of the mode of vibration having wave number $\boldsymbol{\sigma}$ and polarization index t, $\xi_t(\boldsymbol{\sigma})$ is the polarization vector for this mode of vibration, and M is the mass of the atoms of the lattice. Corresponding to this assumption, the perturbing potential satisfies the equation

$$V_p=-\mathbf{R}\cdot\operatorname{grad}V_n(\mathbf{r}). \tag{17}$$

The use of (16) and (17) in the form given implies that we are dealing with a crystal in which the directions of polarization of the elastic waves are the same for all atoms and that the phase relations for the various atoms can be expressed in terms of a continuous function. The first of these conditions is always satisfied for crystals in which all of the atoms are at positions where a point center of symmetry (or inversion center) exists. The second condition also can usually be satisfied in these cases. The atoms in diamond, silicon, and germanium are not at positions of inversion symmetry so that the directions of polarization are usually not the same for all atoms. We shall see later that the conditions corresponding to the use of (16) and (17) can be met for the interesting modes of vibration even in these cases.

Peterson and Nordheim[11] have shown that the

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[9] H. Fröhlich, *Theorie der Metalle* (Julius Springer, Berlin, 1939).

[10] F. Bloch, Zeits. f. Physik **52**, 555 (1928); A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. XXIV 1; A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Teddington, England, 1936).

[11] E. L. Peterson and L. W. Nordheim, Phys. Rev. **51**, 355 (1937).

hypothesis of deformable atoms is only of semi-quantitative value in the case of the simple metals. On the other hand, Bardeen[12] has found that the more accurate interaction potential is very similar to (17) for alkali metals. It is possible that Nordheim's approximation[13] of "rigid atoms" which replaces (15) by the condition

$$V_d(\mathbf{r})=\sum_p v(\mathbf{r}-[\mathbf{r}(p)+\mathbf{R}(p)]), \qquad (18)$$

in which $v(\mathbf{r})$ is the potential of one of the atoms of the lattice, $\mathbf{r}(p)$ is the positional coordinate of the pth atom of the lattice when the crystal is undeformed and $\mathbf{R}(p)$ is the displacement of the pth atoms, determined from (16) by setting $\mathbf{r}=\mathbf{r}(p)$, would be more accurate for the non-polar insulating atomic substances since the electron cloud is not as highly polarizable in these materials as in metals. However, since the two hypotheses are qualitatively similar, we shall adopt the first, which is simpler.

V. CALCULATION OF THE COLLISION FREQUENCY

The matrix component of (17) connecting the electronic states associated with wave numbers k and k', namely,

$$\int \psi_{\mathbf{k}'}{}^*\psi_{\mathbf{k}}\mathbf{R}\cdot\operatorname{grad} V_n d\tau, \qquad (19)$$

in which $\psi_{\mathbf{k}}$ and $\psi_{\mathbf{k}'}$ are the electronic wave functions, may readily be placed in the form,

$$\frac{1}{(NM)^{\frac{1}{2}}}a_t(\boldsymbol{\sigma})\int \chi_{\mathbf{k}'}{}^*\chi_{\mathbf{k}}\xi_t(\boldsymbol{\sigma})\cdot\operatorname{grad} V_n e^{-\mathbf{K}\cdot\mathbf{r}}d\tau, \qquad (20)$$

in which $\mathbf{k}$, $\mathbf{k}'$, $\boldsymbol{\sigma}$, and $\mathbf{K}$ are related by the equation

$$\mathbf{k}'=\mathbf{k}+\boldsymbol{\sigma}+\mathbf{K}, \qquad (21)$$

and $\chi_{\mathbf{k}}$ and $\chi_{\mathbf{k}'}$ are functions having the periodicity of the lattice which are related to $\psi_{\mathbf{k}}$ and $\psi_{\mathbf{k}'}$ by the equations

$$\begin{aligned}\psi_{\mathbf{k}}&=\chi_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}},\\ \psi_{\mathbf{k}'}&=\chi_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{r}}.\end{aligned} \qquad (22)$$

In the case in which $\mathbf{K}=0$, the conventional treatment of the matrix components shows that the coefficient of $a_t(\sigma)/(NM)^{\frac{1}{2}}$ in (20) may be reduced to approximately $2iC\sigma/3$ where

$$C=\frac{h^2}{2m}\int|\operatorname{grad}\chi_{\mathbf{k}}|^2 d\tau. \qquad (23)$$

Since we do not have reliable values of $\chi_{\mathbf{k}}$, we shall treat C as an unknown parameter in the following discussion. The analysis leading to (23) also shows that only longitudinally polarized waves are effective in scattering the electron when $\mathbf{K}=0$. It is to be noted that the coefficient of $a_t(\boldsymbol{\sigma})$ in the matrix component associated with $\mathbf{K}=0$ varies linearly with $\boldsymbol{\sigma}$, so that it becomes vanishingly small in the limiting case of very long waves, that is, in the limiting case in which $\mathbf{k}'$ coincides with $\mathbf{k}$. This behavior of the matrix component can be predicted at once from the fact that $\operatorname{grad} V_n$ is an odd function of the electron coordinates.

When $\mathbf{K}$ is not zero, $\boldsymbol{\sigma}$, as we have seen previously is very nearly equal to $-\mathbf{K}$, or is close to the origin in the reduced zone scheme as long as $\mathbf{k}$ corresponds to the wave number for a thermal electron. Thus we are interested in values of the matrix component for which $\mathbf{k}$ and $\mathbf{k}'$ differ by small amounts. In the limiting case in which $\mathbf{k}$ and $\mathbf{k}'$ are equal, the integral in (20) becomes

$$\int|\chi_{\mathbf{k}}|^2\xi_t(\boldsymbol{\sigma})\cdot\operatorname{grad} V_n e^{-i\mathbf{K}\cdot\mathbf{r}}d\tau. \qquad (24)$$

This integral will generally not vanish, although it may do so under conditions of proper symmetry. If it does not vanish, the absolute value of the integral may be written in the form

$$KD_t, \qquad (25)$$

in which K is the absolute value of $\mathbf{K}$ and D_t is a parameter having the dimensions of energy, analogous to the parameter C introduced for the case $\mathbf{K}=0$. We may use (25) for the case in which $\mathbf{k}$ and $\mathbf{k}'$ are not equal since the higher order terms depending on the difference between $\mathbf{k}$ and $\mathbf{k}'$ will be small in comparison with (25), provided the latter is not zero.

When the integral vanishes for the case $\mathbf{K}\neq 0$ because of the symmetry of the functions ap-

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[12] J. Bardeen, Phys. Rev. **52**, 688 (1937).

[13] L. W. Nordheim, Ann. d. Physik **9**, 607 (1931).

pearing in the integrand, we may expect the integral in (24) to depend linearly on $\boldsymbol{\sigma}$ for small values of this vector when expressed in the reduced zone scheme, just as for the case in which $\mathbf{K}=0$. We may treat this case by assuming that the integral has the absolute value

$$\tfrac{2}{3}C'\sigma, \tag{26}$$

in which C' is a parameter analogous to C and σ is the absolute value of σ in the reduced zone scheme.

We shall now calculate the electronic transitions produced by the lattice vibrations. It is convenient to consider separately the effects arising from the acoustical branch, for which $K=0$, and from the other branches since only the acoustical modes will be effective in scattering electrons under the proper circumstances

(1) $\mathbf{K}=0$ (*acoustical modes*).—In this case[14] the quantity $|V_{12}|^2$ appearing in the expression for the transition probability is

$$|V_{12}|^2=\frac{4}{9}C^2\sigma^2\frac{\hbar}{2NM\omega(\boldsymbol{\sigma})}\left\{\begin{matrix}n(\boldsymbol{\sigma})\\ n(\boldsymbol{\sigma})+1\end{matrix}\right\}. \tag{27}$$

Here the coefficient $4C^2\sigma^2/9$ is the square of the matrix component of $V_p/a_t(\boldsymbol{\sigma})$ connecting the electronic states associated with k and k' satisfying (21), whereas the remainder of (27) is the square of the matrix component of $a_t(\boldsymbol{\sigma})$ connecting the state for which the initial vibrational quantum number is $n(\boldsymbol{\sigma})$ with those for which the quantum numbers are $n-1$ and $n+1$, for which the upper and lower values of the quantity in brackets is to be used, respectively. Since only the longitudinal waves contribute non-vanishing matrix components, the subscript t has been dropped. If the theory of deformable atoms were accurately valid, C would have the value (23).

Using Eqs. (7) and (27) we find that the total differential probability for a transition involving lattice vibrations for which $\boldsymbol{\sigma}$ lies in a range from θ to $\theta+d\theta$ relative to $\mathbf{k}$ is

$$dP(t,\theta)=\frac{2\pi}{\hbar}t\cdot\frac{2\hbar C^2}{9NM}\int\sigma^4(2n(\sigma)+1)\times\frac{\delta(E_1-E_2)}{\omega(\boldsymbol{\sigma})}\rho 2\pi\sin\theta d\theta d\sigma \tag{28}$$

provided the second term on the right-hand side of (13) is neglected, which is a permissible approximation for values of $\epsilon(\mathbf{k})$ that are sufficiently large. Here ρ is the density of values of $\boldsymbol{\sigma}$ in wave number space, namely $V/8\pi^3$, and the integration is to be extended over $\boldsymbol{\sigma}$. Using the relation

$$\begin{aligned}E_1-E_2&=\epsilon(k)-\epsilon(k')\pm\hbar\omega(\sigma)\\&=-\frac{\hbar^2}{2m^*}(\sigma^2+2k\sigma\cos\theta)\pm\hbar\omega(\sigma)\\&=-\frac{8\hbar^2}{2m^*}(\sigma^2+2k\sigma\cos\theta),\end{aligned} \tag{29}$$

we find

$$d\sigma=-\frac{m^*}{\hbar^2}\frac{1}{\sigma+k\cos\theta}d(E_1-E_2). \tag{30}$$

Thus the integration over σ may be carried out very simply because of the presence of the delta-function. It follows from (29) that the integrand is finite only when

$$\sigma=-2k\cos\theta. \tag{31}$$

If we replace $n(\sigma)$ by

$$n(\sigma)=k_0T/\hbar\omega(\sigma) \tag{32}$$

to take account of the fact that the modes of vibration with which the electrons react obey classical statistics, we obtain

$$dP(t,\theta)=\frac{8}{9\pi}t\frac{C^2k_0T}{\hbar^2c^2n_0}\frac{m^*}{M}k\cos\theta\sin\theta d\theta, \tag{33}$$

in which θ varies from 90° to 180° and n_0 is the density of unit cells in the lattice.

It is convenient to replace θ by the angle χ through which the electron is deflected. The two angles are related by the equation

$$\cos\theta=\sin(\chi/2), \tag{34}$$

whence

$$\cos\theta\sin\theta d\theta=\sin\chi d\chi/4. \tag{35}$$

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[14] The writer is indebted to J. Bardeen for pointing out to him that the case of scattering of free electrons in a semi-conductor by the acoustical modes was treated by A. H. Wilson (*The Theory of Metals*, p. 211), for a simple cubic lattice. The results obtained here reduce to Wilson's when appropriate simplifications are made. It is to be noted that the parameter C employed by Wilson is $\frac{2}{3}$ as large as that employed here.

It follows that the electron has equal probability of being scattered into any element of solid angle, that is, the cross section for scattering is independent of ψ.

If we now integrate over all values of θ or ψ, we obtain for the average collision time τ,

$$\frac{1}{\tau}=\frac{4}{9\pi}\frac{C^2k_0T}{\hbar^3c^2n_0}\frac{m^*}{M}k. \qquad (36)$$

Since $\hbar k=m^*v$, where v is the velocity of the electron having wave number k, and $1/\tau=v/\lambda$, where τ is the mean free path for scattering, it follows that λ is independent of v and satisfies the equation,

$$\frac{1}{\lambda}=\frac{4}{9\pi}\frac{C^2k_0T}{\hbar^4c^2n_0}\frac{m^{*2}}{M}. \qquad (37)$$

In other words, the conduction electrons satisfy the following three conditions of the elementary theory of transport: (1) The energy of the electrons is essentially conserved during collisions, (2) the scattering is isotropic, and (3) the mean free path is independent of velocity.

The velocity c may be expressed in terms of the characteristic temperature Θ of the crystal with the use of the approximate relation,

$$c=(k_0\Theta/\hbar)(1/(6\pi^2n_0)^{\frac{1}{3}}). \qquad (38)$$

In the general case in which it is possible to define a collision frequency, the mobility μ is given by the equation

$$\mu=\frac{2}{3}\frac{e}{m^*}\frac{\langle\epsilon\tau\rangle}{k_0T}, \qquad (39a)$$

where $\langle\epsilon\tau\rangle$ is the mean value of $\epsilon\tau(\epsilon)$ averaged over the distribution. This reduces to[15]

$$\mu=\frac{8}{3\pi}\frac{e}{m^*}\frac{\lambda}{\bar{v}} \qquad (39b)$$

when λ is independent of energy and the distribution function has the Maxwell-Boltzmann form. Here

$$\bar{v}=4\left(\frac{k_0T}{2\pi m^*}\right)^{\frac{1}{2}} \qquad (40)$$

is the average velocity. The final expression for μ is

$$\mu=6\frac{e}{m^*}\frac{c\hbar}{C^2k_0T}\frac{M}{m^{*2}}\frac{n_0}{\bar{v}}, \qquad (41a)$$

which, by the use of (38), may be placed in the form

$$\mu=\frac{6}{(6\pi^2)^{\frac{2}{3}}}n_0^{\frac{1}{3}}\frac{e}{m^*}\frac{\hbar^2k_0^2\Theta^2}{C^2k_0T}\frac{M}{m^{*2}}\frac{1}{\bar{v}}. \qquad (41b)$$

It is interesting to note at this point that the product of the Hall constant R and the electrical conductivity σ satisfies the relation

$$R\sigma=\frac{e}{m^*c}\frac{\langle\epsilon\tau^2\rangle}{\langle\epsilon\tau\rangle}, \qquad (42a)$$

in the general case in which λ depends upon energy, and reduces to

$$R\sigma=\frac{e}{m^*c}\frac{\lambda}{\bar{v}}=\frac{3\pi}{8c}\mu \qquad (42b)$$

when λ is constant. This relation, which is commonly used to determine mobilities of semiconductors from experimental measurements of the Hall effect, is only approximately valid when λ is not constant.

According to (41b) the relative mobility of an electron at a given temperature in two different substances, distinguished by subscripts a and b, respectively, for which the only elastic waves causing collisions are those in the acoustical branches, is given by the relation

$$\frac{\mu_a}{\mu_b}=\left(\frac{\Theta_a}{\Theta_b}\right)^2\left(\frac{n_a}{n_b}\right)^{\frac{1}{3}}\left(\frac{C_b}{C_a}\right)^2\left(\frac{M_a}{M_b}\right), \qquad (41c)$$

if we assume the effective electron masses are the same.

It is interesting to compute the value of μ for diamond with the use of Eq. (41a). We shall take the density of diamond to be 3.5, take m^* to be the true electronic mass, set $T=300°$K, and take the velocity of longitudinal waves to be $1.75\cdot10^6$ cm/sec. The last quantity is determined from the equation

$$c_l=(c_{11}/\rho_0)^{\frac{1}{2}}, \qquad (43)$$

in which c_{11} is the elastic constant in conven-

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[15] See for example, F. Sietz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1941), p. 517.

TABLE I. Evaluation of mobility at room temperature with use of Eqs. (41c) and (44). (The mobilities are given in units of cm^2/volt-sec.)

Crystal	Θ(°K)	M	$n\cdot 10^{22}$ (cm^{-3})	C(ev)	C^2	$C^2\mu\cdot 10^{-5}$	μ(calc.)	μ(obs.)
Diamond	1800	12	17.6	30.6	936	1.46	156	($\gtrsim$ 100)
Silicon	600	28	5.21	10.2	104	0.253	243	$\sim$ 300
Germanium	290	72	4.57	4.9	24.0	0.145	605	$\sim$ 130

tional notation and ρ_0 is the density of the crystal. c_{11} is taken to have the value[16] $1.07\cdot 10^{13}$ dynes/cm^2. Using these values, we obtain

$$\mu = \frac{1.46\cdot 10^5}{C^2}\,\frac{\text{cm/sec.}}{\text{volt/cm}} \tag{44}$$

in which C is expressed in units of ev $\bar{v}$, computed with the use of (40) has the value $1.08\cdot 10^7$ cm/sec. The right-hand side of Eq. (44) should be multiplied by $(m/m^*)^{5/2}$ if m/m^* is not unity.

Given the value of the mobility for diamond, we can determine the mobility for silicon and germanium with the use of Eq. (42). The greatest uncertainty in the numerical evaluation of the mobilities evidently lies in the determination of the values of C and of the effective electron mass. For simplicity we shall assume that m and m^* are equal and that C is given by the equation

$$C(\text{ev}) = 1.7\cdot 10^{-2}\Theta, \tag{45}$$

in which Θ is the characteristic temperature, expressed in degrees Kelvin. This relationship is approximately satisfied in the case of the simpler monovalent metals treated by A. H. Wilson[14] and can be employed here at least to determine orders of magnitude. Table I contains values of the mobility of electrons at room temperature derived with the use of Eqs. (42) and (44). The numerical values of the constants employed in the calculation are also given.

The observed values of the mobilities given in Table I are obtained from several sources.[6] That for diamond is a very rough lower limit estimated by the group at the Bell Laboratories from a study of the pulses observed in crystal counters employing diamond. The value for silicon is obtained by extrapolating to room temperature the mobility observed by the group at the Bell Laboratories in fairly pure samples of n-type silicon at temperatures somewhat above room temperature. The mobility is found to depend upon temperature through a factor $T^{-\frac{3}{2}}$ predicted from (40) in this range. The value for germanium is obtained in a similar way from measurements obtained both at the Bell Laboratories and by Estermann at this laboratory. It is rather surprising that the $T^{-\frac{3}{2}}$ relation predicted from (40) for low temperatures should be observed at temperatures as close to the characteristic temperature as is the case in silicon and germanium. This seems to imply that the electron scattering arising from terms for which $\mathbf{K}\neq 0$ is not very strong. This point will be discussed again later in this section.

It may be seen that the agreement between observed and calculated mobilities given in Table I is not very good, only the general order of magnitude being obtained. This is not very surprising in view of the fact that the relation (45) is employed to determine C, that the relative effective electron mass is taken to be unity, and that the fact that the contribution to the scattering from modes of vibration for which $\mathbf{K}\neq 0$ has not been separated from the observed values of the mobility of silicon and germanium.

In passing, it may be noted that the value of the characteristic temperature of diamond determined from Eq. (38) with the use of the value of the acoustical velocity obtained from (43), namely $1.75\cdot 10^6$ cm/sec., is somewhat greater than the observed value (2890°K instead of 1800°) as is usually the case. In deriving μ(calc.) for silicon and germanium it is assumed that the sonic velocities in silicon and germanium bear the same relation to the sonic velocity in diamond that the observed characteristic temperatures of the first two materials do to the characteristic temperature of the latter.

(2) $\mathbf{K}\neq 0$ (*non-acoustical modes*).—We shall now consider the contribution to the collision process from the branches of the vibrational spectrum other than the acoustical branch in the case of the non-polar insulators. In the case of polar insulators, the optical branches are of principal importance, provided the temperature is not so low that interaction with the optical modes is forbidden on purely energetic grounds.

We shall proceed in the following manner: First, we shall adopt the reduced zone scheme,

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[16] See for example, R. F. S. Hearmon, Rev. Mod. Phys. **18**, 409 (1946).

so that $\omega_i(\boldsymbol{\sigma})$ is represented by a multivalued. function of the range of $\boldsymbol{\sigma}$ lying in the first Brillouin zone for the lattice. In this case the values of σ of interest for the scattering process are those lying near the origin of $\boldsymbol{\sigma}=0$. Second, we shall assume that $\omega_i(\boldsymbol{\sigma})$ is a constant for each of the non-acoustical branches in the vicinity of $\boldsymbol{\sigma}=0$. We shall assume that only one mode of vibration is responsible for scattering and drop the subscript on $\omega_i(\boldsymbol{\sigma})$ describing the direction of polarization, as in the previous case. Since there will generally be more than one non-acoustical branch of waves having given polarization if there are more than two atoms per unit cell, we should introduce an index to indicate to which branch a given value of ω belongs. For convenience we shall assume that there is only one non-acoustical branch since the contribution to scattering from additional branches can be obtained by simple addition of the results derived for one branch.

We must now consider the transition probability in two cases, namely, that in which the absolute value of the integral of (24) has the form

$$KD \quad \text{(Case I)}, \tag{45a}$$

and that in which it has the form

$$\tfrac{2}{3}C^{\frac{1}{2}}\sigma \quad \text{(Case II)}. \tag{46}$$

In these two situations, the differential transition probability, analogous to (28) is

$$dP(t,\theta)=\frac{2\pi}{\hbar}t\cdot\frac{D^2}{2NM}\frac{\hbar K^2}{\omega}\left\{\begin{matrix} n \\ n+1\end{matrix}\right\}\rho$$

$$\times\int\sigma^2\delta(E_1-E_2)2\pi\sin\theta d\theta d\sigma \quad \text{(I)} \tag{47a}$$

and

$$dP(t,\theta)=\frac{2\pi}{\hbar}t\cdot\frac{2\hbar C'^2}{9NM}\frac{1}{\omega}\left\{\begin{matrix} n \\ n+1\end{matrix}\right\}\rho$$

$$\times\int\sigma^4\delta(E_1-E_2)2\pi\sin\theta d\theta d\sigma \quad \text{(II)} \tag{47b}$$

in which the integration is to be carried out over the allowed range of σ. In both cases ω is the constant frequency of the modes of vibration with which the electron interacts and n, as previously, is the number of quanta having wave number σ in the branch under consideration. Since n is a function of $\hbar\omega/k_0T$, it can be treated as a constant. The relation between E_1-E_2 and the variables describing the electron and the vibrational waves differs in the case in which the electron receives energy from the lattice and that in which it transmits energy (see Eq. (29)). The relation to be used in the present case is

$$E_1-E_2=-\frac{\hbar^2}{2m}(\sigma^2+2k\sigma\cos\theta)\pm\hbar\omega, \tag{48}$$

in which the upper sign before the last term is associated with transitions in which the electron gains energy, and the lower sign with transitions in which it loses energy. Similarly, the upper value in the expression $\{{}^{n}_{n+1}\}$ before the integrand is to be used with the upper sign and conversely. Since there is a delta function in the integrands appearing in (47a) and (47b), the integrals contribute to dP only for values of σ corresponding to the roots of (48), namely,

$$k[-\cos\theta\pm(\cos^2\theta\pm\hbar\omega/\epsilon)^{\frac{1}{2}}]. \tag{49}$$

The two roots correspond to the two possible signs before the radical (not to the two signs before $\hbar\omega/\epsilon$). As previously, $\epsilon=\hbar^2k^2/2m^*$. Only the positive, real roots are of interest. A simple analysis of the situation shows that the roots are governed by the following rules:

(1) *Electron gains energy* (*positive sign under radical*). In this case there is one positive root for each value of θ between zero and 180°. This root is given by the equation

$$\sigma=k[-\cos\theta+(\cos^2\theta+\hbar\omega/\epsilon)^{\frac{1}{2}}]. \tag{50}$$

(2) *Electron loses energy* (*negative sign under radical*). In this case there are two positive real roots provided θ lies between 90° and 180° and the value for which $\cos\theta=-(\hbar\omega/\epsilon)^{\frac{1}{2}}$. Under these conditions the two roots are

$$k[-\cos\theta\pm(\cos^2\theta-\hbar\omega/\epsilon)^{\frac{1}{2}}]. \tag{51}$$

The corresponding values of the integrals appearing in (47a) and (47b) are $2\pi m^*\sin\theta d\theta/\hbar^2$ times the following quantities.

Case I. (a) Electron gains energy,

$$k\frac{[-\cos\theta\pm(\cos^2\theta+\hbar\omega/\epsilon)^{\frac{1}{2}}]^2}{(\cos^2\theta+\hbar\omega/\epsilon)^{\frac{1}{2}}}. \tag{52}$$

(b) Electron loses energy,

$$-4k\cos\theta. \tag{53}$$

Case II. (a) Electron gains energy,

$$k^3\frac{[-\cos\theta+(\cos^2\theta+\hbar\omega/\epsilon)^{\frac{1}{2}}]^4}{(\cos^2\theta+\hbar\omega/\epsilon)^{\frac{1}{2}}} \tag{54}$$

(b) Electron loses energy,

$$-8k^3\cos\theta(2\cos^2\theta-\hbar\omega/\epsilon). \tag{55}$$

It is evident from these expressions that the angular distribution of scattering is more complex than in the case in which the acoustical waves are responsible for transitions.

As Fröhlich[9] has pointed out, we may obtain the collision frequency of interest for the electrical mobility by taking the integral over-all angles of $dP(\theta, t)/t$ times the quantity

$$\frac{1}{2}\left(\frac{\sigma^2}{k^2}\pm\frac{\hbar\omega}{\epsilon}\right). \tag{56}$$

Actually, it is simpler to carry out the integration over σ and θ completely anew, the integration over θ being carried out first. We readily find that the integrals appearing in (46) and (47) have the following values when (56) is included and the operations are carried out over both θ and σ.

Case I:

$$\frac{\pi m^*}{\hbar^2}k^4\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}. \tag{57}$$

Case II:

$$\frac{\pi m^*}{\hbar^2}k^3\frac{4}{3}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}\left(8\pm5\frac{\hbar\omega}{\epsilon}\right). \tag{58}$$

The upper sign before $\hbar\omega/\epsilon$ corresponds to the case in which the electron gains energy and the lower sign to that in which it loses energy. The result corresponding to Case I is the same as that which would have been obtained if (56) had been replaced by unity, showing that the scattering behaves as if isotropic as far as the average effect is concerned.

The final values for the collision frequency are as follows.

Case I:

$$\frac{1}{\tau}=\frac{1}{\pi}\frac{D^2\hbar^2K^2/2m^*}{\hbar\omega}\frac{m^{*2}}{M}\frac{k}{\hbar^3n\sigma}\times\begin{Bmatrix}n\\ n+1\end{Bmatrix}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}. \tag{59}$$

Case II:

$$\frac{1}{\tau}=\frac{2}{27\pi}\frac{C'^2}{\hbar\omega}\frac{m^*}{M}\frac{1}{\hbar}\frac{k^3}{n_0}\times\begin{Bmatrix}n\\ n+1\end{Bmatrix}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}\left(8\pm5\frac{\hbar\omega}{\epsilon}\right). \tag{60}$$

The total collision frequency is obtained by first adding the frequencies for collisions in which the electron gains and loses energy and then combining the result with the expression (36) for the collisions with acoustical waves. It is interesting to note that (59) involves k linearly in the event that $\hbar\omega/\epsilon$ is so small that the factor $(1\pm\hbar\omega/\epsilon)^{\frac{1}{2}}$ can be replaced by unity. In this case, which is not typical of one of the most stable insulators, the mean free path is independent of velocity, provided Case I prevails, even when the non-acoustical vibrations are important. The mean free path will have a complicated dependence upon velocity in Case II if the term (60) is not negligible compared with that arising from the acoustical vibrations.

We shall now compare the ratio of the collision frequencies (59) and (60) to the frequency (36).

Case I.—In this case the ratio is

$$R=\frac{9}{4}\frac{D^2}{C^2}\frac{\hbar^2K^2/2m^*}{k_0T}\frac{m^*c^2}{\hbar\omega}\begin{Bmatrix}n\\ n+1\end{Bmatrix}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}. \tag{61}$$

Since D should be of the same order of magnitude as C (if it does not vanish) and since $\hbar Kc\sim\hbar\omega$ the ratio has the magnitude

$$R\sim\frac{\hbar\omega}{k_0T}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}\begin{Bmatrix}n\\ n+1\end{Bmatrix}. \tag{62}$$

This will be small compared with unity only if $\hbar\omega/k_0T$ is so large that n is very small. Only the positive sign in (62) will then be of interest since ϵ is of the same magnitude as k_0T if the electron is in equilibrium with the lattice. In the case of a material such as diamond for which the characteristic temperature is in the vicinity of 2000°K, $\hbar\omega/k_0T$ is about 6 at room temperature. Hence n is approximately $2.5\cdot 10^{-3}$ and R is a few percent. On the other hand, n should be near unity for a material such as silicon, germanium, or sulfur. In such a case R will not be negligible near room temperature.

Case II. In this case R has the value

$$R=\frac{1}{3}\frac{C'^2}{C^2}\frac{\epsilon}{\hbar\omega}\frac{m^*c^2}{k_0T}\times\left\{\begin{matrix} n \\ n+1 \end{matrix}\right\}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}\left(8\pm 5\frac{\hbar\omega}{\epsilon}\right). \quad (63)$$

As in Case I, this will be very small if n is very small because $\hbar\omega/k_0T$ is large compared with unity. On the other hand, it may also be quite small if n is near unity, for the factor $C'^2m^*c^2/C^2\hbar\omega$ will be small compared with unity if C' is not substantially larger than C.

In any case, the scattering produced by non-acoustical waves will be negligible if the temperature is sufficiently small that $\hbar\omega/k_0T$ is large compared with unity.

In connection with the discussion of Table I, it was pointed out that the mobilities of relatively pure silicon and germanium seem to obey the $T^{-\frac{3}{2}}$ power law, corresponding to Eq. (41a), at temperatures near their characteristic temperatures. We shall see in the next section that these materials probably belong to Case I described above, so that the expression for the collision frequency of the conduction electrons should contain a term of the type (59) in addition to that arising from the acoustical modes of vibration. If the previous discussion of the influence of the non-acoustical modes is correct, the mobility near the characteristic temperature, for which $\hbar\omega/k_0T$ should be of the order of unity, should be approximately half that which would be observed if only the acoustical modes of vibration were effective, and the temperature dependence should not be exactly $T^{-\frac{3}{2}}$ because the factor

$$\frac{1}{T}\left(1\pm\frac{\hbar\omega}{\epsilon}\right)^{\frac{1}{2}}\left\{\begin{matrix} n \\ n+1 \end{matrix}\right\}$$

in (62) will introduce a more complex dependence. We must conclude either that the foregoing estimate of R (Eq. (62)) is too large or that the experiments which seem to support the $T^{-\frac{3}{2}}$ behavior near the characteristic temperature are not sufficiently accurate to separate the deviation which actually exists.

VI. IMPLICATIONS OF CRYSTAL SYMMETRY

It is interesting to consider the question of whether the integral (20) would vanish for diamond. Kimball[17] has investigated the wave functions for diamond and other crystals, such as silicon and germanium, having the same structure, with the use of the cellular approximation. The lattice contains two atoms per unit cell which can be sent into one another with use of a center of symmetry lying at the midpoint of the line joining the two atoms. The two atoms in the cell have the point symmetry of a tetrahedron and the unit cell may be divided into two symmetrically equivalent polyhedra, having tetrahedral symmetry, at whose centers the atoms are situated. Kimball determined the electronic wave functions on the assumption that the portion contained in each polyhedron could be expressed in terms of a single s-function and three p-functions. He found that in this approximation the lowest conduction state possesses a wave function which has tetrahedral symmetry about each atom and has opposite signs in the two polyhedra of a single unit cell. Kimball's wave function is a pure s-function satisfying the equation $s=0$ at the midpoint of four faces of the cellular polyhedron equidistant from the center and possesses an energy that is unreasonably high. The exact wave function having this symmetry[18] would contain spherical harmonics of higher order than the s-function and would undoubtedly have a much lower energy. In fact, it is easy to show with the use of group theory that the next pair of spherical harmonics which would occur are f and g functions having the same angular symmetry as the functions

$$xyz \text{ and } x^2y^2+y^2z^2+z^2x^2-\tfrac{1}{3}(x^4+y^4+z^4). \quad (64)$$

The addition of these functions would lower the the energy of Kimball's solution by replacing the strong curvature in the radial direction with curvature in the angular direction.

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[17] G. E. Kimball, J. Chem. Phys. **3**, 560 (1935).

[18] The reasoning employed here is described in the paper by D. H. Ewing and the writer, Phys. Rev. **50**, 760 (1936).

In any case, we shall assume that for small values of $\mathbf{k}$, $\chi_{\mathbf{k}}$ has tetrahedral symmetry about each atomic position and that it reverses its sign in passing from one polyhedron of a given cell to the next. According to this assumption, $|\chi_{\mathbf{k}}|^2$ possesses the complete symmetry of the lattice.

Let us now consider the value of the integral (24) for a unit cell of the lattice. We shall assume that one atom is at the origin of coordinates and that the other is at the position $\mathbf{r}_a$ whose components are $(a/2,\ a/2,\ a/2)$, where $2a$ is the length of the edge of the unit cubic cell of the crystal. In terms of this notation the allowed values of K are given by the eight vectors,

$$\frac{\pi}{a}\begin{pmatrix}\pm 1\\ \pm 1\\ \pm 1\end{pmatrix}. \tag{65}$$

In the modes of vibration associated with $\sigma = K$, the two atoms in the unit cell move in opposite directions. For those values of $\mathbf{K}$ for which $\mathbf{K}\cdot\mathbf{r}_a$ is equal to $-\pi/2$ or to $3\pi/2$, the displacement of the atoms is expressible in terms of the function

$$R = \xi A[(1-i)e^{i\mathbf{K}\cdot\mathbf{r}} + (1+i)e^{-i\mathbf{K}\cdot\mathbf{r}}], \tag{66}$$

evaluated at the positions of the atom. Here A measures the amplitude of the wave and the vector ξ is the direction of polarization of the atom at the origin. In the four cases in which $\mathbf{K}\cdot\mathbf{r}_a$ is $\pi/2$ or $-3\pi/2$, the corresponding function is

$$R = \xi A[(1+i)e^{i\mathbf{K}\cdot\mathbf{r}} + (1-i)e^{-i\mathbf{K}\cdot\mathbf{r}}]. \tag{67}$$

Equations (66) and (67) can be used to describe modes of vibration for which $\boldsymbol{\sigma}$ is close to, but not necessarily equal to, $\mathbf{K}$ by replacing $\mathbf{K}$ by $\boldsymbol{\sigma}$.

The integral (24) over the unit cell can be broken into two integrals over the polyhedral cells surrounding the two atoms in the unit cell. If the atom in each cell is chosen to be the center of coordinates for the corresponding integral, the sum of the two integrals is

$$\xi\cdot\left[\int_1 |\chi_{\mathbf{k}}|^2 \operatorname{grad} V_n e^{-i\mathbf{K}\cdot\mathbf{r}} d\tau + e^{-i\mathbf{K}\cdot\mathbf{r}}a_2 \times \int_2 |\chi_{\mathbf{k}}|^2 \operatorname{grad} V_n e^{i\mathbf{K}\cdot\mathbf{r}} d\tau\right], \tag{68}$$

in which the two integrals extend over the two polyhedra. Now the two polyhedra can be brought to congruence after the second has been inverted by reflection in the point at the origin. The same inversion will reverse the sign of the gradient term in the integrand and change the exponential into its complex conjugate. It follows that the second term in brackets in (68) may be transformed to

$$\pm i\int_1 |\chi_{\mathbf{k}}|^2 \operatorname{grad} V_n e^{-i\mathbf{K}\cdot\mathbf{r}} d\tau. \tag{69}$$

The sign before the integral is determined by the sign of $\mathbf{K}\cdot\mathbf{r}_a$ which is equal to $\mp\pi/2$. Thus, if the first integral in (68) is designated by $a = a_r + ia_i$, the second is a^* and the expression in parenthesis in (68) may be written

$$(1\pm i)(a_r \pm a_i). \tag{70}$$

It follows that the integral generally will not vanish so that diamond is a material belonging to the first of the two classes described above. We shall investigate the implications of crystal symmetry on the value of the integral somewhat further.

As we shall see below, even in the case in which $\chi_{\mathbf{k}}$ does not have tetrahedral symmetry about each atomic position, $|\chi_{\mathbf{k}}|^2$ will contain a function belonging to the unit irreducible representation of the tetrahedral group. Hence, the conclusion that diamond belongs to the first of the two classes, for which (68) does not vanish, is valid under more general conditions than that in which $\chi_{\mathbf{k}}$ has pure tetrahedral symmetry. We may conclude, for example, that the holes produced in the filled band of diamond and in other crystals having the same lattice symmetry will also interact with the non-acoustical modes of vibration in accordance with the first of the two rules of the previous section.

The point symmetry at the position of an atom in the diamond lattice is expressible in terms of a twenty-four element group T_d, which possesses five classes. The five types of element in the classes are as follows:

(1) the unit operator (1 element),
(2) the three-fold rotations about (111) axes (8 elements),

(3) the two-fold rotations about (100) axes (3 elements),
(4) the rotary reflections through 90° about (100) axes (6 elements), and
(5) the reflecting planes passing through (100) axes (6 elements).

The five irreducible representations, which may be designated by Γ_1, Γ_2, Γ_3, Γ_4 and Γ_5 have the following character system

	E	$8C_3$	$3C_2$	$6\delta_4$	6ρ
Γ_1	1	1	1	1	1
Γ_2	1	1	1	−1	−1
Γ_3	2	−1	−2	0	0
Γ_4	3	0	−1	−1	1
Γ_5	3	0	−1	1	−1

in which the columns designate the classes in the order given above. It is readily found that the spherical harmonics decompose in the following manner: s: Γ_1, p: Γ_4, d: $\Gamma_3+\Gamma_4$, f: $\Gamma_1+\Gamma_4+\Gamma_5$, g: $\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$, and that the cross products of the representations decompose as follows:

$$\begin{aligned}
&\Gamma_1\times\Gamma_j=\Gamma_j,\\
&\Gamma_2\times\Gamma_3=\Gamma_3,\\
&\Gamma_2\times\Gamma_4=\Gamma_5,\\
&\Gamma_2\times\Gamma_5=\Gamma_4,\\
&\Gamma_3\times\Gamma_4=\Gamma_4+\Gamma_5,\\
&\Gamma_3\times\Gamma_5=\Gamma_4+\Gamma_5,\\
&\Gamma_4\times\Gamma_5=\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5,\\
&\Gamma_2\times\Gamma_2=\Gamma_1,\\
&\Gamma_3\times\Gamma_3=2\Gamma_1+\Gamma_2,\\
&\Gamma_4\times\Gamma_4=\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5,\\
&\Gamma_5\times\Gamma_5=\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5.
\end{aligned}$$

Since $|\chi_{\mathbf{k}}|^2$ and V_n belong to Γ_1, whereas **R** grad belongs to Γ_4, it follows that the coefficient of $e^{i\mathbf{K}\cdot\mathbf{r}}$ in the integrand of (24) can be expanded in terms of spherical harmonics having the symmetry of Γ_4, of which the first four are of the type form:

$$x,\ yz,\ x^3-\tfrac{3}{2}x(y^2+z^2),\ \text{and}\ yz(y^2+z^2-6x^2). \qquad (71)$$

The first real term in the expansion of $\exp(i\mathbf{K}\cdot\mathbf{r})$ with which any one of these harmonics can possess a non-vanishing integral is $-(\mathbf{K}\cdot\mathbf{r})^2/2$, which, for diamond, may take any one of the four independent values given by the expression

$$(K^2/2)(\pm x\pm y\pm z)^2,$$

where K is the absolute value of $\mathbf{K}$. Two of these functions give non-vanishing integrals when multiplied with xy, a d function belonging to Γ_4.

The first imaginary term in the expansion of $\exp(-iK\cdot r)$ is $-i\mathbf{K}\cdot\mathbf{r}$. This will usually give a non-vanishing integral when multiplied by the first of the four representatives of Γ_4 shown in (71).

It is interesting to observe that D would vanish if $|\chi_{\mathbf{k}}|^2$ and V_n were spherically symmetric about the atom in the polyhedron. It would also vanish if Nordheim's hypothesis of rigid ions were employed, for the use of this procedure would be equivalent to replacing the term $\exp(-i\mathbf{K}\cdot\mathbf{r})$ by unity in the integration over a single polyhedron. The integrand would always be a spherical harmonic belonging to the representation of Γ_4 (if $|\chi_{\mathbf{k}}|^2$ belongs to Γ_1) and the integral would vanish. These results suggest that D will probably be small compared with C in any substance in which the atoms are highly symmetric or highly undeformable. In such a case the ratio (59) might be small so that only the acoustical modes of vibration would scatter electrons at any temperature, as is possibly the case in silicon and germanium.

VII. COMMENT ON CRYSTAL COUNTERS

The preceding discussion shows that the mobility of electrons in the non-polar insulating crystals may be of the order of several hundred cm²/volt-sec. or more even at room temperature. It is interesting to consider the implications of this conclusion in connection with the development of crystal counters. In the conventional arrangements of such counters which are under consideration at the present time, the crystal specimen is of the order of 0.1 cm thick in the direction in which the electric field is applied and across which the charges produced by the ionizing radiation move. The applied electric field are usually somewhat less than 10,000 volts per cm, although a field of this magnitude or greater probably could be obtained without serious difficulty. The time T required for electrons to traverse the specimen under these conditions is given by the equation

$$T=d/\mu E=10^{-5}/\mu\ \text{sec.}, \qquad (72)$$

where d is the crystal thickness, E is the electric field intensity, and μ is the mobility expressed in units of cm^2/volt-sec. If it is desired that T be 10^{-7} sec. at maximum, it is necessary under the conditions given that μ be at least 100 cm^2/volt-sec. Since an energetic charged particle which is either stopped by the crystal or passes through it will produce a sufficient number of electrons and positive holes to be detected if all pass to the electrodes, it would appear that any crystal having sufficiently high mobility should be able to act as a counter.

Actually another important factor will enter into the problem. The careful studies on the alkali halide crystals show that the migrating electrons or holes may be trapped in the interior of the crystal so that they do not necessarily reach the electrodes. Actually, a very small amount of impurity of the kind needed for trapping may suffice to cut the ionization pulses to a negligible value. The experiments on the trapping effect of F- and F'-centers in the alkali halides, that is of halogen ion vacancies and halogen ion vacancies neutralized by an electron, show[19] that the cross section for capture in these cases is of the order of magnitude of 10^{-15} cm^2. If the concentration of trapping centers is n_t and if their cross section for capture is σ_t, the time T_t an electron having velocity v will travel before being trapped is

$$T_t = 1/n_t\sigma_t v. \tag{73}$$

In order that this be at least as large as the 10^{-7} sec. necessary for the electron to travel to the electrodes under the conditions described in the previous paragraph, it is necessary that

$$n_t < 10^7/\sigma_t v. \tag{74}$$

We shall take σ_t to have the value 10^{-15} cm^2 and v to be 10^7 cm sec., in which case we must have

$$n_t < 10^{15} \text{ atoms per cc.}$$

This condition implies a very high degree of freedom from any kind of contamination which will provide trapping centers, including lattice defects such as vacancies or interstitial atoms. It is not necessary that all types of contamination provide trapping centers, so that it may only be necessary in a given case to free the crystal from certain elements.

The fact that strong pulses have been observed in silver chlorides and diamond by various investigators indicates that the number of trapping centers was very small in the specimens employed in this work.

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[19] This result can be obtained from the study of the distances moved by photoelectrons in the colored alkali halides before being trapped (see reference 3). It is assumed that the mobility of the conduction electrons is of the order of 5 cm^2/volt-sec. on the basis of the Hall effect measurements of J. Evans, Phys. Rev. **57**, 47 (1940).