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On the Theory of Electron Multiplication in Crystals

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The theory of the multiplication of electrons in strong electrostatic fields is investigated. It is found that the non-polar coupling between electrons and lattice has an important effect on the retardation of electrons in polar materials as well as in non-polar ones if the electron is to be accelerated to an energy at which it may ionize the bulk material. The retardation arising from this coupling is a maximum when the energy of the electron corresponds to a value near the boundary of the Brillouin zone, in contrast with the retardation arising from purely polar interaction in polar crystals which has its maximum when the energy is near the energy of the polar modes. The existence of the non-polar interaction seems to make the difference between the breakdown criteria of von Hippel and Fröhlich of less practical importance than was supposed hitherto. It is found that statistical fluctuations in the velocity of the electrons plays a very important role in determining electron multiplication and that the field required to produce breakdown in a standard specimen actually is no more than twenty percent of the value obtained from the criteria of von Hippel and Fröhlich.

1. INTRODUCTION

THE theory of the production of free electrons in crystals in the presence of high electrostatic fields and relatively low temperatures, where thermal currents do not play a role, has been the subject of relatively intense but somewhat diversified activity during the past fifteen years. In this development principal interest has focused on dielectric breakdown because of its great practical importance.[1] On the other hand there are secondary phenomena which are of equal interest from the standpoint of fundamental development. For example it has been observed by von Hippel[2] and his co-workers that a measurable current exists within the alkali halides for fields somewhat lower than that required to induce breakdown. These pre-breakdown currents grow in magnitude as the field is raised. Although the breakdown current usually appears as a discontinuity on the rising pre-breakdown current, it seems reasonable to suppose that the pre-breakdown current is related to breakdown. Haworth and Bozorth,[3] who studied pre-breakdown phenomena in glass, observed that the current is exceedingly noisy; that is, the current occurs in pulses (Fig. 1) which grow in magnitude as the field increases. Pulses of this type have been observed[4] in a qualitative manner in many cases. Their presence suggests that electron avalanches occur at fields lower than that required to produce breakdown and grow rapidly in magnitude as the breakdown field is approached.

Theoretical developments concerning breakdown phenomena have flowed in three somewhat separate channels, each of which has had its own exponents:

(1) One of the first systematic development along modern lines is that of Zener,[5] who proposed that breakdown occurs when the electrostatic field becomes sufficiently strong to ionize the atoms of the insulator by a process akin to field emission. In effect, the electrons of the bulk solid are able to tunnel from the filled band of levels to the conduction band. This effect was investigated subsequently by Houston[6] and by Franz.[7] The latter focused attention particularly on the problem of breakdown, however, Houston's calculations are somewhat more accurate. These investigators find that the probability per unity time that an electron is ejected from the filled to the empty band when the field intensity is E is

$$P=(2\pi deE/\hbar)(e^{-\alpha}/(1-e^{-\alpha})^2), \tag{1}$$

where

$$\alpha=(\Delta\epsilon)^2md/eE\hbar^2. \tag{2}$$

Here $\Delta\epsilon$ is the gap in energy between filled and empty band, d is the lattice spacing (for the one-dimensional model employed) and e and m are the electron charge and mass. Franz has shown that this leads to a current of the order of 1 amp per cm^2 when E takes the value

$$E=0.33\cdot 10^6(\Delta\epsilon)^2(\text{volts per cm}). \tag{3}$$

Here E is given in volts per cm when $\Delta\epsilon$ is expressed in electron volts. The lattice spacing d is assumed to have the value $3\cdot 10^{-8}$ cm corresponding to the nearest-neighbor spacing in sodium chloride. Now the spacing between filled and empty conduction bands is about 10 ev in the case of sodium chloride, if present interpretation[8] of the ultraviolet absorption spectra of the alkali halides is correct. Thus (3) leads to a breakdown potential of about $3\cdot 10^7$ volts per cm, which is at least

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[1] The principal survey articles on the field of dielectric breakdown in solids are as follows: A von Hippel, J. App. Phys. **8**, 815 (1937); Trans. Faraday Soc. (Conference on Dielectrics) **40**, 78 (1946); W. Franz, Zeits. f. Physik **113**, 607 (1939); H. Fröhlich, Reports on Progress in Physics **6**, 411 (1939); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940); A. E. W. Austen and S. Whitehead, Proc. Roy. Soc. **176**, 33 (1940). More recent papers are as follows: H. Fröhlich, Proc. Roy. Soc. **188**, 521, 532 (1947); J. W. Davisson, Phys. Rev. **70**, 685 (1946).

[2] A. von Hippel, Phys. Rev. **54**, 1096 (1938).

[3] F. E. Haworth and R. M. Bozorth, Physics **5**, 15 (1934).

[4] The writer is indebted to Professor R. J. Maurer for a discussion of observations on pre-breakdown noise.

[5] C. M. Zener, Proc. Roy. Soc. **145**, 523 (1934).

[6] W. V. Houston, Phys. Rev. **57**, 184 (1940).

[7] W. Franz, see reference 1.

[8] N. F. Mott and R. W. Gurney, see reference 1, p. 95.

a factor 10 larger than the observed[9] value at room temperature of $1.5 \cdot 10^6$ volts per cm. Even without this evidence, which is subject to criticism on the ground that the absolute theoretical values may contain large calculational inaccuracies, the measurements of Buehl and von Hippel[9] on the temperature dependence of the breakdown field in the alkali halides seem to rule out the field emission theory. This work shows that the breakdown field decreases with decreasing temperature in the range below room temperature. This effect is very difficult to explain on the field emission theory, whereas it is explained very naturally on an avalanche theory.

The value of $\Delta\epsilon$ is not accurately known in diamond; however it is probably less than 10 ev and probably nearer to 7 ev. Moreover the lattice spacing in diamond is about half the value for sodium chloride. As a result, the field corresponding to that given by Eq. (3) is somewhat less than 10^7 volts per cm. We shall have cause to refer to this value in later sections.

(2) In 1932 von Hippel[10] proposed that breakdown in solids is a by-product of the production of electron avalanches through electron impact. He pointed out that any electron which finds itself free in a solid in the presence of an electrostatic field will be subject to two opposing influences: It will tend to be accelerated by the field and retarded by the "friction" resulting from interaction with the vibrational waves of the lattice. He postulated that breakdown occurs when the average electron gains energy more rapidly from the field than it loses it to the lattice for all velocities of motion less than the value needed to produce ionization by impact. von Hippel also proposed that the electron would encounter the greatest friction in ionic crystals when its energy is of the order of $h\nu_0$ where ν_0 is the frequency of the optically active mode of lattice vibration. In other words the barrier is greatest when the electron has energy in the thermal range.

Seeger and Teller[11] supplemented von Hippel's theory by deriving an expression for the rate at which a conduction electron would lose energy to the lattice. Unfortunately this calculation alone does not provide a very satisfactory test of the theory because the collision frequency is so large in the velocity range where the friction is greatest that there is no reliable method of determining the rate of loss. For example, quantum mechanical perturbation techniques are not accurately applicable. In spite of the fact that von Hippel's theory is not subject to precise treatment, it evidently has many attractive features. For example it does give the correct order of magnitude of breakdown field and it does explain the occurrence of avalanches at least qualitatively. In addition it predicts temperature dependence of the general type that is observed.

(3) In 1937 Fröhlich[12] proposed an independent impact ionization theory which differs from von Hippel's primarily in regard to the condition employed for breakdown. Fröhlich also postulated that breakdown occurs as a result of acceleration of electrons through a friction barrier arising from interaction between electrons and lattice waves. However, he has been guided by the intuitive notion that the critical conditions are determined by the behavior of electrons which have an energy sufficient to ionize the atoms of the solid. As a result he has proposed an equation for the breakdown field which differs from von Hippel's and which states that the field should be sufficiently strong that electrons having energy sufficient to ionize gain more energy from the field than they lose to the lattice waves. As far as the writer can judge, Fröhlich believes that von Hippel's condition is too stringent because it requires that every electron be accelerated on the average. Apparently Fröhlich believes that breakdown will occur when any electron which has by whatever means possible reached the ionization energy will gain more

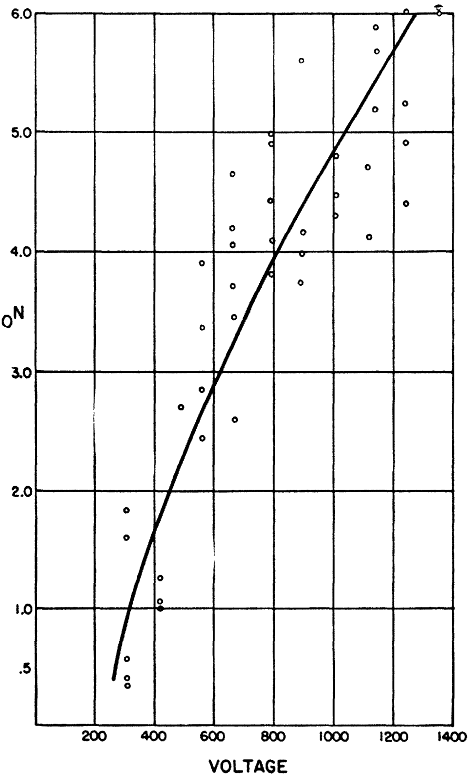

FIG. 1. Variation of the size of electron avalanches in Pyrex with applied voltage (after Haworth and Bozorth). The ordinate is expressed in units of the electron charge.

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[9] A. von Hippel, Zeits. f. Physik **75**, 145 (1932); Ergebn. d. exakt. Naturwiss. **14**, 79 (1935); R. C. Buehl and A. von Hippel, Phys. Rev. **56**, 941 (1939); A. E. W. Austen and S. Whitehead, see reference 1.

[10] A. von Hippel, Ergeb. d. exakt. Naturwiss. **14**, 79 (1935); J. App. Phys. **8**, 815 (1937); A. E. W. Austen and S. Whitehead, see reference 1.

[11] R. J. Seeger and E. Teller, Phys. Rev. **54**, 515 (1938); **56**, 352 (1939).

[12] H. Fröhlich, Proc. Roy. Soc. **160**, 230 (1937); **172**, 94 (1939); **178**, 493 (1941); **188**, 521, 532 (1947); Phys. Rev. **61**, 200 (1942).

energy from the field than it loses to the lattice vibrations. In essense, his theory appears to rest on the assumption that when the breakdown field is reached the distribution function describing the spread of electron energies will have a maximum well below the ionization energy, but will possess some type of tail in the region of the ionization energy. The behavior of the electrons in this tail determines breakdown. In partial support of this viewpoint, Fröhlich has shown recently in a somewhat idealized calculation[12] that the distribution function actually possesses a portion which rises with increasing energy above the ionization energy. This calculation is deficient in the sense that it does not include the influence of the ionization process itself on the distribution function. Inasmuch as this influence is probably great, it must be admitted that Fröhlich's case still rests primarily on intuitive grounds.

Since Fröhlich, like von Hippel and Seeger and Teller, assumed that the maximum friction occurs when the electron has energies near $h\nu_0$ and that the curve describing dissipation of energy to the lattice falls at higher energies, his condition for breakdown would lead to a lower value of the breakdown if both groups of investigators employed in same function. Actually both arrive at about the same values of the breakdown field because they employ functions which differ essentially by a multiplicative constant. The difference arises from the manner in which the screening of electrons by the polarization of the lattice is included. Seeger and Teller assume that the electron is shielded by a polarization charge determined by the dielectric constant of the medium, whereas Fröhlich assumes that this screening is not of great importance for energies near the ionization potential.

As we shall see in Section 4 both groups of investigators neglect the interaction of electrons with non-polar modes of vibration. The calculations of the present paper seem to show that this interaction, which is peaked at energies of the order of several electron volts and which is of primary importance in non-polar crystals, plays a very important role in ionic solids and should modify the application of either of the criteria for breakdown described above. In fact, the present work seems to show that the criteria of von Hippel and Fröhlich do not differ appreciably from a practical viewpoint since the electron friction arising from interaction with lattice vibrations is almost as large when the electron can ionize as it is when the electron has energies near $k_0\theta$ in the case of polar crystals. Moreover the present work indicates that statistical fluctuations are sufficiently important that both criteria are too stringent.

It should be emphasized in connection with this summary that experimental aspects of the topic of breakdown still merit a great deal of further investigation. The best available data on the subject is derived from direct voltage measurements which are carried out to the point at which rupture occurs. It is conventional to assume that the applied electrostatic field is relatively uniform and that the electrodes play a minor role in the breakdown process when relatively reproducible results are achieved. Early work of Gudden and Pohl and more recent work of McKay[13] indicates that the introduction of as few as 10^{10} electrons into a crystal can have an appreciable influence upon the potential distribution through the formation of space charge within the specimen as a result of the trapping of electrons. It is possible that the large electrostatic fields which are achieved near breakdown in the best insulators sweep away this space charge. However this point, as well as the influence of ionic polarization, merits much more study than the topic has received to date. Similarly it is possible that the character of the pre-breakdown currents is determined primarily by the electrode-crystal junction.

These uncertainties will have relatively little influence on the following discussion since we shall be primarily interested in the manner in which electrons may be multiplied as a result of acceleration within the crystal. It seems reasonable to assume at present that this process is intimately related to the breakdown problem in many crystals even though we may not have complete understanding of the relationship between the applied voltage and the distribution of field in a specimen for which the applied voltage is near the breakdown value.

2. VIEWPOINT OF PRESENT ANALYSIS

The present paper is devoted to a re-examination of the impact ionization theory in order to attempt to obtain a somewhat clearer view of the multiplicative process. In the opinion of the writer, von Hippel's approach to the problem of dielectric breakdown provides a more fruitful starting point than Fröhlich's since it attempts to follow the dynamical behavior of a free electron throughout its life cycle as it passes from cathode to anode. It is difficult to believe that it will lead to essentially incorrect results if due attention is paid to all of the effects which influence the electron. It cannot of course be denied that Fröhlich's more formal approach could lead to identical results; however it appears to be very difficult to subject his method to the type of detailed approximation which is so valuable in obtaining a feeling for the inner working of a problem.

In the last analysis the central problem of dielectric breakdown in solids is this: At what field strength are free electrons produced in sufficient numbers to produce disruption? We shall suppose that the free electrons are produced by an avalanche effect in which one initial free electron produces a secondary by impact ionization; the pair then produce a second pair and the process continues through n generations at the end of which

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[13] B. Gudden and R. W. Pohl, Zeits. f. Phys. 7, 69 (1921); K. G. McKay, Phys. Rev. 74, 1606 (1948).

time there are 2^n free electrons. For a given material and field strength n will be proportional to the time the electrons spend within the crystal and hence upon the dimensions of the specimen and the point at which the first electron is initiated, as well as on the bulk properties of the material.

The following arguments may be employed to obtain an estimate of the value n should attain for breakdown to be induced. We shall see in the following sections that a typical free electron will migrate through a crystal with a mobility in the vicinity of 1 cm^2 per volt-sec. when the field is near the breakdown value of say 10^6 volts per cm. Thus the electron will traverse a distance of 1 cm in about 10^{-6} sec. In addition to drifting in the direction of the field, the electron will undergo Brownian motion or diffusion in the plane normal to the field. The diffusion coefficient, which is $\lambda v/3$, where λ is the mean free path and v is the velocity of motion, has a value in the neighborhood of 1 cm^2 per sec. Thus in travelling 1 cm in the direction of the field, the electron will on the average wander through a circle of radius 10^{-3} cm in the plane normal to the field. We shall assume that its progeny, produced by impact ionization, also lie within a circle of this radius. Since the diffusion coefficient of heat in most solids is less than 1 cm^2 per sec., the energy which the electrons transfer to the atoms of the lattice in the collisions between electrons and lattice vibrations will not diffuse out of this tube in the time in which the electrons migrate 1 cm. Now if the field is 10^6 volts per cm, each electron will transfer 10^6 ev to the group of atoms in the tube. The material in the tube would be seriously disrupted if each atom received as much as 10 ev (230,000 cal. per mole). Thus it seems safe to assume that breakdown will occur if the primary electron produces one electron for each 10^5 atoms in the tube. Since there are about 10^{17} atoms in the tube, we conclude that the primary electron will produce breakdown if it generates 10^{12} progeny. The foregoing calculation has been made as if the 10^{12} electrons were present during the entire traversal of the tube. Actually the atoms in the tube will begin to receive energy from the electrons at the estimated rate of 10 ev per atom only after the 10^{12} electrons have been produced. Thus only the material near the end of the tube would be disrupted.

It is clear that if 10^{12} electrons were produced in a distance shorter than 1 cm, and hence in a time less than 10^{-6} sec., the energy transferred per atom to the atoms in the tube having a radius equal to the distance the electron diffuses normal to the field would be greater than 10 ev because this radius varies as the square root of the time. Conversely less than 10^{12} electrons would be needed to produce the desired disruption. We shall neglect this variation of the number of electrons needed with the distance in which they are produced since it is relatively small for the variations in electrode spacing normally employed in experiments.

The value of n for which $2^n = 10^{12}$ is 40. Thus we conclude that about 40 generations of secondary electrons should be produced between electrodes from a single primary if breakdown is to occur as a result of impact ionization. It is evident that this is a fairly approximate value; however it is sufficiently accurate for the purposes for which we shall use it.

The preceding conditions for breakdown may also be expressed in the following way: An average free electron must produce a secondary electron in travelling a distance $L = D/40$ in the direction of the field if D is the spacing between electrodes. Since the electrode spacing enters into this formulation of the condition for breakdown, it follows that the breakdown field should depend upon the electrode spacing, being larger the smaller the spacing. It has been well established for mica[14] that the breakdown field varies inversely as the electrode spacing. However the measurements of Austen and Whitehead do not permit a precise determination of the relation.

If the distance Λ which the electron travels in producing a secondary is greater than L but less than D it will start an avalanche; however this avalanche will not reach sufficient proportions to cause breakdown, even though it may be great enough to be detected relatively easily as a current pulse.

We may expect the distance Λ to decrease continuously with increasing field strength. Thus as the field intensity is increased we may generally expect to find a region in which pre-breakdown avalanches are observed whenever breakdown is caused by impact ionization. The size of the avalanches will increase continuously with increasing field until they become sufficiently large to produce breakdown.

Should the current produced by field emission of the type described by Zener and Franz cause breakdown before Λ is smaller than D, the free electrons will not be able to produce progeny and the pre-breakdown current will not be very noisy, that is, will not contain avalanches larger than those produced by the random arrival of electrons at the anode.

In the following sections an attempt will be made to analyze the factors which determine the ability of electrons to multiply in strong fields in somewhat more detail than has been done hitherto. Since quantum mechanical perturbation methods form the basis for most of this discussion, it is necessary to emphasize, along with other investigators,[15] that these methods cease to be accurate as soon as the collision frequency exceeds a value of about $3 \cdot 10^{13}$ $sec.^{-1}$. Since the collision frequency actually does exceed this value in the most interesting range of electron velocity, the results obtained with perturbation theory have only semiquantitative value and must be employed with full recognition of this limitation. They can be employed only to infer the type of behavior that may be expected

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[14] A. E. W. Austen and S. Whitehead, see reference 1.

[15] The applicability of perturbation theory is discussed in a previous paper by the writer, Phys. Rev. **73**, 550 (1948).

TABLE I. Characteristic energies associated with free electrons at boundary of Brillouin zone (expressed in electron volts).

	ϵ min.	ϵ max.	ϵ_z
Diamond	8.9 ev	11.9	11.5
NaCl	3.6	4.8	4.6

to occur in practice; precise values of the various parameters should be determined either with the use of experiment or by application of methods other than those based on perturbation theory. In spite of these drawbacks the theoretical values to be derived and discussed lead to interesting conclusions.

3. FACTORS EFFECTING FREE ELECTRON

Consider the behavior of an electron which finds itself free in an insulating crystal. We shall assume that the electron possesses thermal energy initially and that there is a uniform electrostatic field of intensity E within the crystal. If the electron did not interact with the crystal, it would be uniformly accelerated at a rate eE/m and would with certainty obtain sufficient energy to excite or ionize the electrons of the insulator provided there is sufficient potential drop between the point of origin of the free electron and the anode toward which the electron is accelerated. As von Hippel has pointed out, the lattice provides in effect a source of "friction" for the motion of the electron which prevents the electron from being accelerated at the rate eE/m. The various sources of friction may be catalogued in the following way.

(1) Excitation of Polar (Optical) Modes of Vibration

In polar crystals the electron will interact strongly with the polar or optical modes of vibration of the lattice. This interaction has been examined in various approximations by von Hippel, Fröhlich and Mott, Seeger and Teller, and Callen who obtain results that are similar semi-quantitatively. The maximum interaction occurs when the electron has an energy of the order of $h\nu_0$, where ν_0 is the frequency of the polar mode of longest wave-length in the reduced zone scheme. The electron may lose energy to the lattice, provided it has sufficient energy to excite the polar modes, or it may gain energy if the lattice is thermally excited. Both types of encounter cause the electron to be scattered so that it undergoes Brownian motion. Fröhlich and Mott have distinguished carefully between the transverse and longitudinal polar modes of vibration, which generally have different frequencies even in a cubic crystal, and have shown that the longitudinal modes are principally responsible for the interaction. As far as the writer is aware all of the investigators who have considered the friction encountered by an electron in being accelerated have placed principal emphasis upon the interaction with polar modes and have neglected a second effect which seems to him to be as important for the problem.

(2) Interaction with Non-Polar Modes

The electron will interact with non-polar modes of vibration even in a polar crystal. This type of interaction is usually considered only in non-polar crystals since the polar modes are absent in these materials and the non-polar modes provide the principal source of scattering. However, the non-polar modes are of considerable interest even for polar crystals, for, as we shall see below, their influence is greatest when the energy of the electron is a hundred or so times larger than $h\nu_0$ and the influence of the polar modes has diminished. The neglect of the non-polar modes of polar crystals is undoubtedly justifiable in a discussion of the ordinary problem of electronic conduction for which the kinetic energy of the electrons does not differ greatly from $h\nu_0 \cong k\theta$ (θ = characteristic temperature). However these modes should be included when the electron has either a high energy or a very low energy. The interaction with these modes evidently is a principal subject of discussion for the problem of electron multiplication in non-polar crystals.

In addition to the foregoing impediments to the acceleration of an electron there are two more obstacles which merit attention.

(3) Laue Scattering

If in the course of being accelerated, an electron passes near to the boundary of a Brillouin zone, it has a finite chance of undergoing Laue scattering. Although such scattering will not alter the energy of the electron, it will alter its direction of motion and hence alter the rate at which the electron gains energy. This process is particularly important if the free electron does not possess sufficient energy to excite the bound electrons when it is in the first Brillouin zone associated with free electrons. If the bands associated with free electrons overlap and if the frequency with which the electron makes collisions with the lattice vibrations is sufficiently great, the electron will jump from one zone to the next without spending an appreciable time near the boundary of zones. However if the frequency of collisions with the lattice vibrations is small once the electron has gained energy, or if the neighboring energy bands associated with free electrons are separated by a gap in energy that is large compared with the energy of the lattice vibrational quanta, as is the case between filled and empty bands for the normal valence electrons of an insulator, the accelerated electron will eventually reach the boundary of the zone and undergo Laue reflection. We shall assume in the following that the conduction bands overlap, as is probably the case for most insulators. We shall see later that the frequency of collisions with lattice vibrations is sufficiently large in this case that the electron probably does not spend appreciable time near the boundary of the Brillouin zone.

The first two columns of Table I show the maximum and minimum energies that would be associated with the boundaries of the first conduction zone in diamond and sodium chloride if the electron were perfectly free. The third column gives an average ϵ_z that will be defined later.

(4) Production of Excitons

As J. B. Sampson and the writer emphasized a number of years ago,[16] the first electronic excitation process of which the accelerated electron may be capable is the production of excitation waves. In fact this should be the case with certainty if our present picture of the electronic states in good insulators is correct. Unless the excitation waves are decomposed into free electrons and holes by the field or by other means, the accelerated electron will lose the energy expended in excitation waves without producing secondary charged particles which can be accelerated in turn

4. ENERGY LOSS BY LATTICE COLLISIONS IN POLAR AND NON-POLAR CRYSTALS

A. Non-Polar Crystals[17]

The interaction between free electrons and the lattice vibrations of non-polar crystals may be treated in a straightforward way if it is assumed that the lattice vibrations alter the potential field of the crystal in the manner first proposed by Bloch which is sometimes called the deformable atom hypothesis. It is assumed in essence that the perturbing potential V_p satisfies the equation

$$V_p(r) = -R\cdot\operatorname{grad}V_n(r). \tag{4}$$

Here $V_n(r)$ is the unperturbed potential and R is a continuous function whose values at the positions of the atoms describe the motion of the atoms as a result of the vibrational waves. The use of the Bloch perturbing potential is supported by the fact that it leads to a $T^{\frac{3}{2}}$ dependence of mobility upon temperature at temperatures below the characteristic temperature, in agreement with experimental observations in pure diamond, silicon, and germanium. As a result, we may feel justified in employing the results of a previous paper to discuss the interaction between the electrons and lattice vibrations in non-polar materials.

It has been shown that the probability per unit time p that the electron will interact with the acoustical modes is

$$p = \frac{2\pi}{\hbar}\frac{2\hbar C^2}{9NM}\int \sigma^4(2n(\sigma)+1)\frac{\delta(E_1-E_2)}{\omega(\sigma)}\rho 2\pi \sin\theta d\theta d\sigma. \tag{5}$$

Here C is an energy parameter describing the coupling between electron and lattice, N is the number of unit cells in the crystal under consideration, M is the mass of the atoms of which the lattice is composed, σ is the wave number vector of the vibrational quanta, $n(\sigma)$ is the number of quanta of each type of vibration that is stimulated as a result of thermal excitation, $\omega(\sigma)$ is the circular frequency associated with the vibrational wave having wave number σ, ρ is the density of values of σ in wave number space, E_1 and E_2 are the energies of the system consisting of electron plus lattice before and after a collision of the electron with the wave having wave number σ. In the collision, the wave number k of the electron is transformed to k' where

$$k' = k+\sigma \tag{6}$$

so that $E_1-E_2=\epsilon(k)-\epsilon(k')\pm\hbar\omega$ if $\epsilon(k)$ is the energy of an electron having wave number k. If we assume that the electrons are completely free so that $\epsilon(k)=\hbar^2k^2/2m$, we find

$$E_1-E_2 = -(\hbar^2/2m)(\sigma^2+2k\sigma\cos\theta)\pm\hbar\omega, \tag{7}$$

in which θ is the angle between k and the vector σ which satisfies (6) and the equation

$$E_1-E_2=0. \tag{8}$$

The integration in (5) extends over all permitted values of σ and θ; however the presence of the delta-function reduces the integration to one dimension. In general when one desires to obtain the total probability per unit time as given by the integral (5) instead of the differential probability as a function of angle, it is convenient to replace the integration over θ by one over the variable E_1-E_2, using (7) to connect the two variables. Equation (5) is then reduced to a single integration over the scalar wave number σ. Provided k lies well within the first Brillouin zone, the integration over σ extends from zero to $2k$ and leads to the results described in I. On the other hand, if k lies so close to the zone boundary that the upper limit of σ required by Eqs. (6) and (7) would lie outside the first zone in σ space, the integration becomes much more involved. The simplest procedure to follow is to set the upper limit of integration of σ equal to a constant σ_m that is of order of magnitude of the average radius of the first zone boundary. This procedure can also be adopted when k lies well outside the first zone.

As long as k lies well inside the first Brillouin zone, so that there is no limitation on the integration over σ imposed by the zone boundaries, the calculations of I show that the electron is scattered isotropically. However once the range of σ is no longer $2k$, forward scattering predominates. The transition between the two cases occurs when k approaches the zone boundary.

When the electron has thermal energy, as was assumed to be the case in I, $n(\sigma)$ may be set equal to $k_0T/\hbar\omega$, where k_0 is Boltzmann's constant and T is the absolute temperature. In this case the 1 appearing with

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[16] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), p. 563. The basic theory of excitons may be found in the following: J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931); Physik. Zeits. Sowjetunion **9**, 158 (1936); R. Peierls, Ann. Physik **13**, 905 (1932); J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936); G. Wannier, Phys. Rev. **52**, 191 (1937).

[17] This paper by the writer, Phys. Rev. **73**, 550 (1948), will be referred to as I in the text.

$2n(\sigma)$ in the integral can be neglected and we find, as in I,

$$p=\frac{4}{9\pi}\frac{C^2k_0T}{\hbar^3c^2n_0}\frac{m_k}{M} \tag{9}$$

in which n_0 is the density of unit cells. If the entire factor $(2n+1)$ in the integrand is included, the result is readily found to be

$$p=\frac{4}{9\pi}\frac{C^2k^2}{\hbar^2n_0c}\frac{m}{M}\left(\frac{k_0T}{\hbar ck}+\frac{2}{3}\right) \tag{10}$$

where c is the velocity of the longitudinal modes of vibration.

Equation (9) and its extended form (10) are valid only when the wave number vector of the electron lies well within the first Brillouin zone associated with the free electrons. When k does approach the edge of the zone or extend beyond it, the range of integration of σ becomes limited as we saw above. This limitation is particularly important when k lies outside the first zone, since it alters entirely the dependence of p upon k. A simple investigation shows that the quantity in parenthesis in (10) becomes independent of k, whereas the coefficient varies as $1/k$. In other words, the collision frequency attains its maximum value when k is near the boundary of the first Brillouin zone.

The rate of energy loss exhibits a similar behavior. This quantity, which we shall designate as $d\epsilon/dt$, may be computed by replacing the factor $2n+1$ in the integral (5) by $\hbar\omega$ and carrying out the corresponding integrals. As long as k lies well within the first zone, the result is

$$(-d\epsilon/dt)=(4/9\pi)(C^2/\hbar)(k^3/n_0)(m/M), \tag{11}$$

whereas this quantity falls off as $1/k$ when k lies outside the first zone. Temperature no longer plays a role because the electron loses and gains energy at the same rate from the temperature-stimulated component of the modes of vibration. If we evaluate the temperature-independent part of (10) for diamond under the assumption that m is the mass of a perfectly free electron, that C^2 has the value 936 ev^2 and that k has the value k_z satisfying the equation

$$(4\pi/3)k_z^3\rho=N, \tag{12}$$

where $\rho=V/8\pi^3$ is the density of points in wave number space and N is the number of cells in the specimen, we obtain

$$\frac{1}{\tau}=\frac{16\pi}{9}\frac{1}{\hbar}\frac{C^2}{(2mc^2\epsilon_z)^{\frac{1}{2}}}\frac{m}{M}=1.9\cdot 10^{15}\ \text{sec.}^{-1}. \tag{13}$$

It is interesting to observe that $\epsilon_z=\hbar^2k_z^2/2m$ has a value of 11.5 ev (see Table I). The collision frequency (13) would give rise to a mobility of the order of magnitude of 0.94 cm^2/volt-sec. which is about 100 times smaller than the value for conduction electrons in thermal equilibrium at room temperature. In fact this value of the mobility is so low that the perturbation methods used to obtain it are no longer accurately valid, for the reasons discussed in I. The mobility and collision frequency may be employed only as rough approximations.

Recently Klick and Maurer[18] have carried out Hall effect measurements in diamond which permit an experimental determination of the mobility. They find a value of 900 cm^2/volt-sec. for thermal electrons instead of the value of 156 cm^2/volt-sec. calculated in I. If we arbitrarily assume that this difference of a factor 6 arises from an overestimate of the coupling constant C^2 in I for diamond by that amount, the collision frequency (13) is lowered to $3.1\cdot 10^{14}$ sec.$^{-1}$ and the mobility for $\epsilon=\epsilon_z$ is 5.6 cm^2/volt-sec.

The interaction of a free electron with the optical modes of vibration in a non-polar crystal possessing two atoms per unit cell was discussed in I. Two cases were treated. If in a reduced zone scheme, we let $\sigma=0$ designate the optical mode of highest energy, that is the mode which would have highest wave number in the extended zone scheme, the conservation of wave number is expressed by the equation

$$k'=k+\sigma. \tag{14}$$

One of the cases considered was that in which the matrix component of interaction does not vanish when $\sigma=0$, whereas the second case was that in which it does. The first case will be the normal one and we shall assume that it is valid. The equation analogous to (5) may readily be integrated as is shown in I and the resulting collision frequency is

$$p=\frac{1}{\pi}\frac{D^2\hbar^2K^22m}{\hbar\omega_0}\frac{m^2}{M}\frac{k}{\hbar^3n_0}\left\{\begin{matrix} n \\ n+1\end{matrix}\right\}\left(1\pm\frac{\hbar\omega_0}{\epsilon}\right)^{\frac{1}{2}}. \tag{15}$$

D is an energy parameter, analogous to C in (5) and K is the first non-vanishing reciprocal vector of the lattice. This result (see Eq. (59) of I) is derived under the assumption that the frequency of the optical modes is essentially constant. The upper value of the quantity in braces is valid in collisions in which the electron gains energy and the lower is valid in collisions in which the electron loses energy. The corresponding signs before $\hbar\omega/\epsilon$ apply in the two cases. n will be very small and may be neglected in comparison with unity, if the temperature of the crystal is small compared with the characteristic temperature. We shall focus attention on this case in discussing the collision frequency since n will be of the order of unity at most and the principal effect of the optical modes can be obtained without considering the thermal quanta.

The rate at which the moving electron loses energy is obtained by multiplying (15) by $\hbar\omega$ and setting $n=0$.

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[18] C. C. Klick and R. J. Maurer, Bull. Am. Phys. Soc. 24, No. 4, 26 (1949).

This result is valid even when n is not zero because of the cancelation of collisions in which the electron loses and gains energy. The ratio of the rate of energy loss in collisions with acoustic modes of vibration to the loss in collisions with optical modes is

$$R=(16/9)(C^2/D^2)(k^2/K^2). \tag{16}$$

When k approaches the boundary of a zone the ratio k^2/K^2 approaches unity. Thus R becomes essentially equal to C^2/D^2. The simplest supposition is that D is nearly equal to C so that R is near unity when k approaches the zone boundary. Unfortunately there seems to be little experimental evidence bearing on the point. If C and D are comparable in materials such as silicon and germanium one would expect the mobility in pure crystals to exhibit deviations from the $T^{\frac{3}{2}}$ law in the vicinity of the characteristic temperatures, which are 600°K and 290°K respectively, as the optical modes of vibration become sufficiently stimulated to scatter the electrons. The fact that such deviations are not observed may mean that D actually is smaller than C and that the influence of the optical modes is almost negligible in these materials. In either case the influence of the optical modes will not effect markedly the qualitative behavior of the function representing the collision frequency of the electrons as a function of energy or wave number: In both cases the collision frequency varies from about 10^{13} sec.$^{-1}$ when the energy of the electron is of the order of $kT=0.025$ ev to about 10^{15} sec.$^{-1}$ when the wave number vector approaches the zone boundary, where the curve has its maximum (Fig. 2).

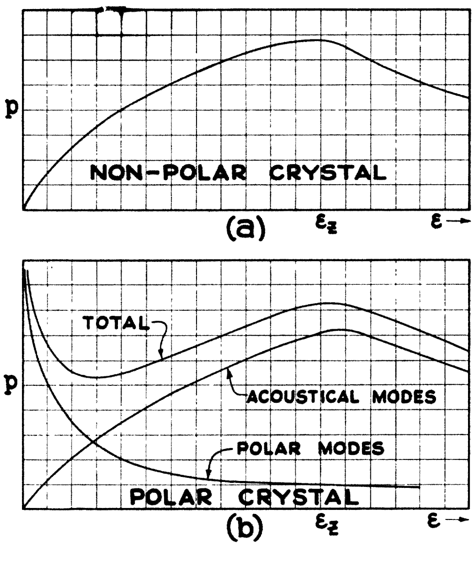

FIG. 2. Schematic representation of the collision frequency p as a function of energy ϵ in polar and non-polar crystals. Figure 2 (a) represents the collision probability in the case of a non-polar crystal such as diamond. The frequency has a maximum for an energy near ϵ_z. Both the optical and acoustical branches contribute to the peak. The collision frequency increases monotonically toward the peak and then falls. In Fig. 2 (b), for a polar crystal, the contributions from the polar and acoustical modes are shown separately, as well as their sums. The collision frequency for polar modes attains its maximum when ϵ is near $k\theta$, that is, of the order of 0.1 ev, whereas the collision frequency for non-polar modes attains its maximum near ϵ_z as in (a). The collision frequency possesses two maxima.

B. Polar Crystals

The most important interaction between electron and lattice in polar crystals is that with the polar modes of vibration when the energy of the electron is not too different from $k\theta$, as has been emphasized by Fröhlich. Mott and Fröhlich[19] have shown that the collision frequency of interest for transport theory is

$$p=\frac{1}{\tau_0}(\exp(h\nu_l/kT)-1), \tag{17}$$

when the energy of the electron is less than $k\theta$ so that it may only gain energy from the polar modes. Here[20]

$$\tau_0=\frac{3}{4\pi}\frac{\hbar v}{e^2(\kappa-\kappa_0)}\frac{\nu_l}{\nu_t^2}\frac{k_\nu}{k}, \tag{18}$$

where ν_l and ν_t are, respectively, the frequencies of the longitudinal and transverse polar modes of longest wave-length. These frequencies are related by the equation

$$\nu_l^2=(\kappa-\kappa_0+1)\nu_t^2, \tag{19}$$

in which κ is the static dielectric constant of the crystal and κ_0 is that arising from electron polarization alone. The v in (18) is the electron velocity, which is also equal to $\hbar k/m$. k_ν is defined by the equation

$$\hbar^2k_\nu^2/2m=h\nu_l. \tag{20}$$

Since τ_0 defined by (18) is independent of k, because of the presence of the ratio v/k, the collision frequency (17) is determined primarily by the temperature of the crystal, and becomes very small at low temperatures. When T approaches θ, (17) leads to values of the collision frequency of the order of $1/\tau_0$, which is of the order of $0.43\cdot10^{15}$ sec.$^{-1}$, and hence is sufficiently great that perturbation theory is not accurately applicable, as Fröhlich and Mott have emphasized.

It is to be stressed that the collision frequencies calculated by Fröhlich and Mott are those of interest for determining the mobility of the electrons and represent the frequency with which the electron is deflected through an angle that is 90° on the average. We shall discuss the true collision frequency later. This point is

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[19] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. 171, 496 (1939).

[20] H. Callen has re-examined the interaction of polar origin in polar crystals more carefully than previous investigators in order to determine the extent to which von Hippel's criterion for breakdown will provide numerical agreement with the observed breakdown measurements. This work employs standard perturbation theory and hence is subject to the uncertainties arising from this source if it is to be employed for quantitative purposes. The writer is indebted to Dr. Callen for an opportunity of seeing a copy of his manuscript prior to publication.

not of major concern in the preceding discussion of non-polar crystals since the scattering is practically isotropic as long as the electron resides in the first zone.

When the energy of the electron exceeds $k\theta$, it may both give to as well as receive energy from the polar modes and the expression, for the transport collision frequency is

$$p=\frac{1}{\tau_0}\left(1+\frac{2}{e^{\theta/T}-1}\right). \tag{21}$$

Fröhlich has found that as long as the wave number vector of the electron lies inside the first zone, but still lies in the range for which the energy of the electron is greater than $k\theta$,

$$\frac{1}{\tau_0}=\frac{e^4 n_0}{\hbar^2 \nu_0 k}\frac{m}{M}, \tag{22}$$

in which n_0 is the density of ions, which is $1/a^3$ in the sodium-chloride lattice if a is the nearest-neighbor distance, and ν_0 is taken as the frequency of the transverse polar modes. Since k appears in the denominator, it follows that the collision frequency decreases as the wave number vector approaches the zone boundary, in contrast with the situation described previously for the interaction in non-polar crystals. We readily find that $1/\tau_0$ is of the order of $1.5\cdot 10^{13}$ for a typical crystal such as NaCl when $k=k_z$. Thus the collision frequency falls from a very high value when the energy of the electron is of the order of $k\theta$ to a relatively low value when the energy is of the order of several electron volts, corresponding to an energy near the zone boundary. In fact the mobility of the fast electron would be comparable to that of a thermal electron in a non-polar crystal if no other influence arose to affect the collision frequency.

Fröhlich has shown that the transport collision frequency falls as $1/k^3$ once the electron has an energy well outside the first zone.

The true collision frequency p', which does not contain an angular weighting factor of the type introduced by Fröhlich, is readily obtained from the material presented in Fröhlich's paper. In fact the derivation follows closely the procedure outlined in Section 5 of his paper in which the rate of energy transfer is calculated. This transfer is the sum

$$h\nu_0(p_+-p_-), \tag{23}$$

in which p_+ is the frequency of collisions in which the electrons transfer energy to the lattice and p_- is the frequency of collisions in which the electron receives energy. It is easily found from Fröhlich's work that

$$p'=2\pi\frac{e^4}{a^3}\frac{m}{M}(2n+1)\frac{1}{h\nu_0}\frac{1}{\hbar k}\int_{\sigma_1}^{\sigma_2}\frac{d\sigma}{\sigma}, \tag{24}$$

in which σ, as previously, is the wave number of the lattice wave (in the reduced scheme) and σ_1 and σ_2 are respectively the minimum and maximum values associated with a given value of k. The value of σ_1 (which Fröhlich calls w') is

$$\sigma_1=\frac{2\pi m\nu_0}{\hbar k}. \tag{25}$$

The maximum is $2k$ when k lies well inside the zone, whereas it may be chosen to be a constant, as an approximation, when k is well outside the first zone. In either case the integral in (24), which has the value $\log(\sigma_2/\sigma_1)$, may be treated as if nearly constant. It is to be noted that the ratio of (24) to (21) is $\log(\sigma_2/\sigma_1)$ which shows that the collisions are nearly isotropic when k is inside the zone. The ratio is much larger when k extends well outside the first zone and increases as $k^2\log(\sigma_2/\sigma_1)$ since the collisions cease to be nearly isotropic.

The preceding scattering is the result of interaction between the electron and the polarization field arising from displacement of the ions. This field is identical with that which would be obtained from a lattice of point ions if they underwent oscillatory motion. Let us now consider the extent to which this scattering is augmented by scattering arising from variations in the local potential field analogous to that considered for non-polar crystals. There is no doubt that any such supplementary scattering is negligible when the energy of the electron is near $k\theta$, however it could be important for other ranges of energy. The simplest procedure to follow is to assume that this additional scattering can be treated by use of the equations derived for non-polar crystals and based on the deformable atom picture. In this case a material such as germanium becomes an approximate stand-in for a crystal such as NaCl since the characteristic temperatures are about the same (Ge: 290°K, NaCl: 281°K) and the density of atoms in the first material is about the same as the density of ions in the second. However, the atomic weight of germanium is about 2.5 times larger than the average atomic weight in the salt. If a correction is made for this, it is found, using the equations derived in I, that the collision frequency for a conduction electron having thermal energy is about $0.7\cdot 10^{13}$ sec.$^{-1}$. This would yield a mobility of about 250 cm^2 volt-sec. in the absence of additional scattering.

If we employ the equations in I which relate the parameters occurring in (10) to the characteristic temperature and employ Eq. (12) for the determination of k_z we find that the collision frequency arising from the acoustical modes is $1.8\cdot 10^{14}$ sec.$^{-1}$ when $k=k_z$. This value is not negligible in comparison with the contribution from the polar modes derived with the use of Fröhlich's equations, namely $1.5\cdot 10^{13}$ sec.$^{-1}$. In other words the non-polar contribution to scattering in polar crystals would be appreciable at energies above the thermal range if it were comparable to that expected in non-polar crystals. This conclusion is valid, even if the contribution from acoustical modes of vibration alone is considered.

It seems entirely reasonable to assume that non-polar scattering is as important in polar crystals as in non-polar materials. The basis for the use of the deformable atom model, which leads to the relation (4) in determining the scattering from non-polar fields, rests on the assumption that the relative distribution of the valence electrons in any unit cell is altered when a vibrational wave passes through the lattice. Since the valence electrons on the negative ions play as important a role in determining the interatomic forces in ionic crystals, principally through the Born repulsive term in the expression for the total energy, as do the valence electrons in non-polar crystals, we may expect non-polar scattering to be of comparable magnitudes in the two materials.

We should also expect the optical branches as well as the acoustical to contribute to the non-polar component of scattering in polar crystals by an amount comparable with that found in non-polar crystals if the surmise of the preceding paragraph is correct. Since the non-polar component becomes most important in polar crystals when the electron has a wave number near the zone boundary and since the magnitudes of the scattering associated with the two branches of the vibrational spectrum are then comparable (Eq. 16), the inclusion of the higher branch will at most multiply the collision frequency computed from the acoustical branch by a factor two.

To summarize, the collision frequency when plotted as a function of energy should have the form shown in Fig. 2 for polar and non-polar crystals. In the first case the curve has two maxima of comparable height, whereas only one maximum occurs in the second case.

5. BEHAVIOR OF AN AVERAGE ELECTRON

Let us now consider the field E_H at which a free electron would receive on the average more energy from the applied field than it expends in exchange with lattice vibrations for all values of its kinetic energy. This is the field at which breakdown would occur, according to von Hippel's theory. The condition satisfied by E_H is

$$d\epsilon/dt)_E + d\epsilon/dt)_L = 0 \tag{26}$$

for the energy ϵ at which $d\epsilon/dt)_L$ is a maximum. Here $d\epsilon/dt)_E$ is the rate of gain of energy from the field and $d\epsilon/dt)_L$ is the rate of transfer of energy to the lattice vibrations. We shall assume that the average electron undergoes Brownian motion and possesses a mobility

$$\mu = (e/m)\tau_m \tag{27}$$

in which τ_m^{-1} is the transport collision frequency. The rate of gain of energy from the field is thus

$$d\epsilon/dt)_E = (e^2/m)E^2\tau_m. \tag{28}$$

Since the largest values of $d\epsilon/dt)_L$ occur in the range of energy in which the collisions are essentially isotropic, the transport collision frequency and the true value do not differ greatly. The source of error that would result from the assumption that they are equal would probably not be larger than that made in employing perturbation theory in calculating the collision frequency. As a result, we shall occasionally replace τ_m by the true value τ_t.

The rate of transfer of energy to the lattice was discussed in the previous section and is given in various cases by Eqs. (11), (16), and (23) which may be placed in the form

$$-d\epsilon/dt)_L = \hbar ck(1/\tau_1), \tag{29}$$

$$1/\tau_1 = (4/9\pi)(C^2k^2/\hbar^2 n_0 c)(m/M) \times[1+(9/16)(D^2K^2/C^2k^2)], \tag{29a}$$

$$-d\epsilon/dt)_L = h\nu_0(1/\tau_2), \tag{30}$$

$$1/\tau_2 = (1/\tau_0)\log(\sigma_2/\sigma_1), \tag{30a}$$

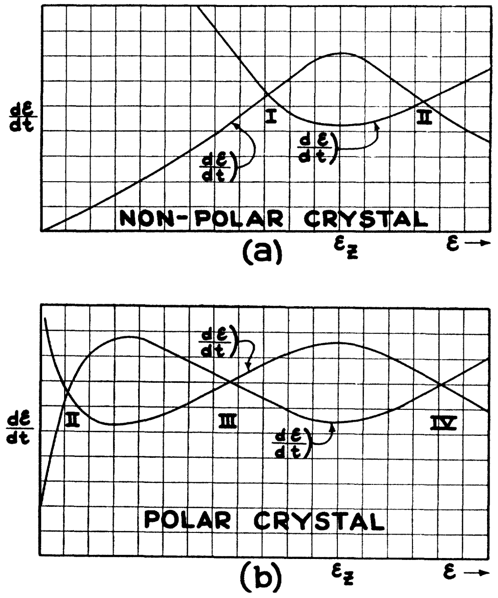

FIG. 3. Schematic picturization of the curves representing energy gain and loss as a function of time in polar and non-polar crystals. Figure 3 (a) shows the gain and loss curves corresponding to the two terms in Eq. (26). The case illustrated represents one in which the electrostatic field is less than but nearly equal to E_H, so that $d\epsilon/dt)_E$ crosses $d\epsilon/dt)_L$ twice. An electron having energy less than that associated with the first crossing, namely I, will be accelerated on the average. The second crossing, designated as II, represents a point of instability. If the electron has greater energy it will be accelerated on the average. Electrons having energy between the cross-points will move toward I on the average. Figure 3 (b) shows the corresponding case for a polar crystal. In this case there are four cross-points, of which only three are shown (designated as II, III, and IV). The cross-point of lowest energy which could be designated as I, is not shown since it occurs too close to the origin. The cross-points I and III represent energies of relative stability for the electron distribution whereas II and IV are unstable points. III and IV evidently are the analogues of I and II in Fig. 3 (a). (*Note:* Through an error the subscripts are omitted in the quantities $d\epsilon/dt$ which designate the gain and loss curves. The lower symbol designates the loss curve in both figures.)

in which τ_0 is given by (18) or (22). Equation (29) is to be employed for the non-polar interaction in polar and non-polar crystals when k is near the zone boundary, whereas (30) is to be employed for the polar interaction in polar crystals when the electron energy is near $k_0\theta$.

In terms of the quantities defined above $E_H{}^2$ is given by the maximum value of the quantity

$$m/e^2(\hbar ck/\tau_m\tau_1) \tag{31}$$

in non-polar crystals, and by the maximum value of either (31) or

$$m/e^2(h\nu_0/\tau_m\tau_2) \tag{32}$$

in polar crystals.

In diamond, the maximum value of (29a) is about $3.8\cdot 10^{15}$ sec.$^{-1}$ and E_H is about $4.0\cdot 10^7$ volts per cm if we take $C^2=936$ ev^2. It should be emphasized again that the absolute value of this may be considerably in error because of the inaccuracy accompanying the use of perturbation theory and inaccuracies in the numerical values used for various parameters. For example, the values are $0.6\cdot 10^{15}$ sec.$^{-1}$ and $6.7\cdot 10^6$ volts per cm if we decrease C^2 by a factor of 6 as suggested by the experiments of Klick and Maurer.

In sodium chloride, the peak in scattering frequency near thermal energies leads to a value of E_H of about $1.6\cdot 10^6$ volts per cm, whereas the peak arising from non-polar scattering produces a value of about $1.2\cdot 10^6$ if we assume the collision frequency is $3.6\cdot 10^{14}$ sec.$^{-1}$. In other words the values are essentially equal within the accuracy of the present analysis.

In the absence of an external electrostatic field, the free electrons which occur in an insulator will possess a velocity distribution given by the Maxwell-Boltzmann distribution function. As the field intensity grows, however, the distribution may be radically altered because an electron possessing thermal energies may gain energy from the field more rapidly than it loses it to the lattice. This rate of gain is given by Eq. (28) which may be expressed in the approximate form

$$d\epsilon/dt)_E=(e^2/m)(E^2/p), \tag{33}$$

since $1/\tau_m$ is closely equal to the true collision frequency. Thus, as E increases toward E_H, the distribution function will be affected first in ranges of energy most distant from the peaks in p. This means that the Maxwell-Boltzmann distribution will be altered most easily in non-polar materials, which have high mobilities in the thermal range of energies. The mobility of diamond is about 900 cm^2 volt-sec. at room temperature according to Klick and Maurer. In this case the thermal electrons begin to gain energy from the field more rapidly than they lose it when the electrostatic field is about 5 kv per cm. Hence, the distribution is pushed to higher energies when the field exceeds this value and the electrons are no longer in thermal equilibrium with the lattice. The distribution which does obtain may be expected to be stable as long as E is small compared to E_H, which has been estimated above to lie between $6\cdot 10^6$ and $4\cdot 10^7$ volts/cm, because p increases and hence $d\epsilon/dt)_E$ decreases with increasing energy. The average energy of the electrons in this type of stable distribution is determined by the value of ϵ at which Eq. (26) is satisfied for the value of E applied to the crystal. This energy is 1 ev for diamond when E is about $3\cdot 10^5$ volts per cm, if we assume the room temperature mobility is 900 cm^2/volt-sec.

The Maxwell-Boltzmann distribution should be much more stable in ionic crystals than in non-polar substances because the collision frequency possesses a maximum for energies near $k\theta$. The mobility of electrons in sodium chloride is about 100 times less than in diamond at room temperature. It follows that the Maxwell distribution will be radically distorted only when E becomes comparable to E_H.

We saw in the previous section that the collision frequency of electrons in ionic crystals possesses two maxima (see Fig. 2) when regarded as a function of energy. Equation (26) may possess four roots, two lying on each side of the maxima of $p(\epsilon)$ (Fig. 3) when E is sufficiently large, but still smaller than E_H. An electron which finds itself on the high energy side of the second root, which lies on the high energy side of the maximum in $p(\epsilon)$ occurring near $k\theta$, will gain energy from the field on the average and eventually reach the energy corresponding to the third root which lies on the low energy side of the peak that occurs near ϵ_z. Thus just as in non-polar crystals, there may be a group of electrons which possess energies that are large compared with kT and yet preserve an energy balance. The difference between the behavior in the two crystals lies in the fact that the high energy group is the only one in non-polar crystals whereas it contains only those electrons which escape the thermal distribution in polar crystals.

6. EXTENT OF DEVIATIONS FROM AVERAGE BEHAVIOR

In the preceding section we discussed the average behavior of a free electron. We shall now examine the extent to which an appreciable deviation from the average behavior can occur. This problem is of interest in trying to decide whether or not breakdown and related properties are determined by the average electron or by improbable fluctuations.

As a typical problem let us consider an electron which moves in the direction of the force exerted by the field and which starts with energy ϵ_1. Consider the probability that it will be accelerated to energy ϵ_2 without making any collisions. An electron of this type would be accelerated at the rate eE/m, where E is the field intensity. Hence it would gain energy from the field at the rate

$$d\epsilon/dt=eEv=eE(2\epsilon/m)^{\frac{1}{2}}. \tag{34}$$

The probability $P(t)$ that it will move for a time t without making a collision satisfies the differential equation

$$dP/dt = -pP \tag{35}$$

in which p is the average frequency of collision, which we have discussed in previous sections. Since p is known as a function of energy and since the energy is known as a function of time in the problem of interest to us in this paragraph, p may be regarded as a function of time. Hence,

$$P(t) = \exp\left(-\int_0^t p\,dt\right) = \exp\left(-\int_{\epsilon_1}^{\epsilon_2} \frac{p\,d\epsilon}{d\epsilon/dt}\right). \tag{36}$$

In the following, we shall assume that fluctuations in which the electrons make no collisions, or at most a very small number of collisions, are the most important group and shall employ (36) to estimate the probability for the group. It is apparently very difficult to treat quantitatively the frequency of collisions intermediate between the average and the extreme case represented by (36) because of the absence of a simple relation of the type (34). We shall see below that fluctuations of the type (36) play an important role in lowering the breakdown field below the value E_H determined by assuming that only the average behavior of electrons is important. If intermediate distributions of collisions are more important than those in which essentially no collisions occur, the breakdown field will be lowered even further, so that the following discussion can be viewed as giving a lower limit to the importance of fluctuations.

The following semi-quantitative argument seems to indicate that the fluctuations which are most important in determining breakdown in practice probably are those in which the electron is accelerated essentially from rest to the energy required for breakdown without making any collisions. Let us consider a somewhat idealized situation in which the collision frequency p is independent of energy. This assumption actually represents, to a fair approximation, the situation which occurs in ionic crystals if the curves of Fig. 2 are similar to the actual case. We shall also assume that the electron loses all of its forward momentum on the average each time it makes a collision with the lattice so that the kinetic energy it gains from the field between two collisions a time t apart is $(eEt)^2/2m$, irrespective of its kinetic energy at the time of the first collision. Thus if the electron starts from rest and makes n collisions spaced a distance t apart, the kinetic energy gained from the field is $(eEt)^2/2m$. In the following we shall consider time intervals between collisions which are sufficiently long and applied fields that are sufficiently strong that the collisions can be regarded as elastic. This means, of course, that we will be treating cases well removed from the average behavior in which gain and loss balance one another.

If I is the energy required to produce ionization and if this energy is obtained after n collisions, which we shall regard for simplicity as equally spaced, the time t between collisions must satisfy the equation

$$I = n(\epsilon Et)^2/2m.$$

Thus the time required to gain the energy I after a sequence of n collisions is $(n)^{\frac{1}{2}}t_1$, where t_1 is the time that would be required if the electron were accelerated with no collisions.

The probability that the electron shall undergo n collisions in the time $(n)^{\frac{1}{2}}t_1$ is given by the expression

$$P_n = \frac{(pt_1)^n n^{n/2}}{n!}\exp(-(n)^{\frac{1}{2}}pt_1) \tag{A}$$

in which p is the average number of collisions per unit time. Moreover the probability that the electron shall spend a time t_1 without making a collision in the time interval $(n)^{\frac{1}{2}}t_1$ is

$$G = p((n)^{\frac{1}{2}}-1)t_1\exp(-pt_1). \tag{B}$$

The ratio of (A) to (B) may be placed in the form

$$P_n/G = ((n)^{\frac{1}{2}}-1)^{-1}\exp(-((n)^{\frac{1}{2}}-1)pt_1-(n/2)\log n \\ +n+(n-1)\log pt_1) \tag{C}$$

if Stirling's approximation is employed. We shall set

$$n = \lambda^2 \quad \text{and} \quad pt_1 = \alpha$$

so that the exponent in (C) becomes

$$-\alpha\lambda+\lambda^2-\lambda^2\log\lambda+\lambda^2\log\alpha+\alpha-\log\alpha. \tag{D}$$

For given α this function has roots at the points

$$\lambda = \alpha(1-x) \quad \text{and} \quad \lambda = 1+y,$$

where

$$x = \left(\frac{2\alpha-\log}{3\alpha^2}\right)^{\frac{1}{2}}, \quad y = \frac{1}{\alpha-1-2\log\alpha}.$$

There is a minimum between these roots at $\lambda = 0.3\alpha$ in which we are principally interested. Equation (C) has the value

$$-0.11\alpha^2+\alpha-\log\alpha$$

at this minimum. At fields near observed breakdown values α varies between about 10 and 30 if p is assumed to have a constant value near 10^{15} sec.$^{-1}$. For $\alpha = 10$, (D) has the value -3.3, so that G is only slightly larger than P_n and we may expect a mixture of fluctuations to be important, those in which the electron is accelerated to the ionization energy with very few collisions being only moderately preferred if at all. On the other hand, (D) is -13 and -74 when α is 15 and 30, respectively, so that G is then far larger than P_n for values of n near the minimum.

The quantity (D) possesses a positive maximum when $\lambda = \alpha$ or when $n = p^2t_1^2$. In this case the time interval $(n)^{\frac{1}{2}}t_1$ is pt_1^2 for which the mean number of collisions is $p^2t_1^2$. Thus this maximum corresponds to the average situation and not one in which fluctuations are occurring.

The previous calculation for the case in which p is constant shows that the group of statistical fluctuations in which the electron is accelerated to the energy I with very few collisions is favored strongly over types intermediate between this and average behavior whenever α is 15 or greater. We may assume that the same conclusion is valid when the integral in the exponent of (36) is 15 or larger.

Let us consider the special case of interaction with the acoustical modes of vibration when the crystal is at the absolute zero of temperature. In this event we see from Eq. (10) that

$$p = A\epsilon, \quad A = \frac{16}{27\pi}\frac{C^2}{\hbar^4 n_0 c}\frac{m^2}{M}. \tag{37}$$

Combining this with (34), we readily find that the integral in (36) is

$$(2/3)(1/Ee)(m/2)^{\frac{1}{2}}(\epsilon_2)^{\frac{1}{2}}p_2-(\epsilon_1)^{\frac{1}{2}}p_1), \tag{38}$$

in which p_1 and p_2 are the values of p when the electron energy has the values ϵ_1 and ϵ_2, respectively. If we take ϵ_1 to be of the order of thermal energy and ϵ_2 to be of the order ϵ_z, the second term in parenthesis is completely negligible in comparison with the first. Moreover, if we assume $p_2=3.8\cdot 10^{15}$ sec.$^{-1}$ and $\epsilon_z=11.5$ which are essentially the values for diamond used in the previous section, (38) is

$$4.8\cdot 10^5/E, \tag{39}$$

or $1.5\cdot 10^8/E$, if E is expressed in units of volts per cm. If E is taken to have the value of $4\cdot 10^7$ ev found in the last section for E_H, the integral becomes about 3.8. Hence

$$P=\exp(-3.8)=0.023. \tag{40}$$

This result is valid not only for the hypothetical example chosen. We note from Eqs. (31) and (32) that $E_H{}^2$ is proportional to $1/\tau_m\tau_t$ where τ_m is the collision time of interest for determining the mobility and other transport coefficients and τ_t is the true collision time. Since τ_t and τ_m are nearly equal for the electron energies of interest to us, it follows that E_H is proportional to the quantity p_2 appearing in (38). As a consequence P may generally be expressed in the approximate form

$$P=\exp(-3.8E_H/E) \tag{41}$$

for fields near E_H in any material for which (38) is valid.

The integral appearing in (36) may be evaluated by methods similar to those used above in the case in which the collision frequency p is determined by polar modes of vibration. In this case p varies as $1/(\epsilon)^{\frac{1}{2}}$ when ϵ exceeds the peak value which occurs near $\epsilon=k\theta$. The expression analogous to (38) is

$$(1/Ee)(m/2)^{\frac{1}{2}}(\epsilon_1)^{\frac{1}{2}}p_1\log(\epsilon_2/\epsilon_1). \tag{42}$$

Here ϵ_1 may be taken to be $k\theta$, $\epsilon_2=\epsilon_z$ and p_1 is the peak value of the collision frequency. The value of P derived from this expression when $E=E_H$ does not differ substantially from that derived with the use of (38) if values of the constants are chosen to correspond to the case of NaCl described in the previous sections.

We may note in passing that the time required to accelerate an electron from rest to an energy of 10 ev when the field is E, is mv/eE, where v is the terminal velocity namely $2\cdot 10^8$ cm sec. The time has the value $3\cdot 10^{-15}$ sec. for the example employed in the previous paragraph when $E=E_H=4\cdot 10^7$ volts per cm.

The time required for an electron to drift 1 cm in a field of strength E is approximately $m/eE\tau_m$, where, as previously, τ_m is the collision frequency of interest for transport. During this time the electron will make $m/eE\tau_m\tau_t$ collisions. This is also the number of "trys" the electron will have to be accelerated to an energy of the order of 10 ev without making a collision during the period in which it migrates 1 cm. The product of the number of trys and the probability P of success per try is the number of times the electron would actually be accelerated to 10 ev without a collision in travelling unit distance. The reciprocal of this quantity is simply Λ, the average distance the electron travels before receiving sufficient energy to produce a secondary (see Section 2):

$$\Lambda=E(e/m)\tau_m\tau_t\exp(3.8E_H/E). \tag{43}$$

This equation may also be placed in the form

$$\Lambda=\frac{E\epsilon'}{eE_H{}^2}\exp(3.8E_H/E), \tag{44}$$

with the use of (31) and (32). ϵ' designates the quantity $h\nu_0$ appearing in (32) in the case in which E_H is evaluated from the polar modes and designates an appropriate mean value of $\hbar ck$ in the case when E_H is evaluated from the non-polar ones.

In the example cited early in this section, for which E_H is taken to be $4\cdot 10^7$ ev and p_2 is $3.8\cdot 10^{15}$ sec.$^{-1}$, corresponding to diamond, the time required for an electron to drift 1 cm on the average in a field of magnitude E_H is about $5.3\cdot 10^{-8}$ sec. The electron would make about $2\cdot 10^8$ collisions during this period of time. Correspondingly the coefficient of the exponential in (44) is of the order of $8\cdot 10^{-9}$ cm if ϵ' is taken to be of the order of 0.1 ev. Thus, Λ is about $4\cdot 10^{-7}$ cm when $E=E_H$.

The dependence of Λ upon E evidently arises principally through the exponential term in (44). For practical purposes the coefficient may be taken to be equal to ϵ'/eE_H when E is near E_H. Λ is of the order of 1 cm when $E=0.2E_H$.

Thus the present calculations show that in general the distance which the electron travels before producing a secondary electron varies from about 1 cm to about 10^{-6} cm as E varies from $0.2E_H$ to E_H. Evidently the field for which $\Lambda=D/40=0.025D$ lies within this range when D has the value associated with a normal test specimen. In other words the value of the field for which breakdown occurs is usually less than E_H, although it is close to this value, when the impact ionization theory is valid. Statistical fluctuations play an important role in the sense that they permit breakdown to occur before the field reaches E_H provided the specimen is larger than about 10^{-6} cm. As described in Section 2, we may expect to observe avalanches in the range of field strength between that for which $\Lambda=D$ and that for which it is $0.025D$.

The value of E at which Λ is $0.025D$, which we may call E_B, is determined by the equation

$$E_B=3.8E_H/\log\frac{0.025eE_H{}^2D}{E_B\epsilon'}. \tag{45}$$

It follows readily from (43) that Λ will decrease by a factor 40 if E is increased by about 20 percent when E is in the vicinity of $0.2E_H$. Hence the value of the field strength at which avalanches begin should be only about 20 percent smaller than the breakdown field if the coefficient 3.8 appears in the exponent of (44). Now this coefficient was derived from (38) by setting $E=E_H$ and is essentially the ratio $(\epsilon_z/mc^2)^{\frac{1}{4}}$ where c is the velocity of the longitudinal sound waves. As a result, it should be relatively insensitive to the errors in the various quantities computed in the previous sections.

Figure 1, which shows the avalanches observed by Haworth and Bozorth in Pyrex, indicates that the field must change by a factor of about 5 in order to have the avalanches change in size from one electron to a value of the order of 10^6 electrons. This dependence on field strength corresponds to a coefficient in the exponent of (44) that is of the order of 50 times smaller than that we have derived. In other words, the avalanches observed by these investigators seem to be much less sensitive to field strength than those predicted from Eq. (44). The electronic pre-breakdown currents observed by von Hippel and others also appear to be much less sensitive to field than currents based on Eq. (44) would be.

The behavior of the avalanches observed by Haworth and Bozorth would be readily understood if it could be postulated that the electrons involved need tunnel through a much smaller portion of the friction barrier than that considered in the evaluation of (38). This would be the case, for example, if these avalanches were produced as the result of the freeing by impact of relatively loosely bound electrons which are attached to foreign atoms. In this case the electron being accelerated would require a lower energy than is needed to ionize the atoms of the bulk material. Hence the electron would be required to make a much less improbable transition through the friction barrier. This point would be worth detailed experimental investigation, for it may prove possible to obtain pre-breakdown avalanches of controlled size by selected contamination of suitably chosen solids.

The value of the breakdown field for diamond determined from the foregoing avalanche theory is about $8\cdot 10^6$ volts per cm. This is very close to the value to be expected from the field ionization theory of Zener and Franz. The absolute values of the breakdown fields obtained from the approximate equations which have been derived for the two types of theories cannot be given great credance. However the results suggest that breakdown may actually occur by field ionization in diamond.

7. THE EXCITATION PROCESS

Consider now the behavior of an electron which has an energy near to or greater than ϵ_z and which is in a field sufficiently strong that it will gain more energy from the field than it loses to the lattice. An electron of this type will be accelerated until it is sufficiently energetic to excite or ionize the electrons of the lattice, the process on which attention will be focused in this section.

For simplicity, we shall assume that the cross section for excitation when regarded as a function of energy can be expressed in the form

$$\sigma(\epsilon)=\sigma_m(\epsilon_m/\epsilon)\log(\epsilon/\epsilon_e)\quad(\epsilon\geqslant\epsilon_e). \tag{46}$$

Here σ_m is the maximum value of the cross section, ϵ_e is the threshold energy at which excitation is possible and $\epsilon_m=2.71\epsilon_e$ is the energy at which the maximum in σ occurs. This expression is to be employed only when $\epsilon\geqslant\epsilon_e$.

The probability dq that the electron will make a collision resulting in excitation of the bulk atoms of the solid in time dt is

$$dq=\sigma n_0 v dt \tag{47}$$

where n_0 is the density of atoms and v is the velocity of the electron. We shall assume that the electron gains energy from the field at the rate veE, so that (47) may be written

$$dq=(\sigma n_0 d\epsilon/Ee). \tag{48}$$

An electron which starts with an energy less than ϵ_e will have unit probability of producing excitation when its energy has attained the value satisfying the equation

$$\log^2(\epsilon/\epsilon_e)=(2Ee/\sigma_m n_0\epsilon_m). \tag{49}$$

The quantity on the right has a value between 0.1 and 0.01 for diamond when E has the range of values of $0.2E_H$ estimated previously provided σ_m is given the value 10^{-16} cm^2 corresponding to a typical atomic cross section. The values for sodium chloride lie in the same vicinity. In both of these cases, Eq. (49) is satisfied when ϵ/ϵ_e lies between 1.3 and 1.1. The principal conclusion to be drawn is that the electron does not produce excitation or ionization as soon as its energy reaches the threshold value ϵ_e when σ_m has a more or less normal value. Instead the electron continues to be accelerated and produces excitation or ionization only when the energy is somewhat larger than ϵ_e. It follows that the primary electron will be left with an energy larger than $k\theta$ on the average after the excitation process although it may not have an energy as large as ϵ_z. Thus even in an ionic crystal the primary electron will usually end with an energy in the range where it can be accelerated further until it is blocked by the peak associated with lattice collisions occurring near ϵ_z. This conclusion evidently is valid only if E is near to E_H.

If the excitation collision produces a second free electron, the primary and secondary electrons should divide the energy in excess of that needed to produce ionization so that both will end up with an energy larger than $k\theta$.

One of the most important conclusions to be drawn from the preceding discussion is the following: Once an electron which is free in an ionic crystal has escaped from the portion of the velocity distribution which occurs on the low energy side of the peak in collision frequencies near $\epsilon=k\theta$, it will continue to remain out of this portion of the distribution during its subsequent history. This conclusion is valid provided E is sufficiently close to E_H that the electron gains more energy from the field than it loses to the lattice in the range of energy between the two peaks occurring near $k\theta$ and ϵ_z. Moreover, any secondary electrons it produces will not join the distribution on the low energy side of $k\theta$. This means that a free electron and its progeny will behave in essentially the same way in polar and non-polar crystals when the field is strong once the electron has been accelerated beyond the low energy range.

Consider next the excitation of impurity atoms which are present in concentration n_i, which we shall suppose to be appreciably smaller than n_0. Let us suppose that the primary electron has been accelerated to an energy sufficient to ionize the impurity atom as a result of an unusual fluctuation, the energy of this electron being of the order of 2 ev above that of the average electron which is at energy equilibrium. If σ_i is the cross section for ionization of the impurity atom, the probability that the unusually energetic primary will produce ionization of one of the impurity atoms in time t is

$$\pi(t)=n_i\sigma_i vt, \tag{50}$$

in which v is the average speed of the electron.

The unusually energetic electron will eventually lose its excess energy since on the average it suffers an unfavorable balance of exchange of energy with the lattice. For example, if its energy is 2 ev higher than average and if it loses about 0.1 ev on the average in each collision with the lattice, it will fall back among the average electrons in the time required for about 20 collisions. If T is the time the electron has the excess energy, the probability that it will ionize an impurity atom during this period is

$$\pi_i=n_i\sigma_i vT. \tag{51}$$

This is of the order of 10^{-6} if we assume that $n_i=10^{16}$ per cc, $\sigma_i=10^{-16}$ cm^2, $v=10^8$ cm per sec. and $T=10^{-14}$ sec.

Consider now the distance Λ_i that the electron must travel in order to ionize an impurity atom. Equation (44) was derived under the assumption that the primary electron will ionize an atom of the bulk material the first time it has been accelerated to the region where it has sufficient energy to do so. The discussion which centers about Eq. (49) of the present section shows that this assumption is reasonable as long as σ_m has a typical atomic value. The equation for Λ_i which replaces (44) will have the approximate form

$$\Lambda_i=\frac{1}{\pi_i}\frac{E\epsilon'}{eE_H^2}\exp(\alpha E_H/E). \tag{52}$$

Here α is a constant considerably smaller than the corresponding constant 3.8 which appears in (44) since it assumed that the primary electron need not experience as radical a fluctuation in gaining energy sufficient to ionize an impurity atom as is necessary to ionize an atom of the bulk solid. The coefficient $1/\pi_i$ takes account of the fact that the primary electron which gains sufficient energy to ionize the impurity atom as the result of a fluctuation need not actually produce ionization. The remaining coefficient in (52) is assumed to be the same as in (44) since the frequency of collisions with the lattice will be nearly the same when the electron has energy sufficient to ionize impurities and to ionize the atoms of the bulk material.

Λ_i has the value D when E satisfies the relation

$$E=\alpha E_H/\log(eE_H^2\pi_i D/E\epsilon'). \tag{53}$$

This in turn is about $\alpha E_H/10$ if π_i is assumed to be 10^{-6} and the other quantities are given typical values. In other words, avalanches which result from the ionization of impurity atoms by electron impact will begin to be observed at fields that are much smaller than E_H. Moreover, the size of these avalanches should grow much less rapidly with field strength than those which originate in the ionization of the bulk material. It seems possible that avalanches of this type were observed by Bozorth and Haworth, and that the noisy pre-breakdown currents observed in other materials originate in the same way. It has also been suggested that these avalanches are associated with sudden changes in the electrode-crystal contact as a result of the strong field there.

8. THE FIELD-DECOMPOSITION OF EXCITONS

It is generally supposed at the present time that the first excited states in an insulating solid correspond to excitation waves which are the analogue of the discrete excited electronic levels of an atomic or molecular system in which the electrons remain bound to the nuclei. Unless the excitation waves become decomposed into free electrons and holes by some agency, the accelerated electron which has produced the wave will have expended its energy without having produced a secondary charged particle. In this case the first excitation process would present a barrier analogous to the processes in which the electron transfers its energy to the lattice vibrations described previously. The electron would need to pass the excitation barrier in order to obtain sufficient energy to produce secondary free electrons.

Let us consider the possibility that the excitation waves are decomposed by the applied field in the manner first proposed by Oppenheimer[21] for the hydrogen atom. The theory of this effect has been highly developed for atomic hydrogen by Lanczos[22] who obtained excellent agreement with observations of von Traubenberg[23] on the disappearance of the spectral lines of atomic hydrogen in the presence of an electrostatic field. These investigators find that the $H\gamma$ line of the Balmer

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[21] J. R. Oppenheimer, Phys. Rev. **31**, 66 (1928).

[22] C. Lanczos, Zeits. f. Physik **62**, 518 (1930); **68**, 204 (1931).

[23] H. Rausch v. Traubenberg, Zeits. f. Physik **54**, 307 (1929); **56**, 254 (1929); **62**, 289 (1930); **71**, 291 (1931).

spectrum, which originates in a transition from the level having total quantum number $n=5$ to the level for which $n=2$, vanishes when the field intensity is about 700 kv per cm. The lifetime of the level for which $n=5$ then becomes less than the time required for emission of radiation (about 10^{-8} sec.). The level for which $n=5$ has a binding energy of 0.54 ev in the field-free atom. An analysis of Lanczos' results for levels in the neighborhood of $n=5$ shows that the critical field varies about as $1/n^4$. In other words, it varies essentially as the square of the ionization energy of the level.

The binding energy of the excitation states of the crystals are not accurately known. To obtain approximate values, we may assume that the electron and hole attract one another with a Coulomb force that is screened as a result of the high frequency dielectric polarization of the lattice. The energy states of the excitation wave associated with zero translational momentum are then given by an equation of the hydrogenic form:

$$E_n=\frac{e^4m}{2\mu^4\hbar^2n^2}. \tag{54}$$

Here μ is the refractive index of the crystal and n is a quantum number which may take the values $n=1, 2, 3, \cdots$. The factor two in the denominator enters because the reduced mass of the system is half the electronic mass. This expression should be more nearly valid for large quantum numbers than for small. Relative to the dissociated state the first excited state possesses the energy

$$E_2=-(1.7/\mu^4)(\text{ev}). \tag{55}$$

Since the indices of refraction of diamond and sodium chloride are 2.42 and 1.54, respectively, E_2 is 0.049 ev and 0.30 ev in the two cases.

In the case of diamond, the excitation states would be dissociated by a field well under 100 kv per cm, that is by a field that is very small compared with E_H. In fact the excitation waves should be dissociated as a result of thermal fluctuations in the vicinity of room temperature if this estimate of the binding energy of electron and hole is at all reliable.

The case of sodium chloride is more questionable since E_2 does not differ greatly from the value for the level $n=5$ in hydrogen. In fact, Mott[8] has proposed on the basis of an analysis of the ultraviolet absorption bands of the alkali halides that the energy of the first excitation state is about -1.7 ev relative to the dissociated state. Presumably the field required to dissociate this excitation state would be near to if not actually greater than E_H.

The calculations of the preceding section show that if σ_m is in the neighborhood of 10^{-16} cm^2, which is a typical value, the average accelerated electron makes its first exciting collision with the electrons of the bulk material when its energy is about 1.2 times larger than the threshold value. The threshold is about 7.5 ev in sodium chloride, according to measurements of optical absorption. It follows that the electron may well have sufficient energy, namely 9 ev, to produce ionization when it first transfers energy to the electrons of the bulk solid. In other words the probability that the electron which has been accelerated will produce a free electron and hole instead of an excitation wave is not negligible compared with unity. This process will be of major importance for breakdown in the alkali halides and other ionic crystals. It will also occur in non-polar materials, but need not occupy the same critical position if excitation waves are decomposed as easily as the results derived from (51) suggest.

To summarize, it appears reasonable to suppose the excitation waves which are stimulated by an accelerated electron will decompose in fields that are much smaller than E_H in a non-polar insulator such as diamond. On the other hand, the situation seems to be much more nearly on the border line in the case of an ionic crystal such as sodium chloride. In this case it is possible that the primary electron is able to produce secondaries when the field is below or near E_H only as a result of fluctuations in which the electron succeeds in obtaining sufficient kinetic energy to produce pairs directly, or at least to produce excitation waves which are sufficiently high in the spectrum that they can be dissociated by the field.

9. INFLUENCE OF BRILLOUIN ZONE

The calculations of Section 3 (Table I) show that a perfectly free electron would meet the first Brillouin zone when its energy lies between 3.6 ev and 4.8 ev in sodium chloride, depending upon its direction of travel. In diamond the corresponding energies are 8.9 ev and 11.9 ev. The crystalline potential will modify these values to some extent. In any event, it seems probable that the accelerated electron must cross a zone boundary before it can produce electronic excitation or ionization in sodium chloride, whereas this is probably not the case in diamond.

The semi-quantitative features of this problem have been investigated by Houston[6] in the case in which lattice collisions can be neglected. He has shown that the wave number vector of the electron approaches the zone boundary and undergoes a Bragg reflection as it reaches the plane boundary when the field is not too strong. Thus, in the absence of other disturbances, the electron alternately would be accelerated and decelerated by the field and the action of Bragg reflections. Two disturbances are provided by the fact that the electron may either undergo field "emission" from one zone to the next or be transferred by a collision with lattice waves. The second process will occur only if the bands overlap or at least are not separated by more than the energy of the highest lattice vibrational quantum. It seems safe to assume that the conduction bands overlap in the insulators of interest to us.

The probability of the electron tunneling across the zone boundary is determined by the quantity α appearing in Eq. (1) in the theory of Zener, Houston, and Franz. If we select $\Delta\epsilon$ to be 0.5 ev, α is close to unity in both diamond and sodium chloride when $E=E_H$. Thus, the electron has an appreciable probability of jumping the gap through field perturbation in one cycle of motion, provided the gap is 1 ev or less and the field is near E_H.

Now we know from the discussion of Section 6 that on the average an electron will make several inelastic collisions with the lattice waves during the time in which it is being accelerated to an energy near ϵ_z. Thus if the bands overlap, as we assume to be the case, the collisions with lattice waves should bring about a transfer from one zone to another.

In other words the barrier presented by the zone boundaries does not appear to offer a serious impediment to the acceleration of electrons. Apparently it may be surmounted either by field perturbation when E is near E_H or as a result of collisions with lattice waves.

10. ANISOTROPY OF BREAKDOWN FIELD

The disruption that accompanies breakdown in almost all crystalline substances exhibits crystalline symmetry.[24] In brief, the breakdown paths usually are oriented along very definite crystallographic directions. On the other hand, the measurements of von Hippel and Davisson[25] on the influence of the breakdown field on crystallographic orientation seem to show that the field is isotropic. In any event this appears to be the case in sodium chloride at room temperature. It seems very difficult to reconcile these two facts on the basis of any of the theories of breakdown proposed to date. As von Hippel and Davisson have emphasized, one would expect both the tunnelling theories of Zener and Franz and the impact-ionization theories to lead to anisotropy in the general case. It is possible that sodium chloride is a special exception. It is also possible that the actual breakdown field in the alkali halides is determined by the condition that the field be sufficiently strong to decompose the excitons produced as a result of impact excitation. In the latter case it is possible that the field required is independent of crystal orientation.

11. SUPPLEMENTARY COMMENTS

Professor R. de L. Kronig[26] has pointed out to the writer that liquid argon exhibits breakdown at fields of about $1\cdot 10^6$ volts per cm. Kronig has interpreted this breakdown in terms of Zener's theory, although it is by no means certain that the avalanche theory is not valid. To obtain agreement with Zener's theory it is necessary to assume that $\Delta\epsilon$ in Eq. (2) is about 3 ev. It is possible that the nature of the breakdown could be determined by studying the dependence of the breakdown field upon temperature since this field would fall with decreasing temperature if the avalanche theory is correct. Since liquid argon is definitely a non-polar substance, one would expect only a single peak in the electron friction curve; moreover this should occur at energies of several electron volts. We may infer from the experimental results on argon that the collision frequency at this maximum would be of the order of $5\cdot 10^{14}$ sec.$^{-1}$ if the preceding theory is correct. The corresponding mobility is about 3 cm^2 volt-sec.

Hutchinson[27] has measured the mobility of conduction electrons in liquid argon in fields of the order of 10 kv per cm by measuring transit times and finds values of 40 cm^2/volt-sec., which are reasonable for a non-polar material for electrons having energies in the thermal range. Hutchinson also reports electron multiplication in solid argon; however it is difficult to say whether or not this multiplication is the result of volume avalanches.

12. CONCLUSION

The principal conclusions to be drawn from the preceding investigation are as follows:

(1) The interaction between a free electron and the lattice vibrations is qualitatively different in polar and non-polar crystals. In non-polar crystals, such as diamond, silicon, and germanium, there is a single peak in "electron friction" which occurs when the free electron is near the boundary of the first Brillouin zone and its energy is of the order of several electron volts, depending upon the crystal. The previous treatments of the interaction between an electron and the lattice in an ionic crystal have neglected the influence of non-polar modes of vibration and have taken into account only the interaction with polar modes, which is a maximum when the electron energy is near $k_0\theta$ ($k_0=$Boltzmann's constant, $\theta=$characteristic temperature). It is proposed that the influence of non-polar modes is as large as that of the polar modes. The function describing electron friction in polar crystals has two peaks. One peak, arising from polar interaction, occurs for energies near $k_0\theta$ and the second, arising from non-polar interaction, occurs for energies near the zone boundary. The existence of the second peak reduces considerably the practical difference between the criteria for breakdown proposed by von Hippel and by Fröhlich since the high energy peak occurs near the energy at which ionization begins.

(2) The lowest value of an applied electrostatic field

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[24] L. Inge and A. Walther, Zeits. f. Physik **64**, 830 (1930); **71**, 627 (1931); A. von Hippel, Zeits. f. Physik **67**, 707 (1931); **68**, 309 (1931); J. Lass, Zeits. f. Physik **69**, 313 (1931). The most extensive work in the field has been carried out by J. W. Davisson, Phys. Rev. **70**, 685 (1946).

[25] A. von Hippel and J. W. Davisson, Phys. Rev. **57**, 156 (1940).

[26] R. de L. Kronig and A. E. van der Vooren, Physics **9**, 139 (1942); R. de L. Kronig, Zeits. f. Physik **118**, 452 (1942).

[27] G. W. Hutchinson, Nature **162**, 610 (1948).

for which a free electron of arbitrary energy will gain energy more rapidly from the field than it loses energy to the lattice vibrations is determined. This field strength, which is designated E_H, is the value at which breakdown would occur according to von Hippel's theory of the breakdown process. It is found that statistical fluctuations in the energies which free electrons possess in the presence of a field are so great that breakdown actually can occur when the field is as small as $0.2E_H$ for specimens of normal size. Calculations have been made on the assumption that fluctuations in which the electron makes very few collisions are the most important. This breakdown occurs as the result of the production of electron avalanches in which 10^{12} electrons are freed by impact collisions. E_H is estimated to lie between $4.0 \cdot 10^7$ and $6 \cdot 10^6$ volts per cm in diamond depending upon the coupling constant employed between lattice and electron. The corresponding value is about $1.5 \cdot 10^6$ volts per cm in sodium chloride. Since the derivation of these values involves improper use of perturbation theory they can be regarded only as rough approximations, as is true of the theoretical results of previous investigators. The breakdown field for diamond, estimated with the use of avalanche theory thus lies between $8 \cdot 10^6$ and $1.2 \cdot 10^6$ volts per cm, whereas the theoretical value for NaCl is about $0.3 \cdot 10^6$ volts per cm. The difference between the calculated value for NaCl and the observed value of $1.5 \cdot 10^6$ volts per cm near room temperature indicates the approximate character of the calculations. The value of the breakdown potential calculated for diamond with the use of the impact theory is not very different from the value estimated with the use of the field emission theory of Zener and Franz. The calculations are not sufficiently accurate to be decisive.

(3) An investigation of the dependence of the size of energy fluctuations on field strength shows that the size of avalanches caused by impact ionization of the bulk material should increase by a factor of 10^{12} when the electrostatic field changes by about 20 percent if the field is near the breakdown value. The avalanches observed by Haworth and Bozorth in Pyrex correspond to an exponent about 50 times smaller. It is concluded that these avalanches may arise from the ionization by impact of impurity atoms which have relatively loosely bound electrons. The pre-breakdown currents observed by von Hippel and his co-workers may have the same origin.

(4) Since the electron friction is relatively small for electrons having thermal energies in non-polar crystals, the free electrons cease to be at thermal equilibrium with the lattice at relatively weak fields. It is estimated that the average energy of free electrons in diamond is 1 ev when the applied field is about $3 \cdot 10^5$ ev. It is evident that electrons in this distribution should be able to excite impurity atoms in such a way as to produce effects such as ionization and luminescence. Two groups of free electrons will be a quasi-equilibrium in polar crystals in strong fields somewhat below the value for breakdown. One of these groups is essentially in thermal equilibrium with the lattice, whereas the second group resembles the average group present in non-polar crystals in having a much higher average energy.

(5) It is concluded that excitation waves are decomposed by the applied field in diamond when the field is near the breakdown value. The theoretical evidence is less conclusive in the case of the alkali halides. It is possible that breakdown occurs in these materials only when the field is sufficiently strong that the electron has an appreciable probability of running through the excitation range associated with the production of excitation waves without actually producing such waves and produces ionization instead.

(6) The barrier presented by the gaps at the boundaries of the Brillouin zones does not offer an appreciable impediment to the acceleration of electrons. The electron can jump between zones as a result of scattering collisions with the lattice if the zones overlap. In any case the perturbation produced by the field probably will permit the electron to leak through the barrier as long as the field is near the breakdown value.

(7) Experiments of Kronig and van der Vooren and of Hutchinson on the breakdown field of rare-gas liquids and solids support the viewpoint that non-polar coupling between electron and lattice is large when the energy of the electron is near a value associated with the Brillouin zone if it is assumed that breakdown in these materials is the result of electron avalanches. Unfortunately the experiments do not make it possible to determine whether this mechanism or that of Zener and Franz prevails.