

Electric Breakdown in Ionic Crystals*

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The electric breakdown strength of ionic crystals at low and moderate temperatures is calculated on the basis of von Hippel's low energy criterion. Fröhlich's method of calculation, modified to take account of the electronic polarizability of the ions, is employed. The breakdown strength at $T=0^\circ$ is F_0 (volts/cm) $= 134 \times 10^6 (\hbar\omega_i)_{ev} [(\epsilon_s - \epsilon_0)/(\epsilon_s \epsilon_0^2)]^{1/2} (m^*/m)$ where $(\hbar\omega_i)_{ev}$ is the reststrahl energy in electron volts, ϵ_s and ϵ_0 are the static and optical values of the dielectric constant, and (m^*/m) is the ratio of the effective mass to the free electron mass. The breakdown strength increases slowly with increasing temperature. The lack of dependence of the breakdown strength on crystallographic orientation and the strong directional dependence of the breakdown paths are qualitatively accounted for.

I. INTRODUCTION

TWO distinct mechanisms have been proposed for the breakdown process in ionic crystals under high field-strengths, at low and moderate temperatures. It has been proposed by von Hippel¹ that breakdown occurs when the applied field is high enough to accelerate electrons of *any* given energy in the conduction band to sufficient energy to further ionize the ions of the crystal by collision, thus leading to an exponential increase in the number of electrons in the conduction band. It may be easily seen that the applied field necessary to accelerate (on the average) an electron of given energy has a maximum when considered as a function of electron energy, as indicated schematically in Fig. 1. For, in order to accelerate an electron, the applied field must compensate the energy lost by this electron to the lattice; but slow electrons have insufficient energy to excite the vibrational modes of the lattice, whereas very fast electrons interact for too short a time with the ions which they pass to transfer energy to them with appreciable probability. The break-

down strength, according to von Hippel's "low energy" criterion, therefore corresponds to the maximum in Fig. 1, and an electron brought into the conduction band with low energy is immediately accelerated to the ionization energy and produces an additional conduction electron, the process thus building up in the form of an avalanche. Alternatively, Fröhlich² has suggested that an applied field sufficient only to accelerate electrons already having the ionization energy may lead to an instability and to electric breakdown.

Unfortunately it does not seem possible as yet to give a definitive *a priori* proof of the necessity of von Hippel's low energy criterion or of the sufficiency of Fröhlich's high energy criterion. It therefore seems desirable to compute the breakdown strength of crystals on the basis of each criterion, and to make an *a posteriori* choice of the criterion which most closely predicts the experimental facts.

Fröhlich² has developed a method of treatment of the interaction between a conduction electron and the vibrational modes of an ionic lattice, the method being a modification of the methods developed in the electron theory of metals. Utilizing this method he has given a breakdown theory based on the high energy criterion. Seeger and Teller³ have given a low energy breakdown theory based on Bohr's classical calculation of the energy loss of alpha-particles in a gas. The calculations of Fröhlich and of Seeger and Teller differ in two fundamental respects. Firstly, as discussed above, Fröhlich adopts what we have called the high energy criterion, whereas Seeger and Teller adopt the low energy criterion. Secondly, Fröhlich has explicitly considered the effect of the tortuosity of the path of the electron, and has given a treatment of this effect in terms of an electronic relaxation time. In the present paper Fröhlich's method,⁴ modified to take account of the

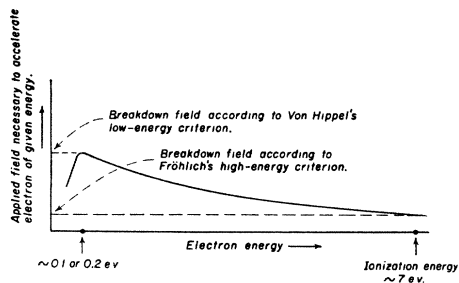


FIG. 1. The field necessary to accelerate an electron of given energy (schematic).

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¹ See A. von Hippel, Trans. Faraday Soc. **42A**, 78 (1946), and A. von Hippel and R. S. Alger, Phys. Rev. **76**, 127 (1949) for recent accounts of this point of view and for a more complete bibliography.

² H. Fröhlich, Proc. Roy. Soc., London, **A160**, 230 (1937).

³ R. J. Seeger and E. Teller, Phys. Rev. **54**, 515 (1938).

⁴ Fröhlich has pointed out (Phys. Rev. **61**, 200 (1942), and private communication with the author) that certain qualitative consequences of his breakdown theory follow from the treatment

electronic polarizability, is applied to the low energy criterion, leading to results in fair agreement with experiment. The structure of the calculation follows closely that of Fröhlich's paper, and many of the equations are modifications of equations obtained by him. We have, however, thought it preferable to present a complete and self-contained account of the theory, rather than to attempt to refer to and modify Fröhlich's equations in those cases where such a procedure would be possible.

The electric field required to accelerate an electron of given energy is determined by the condition that the rate of energy loss from the electron to the lattice is just compensated by the rate of energy input from the field to the electron. This latter energy input is, however, simply Fev_d , where F is the field and v_d is the drift velocity. It is thus necessary to calculate the rate of energy loss from electron to lattice, and the drift velocity, as functions of electronic energy. These calculations are accomplished by treating the effect of the lattice vibrations on the electron as a time-dependent perturbation. The breakdown field is identified with the maximum value of the field so obtained.

II. THE VIBRATIONAL MODES OF THE LATTICE

According to the lattice dynamics of Born and von Karman⁵ the normal vibrational modes of a diatomic crystal may be represented in the form of plane waves. The wave-vectors σ ($|\sigma| = 1/\lambda$) take N discrete values lying within the first Brillouin zone, where N is the number of unit cells in the crystal. To each value of σ there correspond six modes, which can be grouped into three "optical" modes of relatively high frequency and three "acoustical" modes of relatively low frequency. Of the three modes of each type, one is longitudinal and two are transverse.

For a mode of wave vector σ let $\mathbf{u}_{1\sigma}(\mathbf{r})$ or $\mathbf{u}_{2\sigma}(\mathbf{r})$ be the deviation from its equilibrium position of the ion at the point \mathbf{r} , if the ion is of type 1 or type 2, respectively. Then a standing wave description of the longitudinal mode of wave-vector σ may be written as⁵

$$\begin{cases} \mathbf{u}_{1\sigma}(\mathbf{r}) = -\frac{\sigma}{\sigma} \left(\frac{2}{M_1 N} \right)^{\frac{1}{2}} b_{\sigma}(t) \xi_{1\sigma} \begin{Bmatrix} \sin \\ \cos \end{Bmatrix} (2\pi\sigma \cdot \mathbf{r}), \\ \mathbf{u}_{2\sigma}(\mathbf{r}) = -\frac{\sigma}{\sigma} \left(\frac{2}{M_2 N} \right)^{\frac{1}{2}} b_{\sigma}(t) \xi_{2\sigma} \begin{Bmatrix} \sin \\ \cos \end{Bmatrix} (2\pi\sigma \cdot \mathbf{r}), \end{cases} \quad (1)$$

where $\xi_{1\sigma}$ and $\xi_{2\sigma}$ determine the relative amplitudes of $\mathbf{u}_{1\sigma}$ and $\mathbf{u}_{2\sigma}$ and are so defined that

$$\xi_{1\sigma}^2 + \xi_{2\sigma}^2 = 1. \quad (2)$$

of the relaxation time rather than from what we have termed the high-energy criterion. Thus the temperature dependence and the dependence of breakdown strength on impurity content are similar in the present theory to that in Fröhlich's high energy theory.

⁵ See, for instance, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

According to our convention, if the cosine function in Eq. (1) is adopted for the mode σ , the sine function must be adopted for the mode $-\sigma$ to insure orthogonality of the modes. Both the natural frequency of the mode (ν_{σ}) and $\xi_{1\sigma}$ depend on σ in a fairly complicated manner. The total deviation of the ion at \mathbf{r} is, of course,

$$\mathbf{u}_1(\mathbf{r}) = \sum_{\sigma} \mathbf{u}_{1\sigma}(\mathbf{r}), \quad \mathbf{u}_2(\mathbf{r}) = \sum_{\sigma} \mathbf{u}_{2\sigma}(\mathbf{r}), \quad (3)$$

where the summations are over all $6N$ modes.

If the kinetic and potential energies of the lattice are expressed in terms of the variables b_{σ} and \dot{b}_{σ} , a Lagrangian and a Hamiltonian function can be obtained, and \dot{b}_{σ} is found to be the momentum conjugate to b_{σ} . The Hamiltonian is

$$H = \frac{1}{2} \sum_{\sigma} [\dot{b}_{\sigma}^2 + \omega_{\sigma}^2 b_{\sigma}^2], \quad (4)$$

which is formally identical to the Hamiltonian of a collection of $6N$ one-dimensional, independent, harmonic oscillators. The wave function describing the vibrational state of the lattice is the product of $6N$ harmonic oscillator wave functions of individual quantum numbers $n_1, n_2, \dots, n_{\sigma}, \dots$. The corresponding energy eigenvalue is

$$E_{n_1, n_2, \dots, n_{\sigma}, \dots} = \sum_{\sigma} (n_{\sigma} + \frac{1}{2}) \hbar \omega_{\sigma}. \quad (5)$$

Neglecting the fine structure of the dielectric, the mode σ can be considered as producing a polarization \mathbf{P}_{σ} ;

$$\mathbf{P}_{\sigma} = \frac{e^*}{2a^3} (\mathbf{u}_{+\sigma} - \mathbf{u}_{-\sigma}), \quad (6)$$

and consequently a charge density ρ_{σ} ;

$$\rho_{\sigma} = -\nabla \cdot \mathbf{P}_{\sigma}, \quad (7)$$

where e^* is an effective charge per ion (see Section II) and where a is the interionic distance ($2a^3$ is the volume of a unit cell). This charge density ρ_{σ} represents the accumulation of positive and of negative ions at the alternate nodes of a longitudinal wave and it is easily seen from the form of Eqs. (1) that ρ_{σ} differs from zero only for a longitudinal mode. The Coulomb interaction between a conduction electron and the charge density ρ_{σ} supplies a means of interaction whereby the electron can be scattered by the vibrational modes. Of course this is not the only interaction energy between a conduction electron and a phonon, and any vibrational mode alters the periodicity of the potential in which the electron moves and therefore scatters the electron, even though the mode may not give rise to a charge density ρ_{σ} . However, the Coulomb interaction with ρ_{σ} is the dominant term⁶ in the complete interaction, as indicated by the empirical fact that the mean free path of elec-

⁶ F. Seitz, in a paper presented to the New York meeting of the American Physical Society, January 28, 1949, has pointed out that for very fast electrons the Coulomb interaction with ρ_{σ} ceases to be the dominant term.

trons in polar crystals is very much shorter than that in non-polar crystals. We therefore neglect other interaction terms, and we consider the conduction electrons to be scattered only by the longitudinal modes. For the longitudinal modes

$$\mathbf{P}_\sigma = \frac{e^* \sigma}{2a^3 \sigma} \left(\frac{2}{N} \right)^{\frac{1}{2}} b_\sigma \left(\frac{\xi_{+, \sigma}}{M_+^{\frac{1}{2}}} - \frac{\xi_{-, \sigma}}{M_-^{\frac{1}{2}}} \right) \left\{ \frac{\sin}{\cos} \right\} (2\pi \sigma \cdot \mathbf{r}). \quad (8)$$

For every value of σ there are two longitudinal modes, one in the acoustical branch and one in the optical branch. The acoustical modes are characterized by the fact that $\xi_{+, \sigma}/\xi_{-, \sigma}$ is positive, whence neighboring positive and negative ions vibrate in phase. For the optical modes $\xi_{+, \sigma}/\xi_{-, \sigma}$ is negative, and neighboring positive and negative ions vibrate 180° out of phase. The optical longitude modes therefore produce a much larger polarization \mathbf{P}_σ and a much larger charge density ρ_σ than do the acoustical longitudinal modes. In fact, for the acoustical longitudinal modes of long wave-length, which are of principal importance in our theory, the ratio of the amplitudes of positive and negative ions is unity so that $\xi_{+, \sigma}/M_+^{\frac{1}{2}} = \xi_{-, \sigma}/M_-^{\frac{1}{2}}$, and $\mathbf{P}_\sigma = \rho_\sigma = 0$. For the optical longitudinal modes of long wave-length the ratio of amplitudes is

$$u_{+, \sigma}/u_{-, \sigma} = -M_-/M_+ \quad (9)$$

whence

$$\xi_{+, \sigma}/M_+^{\frac{1}{2}} - \xi_{-, \sigma}/M_-^{\frac{1}{2}} = (1/M_+ + 1/M_-)^{\frac{1}{2}} = 1/M^{\frac{1}{2}}, \quad (10)$$

where M is the reduced mass of the ions. As a simplifying assumption we take $\mathbf{P}_\sigma = \rho_\sigma = 0$ as true for all the acoustical longitudinal modes, and Eqs. (9) and (10) as true for all the optical longitudinal modes. In this way the longitudinal modes of long wave-length, which are of principal importance in the theory, are treated correctly, and the over-estimation of the polarization produced by the short optical modes is compensated by the underestimation of the polarization due to the short acoustical modes. Only the optical longitudinal modes are effective in scattering a conduction electron.

In the optical branch the frequency is a fairly insensitive function of wave-length and may, to a good approximation, be taken as constant, independent of wave-length. We therefore attribute to every optical longitudinal mode the frequency of the optical longitudinal modes of long wave-length, which we denote by ν (or by $\omega \equiv 2\pi\nu$). The relation of ν to the reststrahl frequency ν_i , or to the frequency of the long wave-length optical transverse modes, will be considered in the next section.

III. THE FREQUENCY OF THE LONG WAVE-LENGTH LONGITUDINAL OPTICAL MODES

It has been shown by Lyddane and Herzfeld⁷ and by Fröhlich and Mott⁸ that the frequency of the long**

⁷ R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938).

⁸ H. Fröhlich and N. F. Mott, Proc. Roy. Soc. **A171**, 496 (1939).

** A mode of long wave-length is to be considered as one for which $\lambda \gg a$ (a is the inter-ionic distance), but it is assumed that λ

wave-length optical longitudinal modes exceeds the frequency of the long wave-length optical transverse modes in ionic diatomic crystals. In a longitudinal mode there are regions of charge accumulation which set up electric fields within the crystal, and these fields contribute to the restoring force-constant. In a transverse mode of long wave-length, however, the electric fields are "short-circuited" at the crystal boundaries and do not contribute to the restoring force-constant. Lyddane, Sachs, and Teller⁹ have computed the relation between these frequencies taking proper account of the electronic polarizability of the ions.† We now reformulate this analysis in a form appropriate for the calculation, in the next section, of the phonon-electron interaction energy.

Following Lyddane, Sachs, and Teller, consider the ions of the crystal to be given the displacements corresponding to a long wave-length longitudinal optical mode, so that the relative displacement of the positive and negative ions is

$$\mathbf{X}_\sigma = \mathbf{u}_{+, \sigma} - \mathbf{u}_{-, \sigma}. \quad (11)$$

This displacement produces a polarization which, to the first order, is linear in \mathbf{X}_σ . Accordingly we write

$$\mathbf{P}_\sigma = (e^*/2a^3)\mathbf{X}_\sigma, \quad (12)$$

where e^* is an effective charge, which differs from the true ionic charge because of the distortion of the electronic shells and the electronic polarization caused by the internal fields which are set up by the displacement. This polarization is associated with an internal field

$$\mathbf{E}_\sigma = -4\pi\mathbf{P}_\sigma = -(2\pi e^*/a^3)\mathbf{X}_\sigma, \quad (13)$$

and this field is associated with an electrostatic energy density

$$U_\sigma' = \epsilon_0/8\pi[(2\pi e^*/a^3)\mathbf{X}_\sigma]^2. \quad (14)$$

In a transverse mode the electrostatic field of Eq. (13) is absent, so that U_σ' represents the difference in energy density of longitudinal and transverse modes with the same values of \mathbf{X}_σ . Writing the total energy density associated with a mode in the form

$$U = (\frac{1}{2}M\omega^2/2a^3)X_\sigma^2, \quad (15)$$

where M is the reduced mass of the ions and ω is the natural angular frequency we thus find

$$(\frac{1}{2}M\omega^2/2a^3)X_\sigma^2 = \frac{1}{2}M\omega_i^2/2a^3X_\sigma^2 + \epsilon_0/8\pi[(2\pi e^*/a^3)\mathbf{X}_\sigma]^2$$

or

$$\omega^2 = \omega_i^2 + 2\pi\epsilon_0 e^{*2}/Ma^3, \quad (16)$$

where ω is the natural angular frequency of the longi-

is small compared with the dimensions of the crystal in order that the boundary conditions shall not be significant.

⁹ Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941). The author is indebted to Dr. Sachs for calling his attention to this paper.

† Fröhlich and Mott (see reference 8) have also obtained an equation relating the two frequencies, neglecting the effect of electronic polarizability.

tudinal mode and ω_t is the natural angular frequency of the transverse mode.

An equation analogous to the familiar Born¹⁰ formula, relating ω_t to ϵ_0 , ϵ_s and e^* , may be obtained by similar reasoning. Consider a crystal in which the ions are given the relative displacement \mathbf{X} . The energy density is then

$$U = (\frac{1}{2}M\omega^2/2a^3)X^2 = (M/4a^3)[\omega_t^2 + (2\pi\epsilon_0 e^{*2}/Ma^3)]X^2. \quad (17)$$

As in Eq. (13) the internal field is

$$\mathbf{E} = -(2\pi e^*/a^3)\mathbf{X}, \quad (18)$$

and the electrostatic energy density is

$$U' = (\epsilon_0/8\pi)[-(2\pi e^*/a^3)\mathbf{X}]^2. \quad (19)$$

If an external field \mathbf{D} , parallel to \mathbf{X} , is now imposed on the crystal it will induce an additional electronic polarization, the total polarization now being

$$\mathbf{P} = (e^*/2a^3)\mathbf{X} + (1/4\pi)[(\epsilon_0 - 1)/\epsilon_0]\mathbf{D}, \quad (20)$$

and the internal field becoming

$$\mathbf{E} = -(2\pi e^*/a^3)\mathbf{X} + (1/\epsilon_0)\mathbf{D}. \quad (21)$$

The electrostatic energy density is thus increased to

$$U' = (\epsilon_0/8\pi)[(1/\epsilon_0)\mathbf{D} - (2\pi e^*/a^3)\mathbf{X}]^2, \quad (22)$$

and consequently the total energy density becomes

$$U = (M/4a^3)\omega_t^2 X^2 + \epsilon_0/8\pi[(1/\epsilon_0)\mathbf{D} - (2\pi e^*/a^3)\mathbf{X}]^2. \quad (23)$$

If the displacement \mathbf{X} is allowed to adjust itself the equilibrium value will be that which minimizes the energy, or

$$\mathbf{X} = [a^3 e^*/(Ma^3\omega_t^2 + 2\pi\epsilon_0 e^{*2})]\mathbf{D}. \quad (24)$$

With this value of \mathbf{X} the equilibrium polarization becomes, from Eq. (20),

$$\mathbf{P} = \frac{1}{2}[e^{*2}/(Ma^3\omega_t^2 + 2\pi\epsilon_0 e^{*2})]\mathbf{D} + (1/4\pi)(\epsilon_0 - 1/\epsilon_0)\mathbf{D}. \quad (25)$$

But, by definition of ϵ_s (the static dielectric constant),

$$\mathbf{P} \equiv (1/4\pi)[(\epsilon_s - 1)/\epsilon_s]\mathbf{D}, \quad (26)$$

whence

$$\omega_t^2 = (2\pi e^{*2}/Ma^3)[\epsilon_0^2/(\epsilon_s - \epsilon_0)], \quad (27)$$

which reduces to the Born equation if $(e^*\epsilon_0)^2$ is put equal to e^2 . Combining Eq. (26) with Eq. (16) we find

$$\omega^2 = (2\pi e^{*2}/Ma^3)[\epsilon_0\epsilon_s/(\epsilon_s - \epsilon_0)] \quad (28)$$

and

$$\omega^2/\omega_t^2 = \epsilon_s/\epsilon_0. \quad (29)$$

Equations (29) and (27) allow us to compute both ω and e^* in terms of the experimentally observed reststrahl frequency, which is practically identical to ω_t .

¹⁰ See M. Born and M. Goepfert-Mayer, *Handbuch der Physik*, Vol. 24/2, p. 646.

IV. THE PHONON-ELECTRON INTERACTION ENERGY

We have seen that, within our approximations, the interaction energy between an electron and any vibrational mode other than those of the longitudinal optical branch, is zero. Using the method of the previous section we can now evaluate the interaction energy of an electron and a longitudinal optical mode. Consider a crystal in which we establish the ionic displacements \mathbf{X}_σ and into which we insert an excess conduction electron. If the conduction electron produces an electric displacement \mathbf{D} the energy density is, by Eq. (23),

$$U = (M/4a^3)\omega_t^2 \mathbf{X}_\sigma^2 + (\epsilon_0/8\pi)[(1/\epsilon_0)\mathbf{D} - (2\pi e^*/a^3)\mathbf{X}_\sigma]^2 \quad (30)$$

so that the increment in energy density due to the interaction is

$$\Delta U = \frac{e^*}{2a^3}\mathbf{X}_\sigma \cdot \mathbf{D}. \quad (31)$$

By Eqs. (1) and (16) the relative displacement has the form

$$\mathbf{X}_\sigma = -\frac{\sigma}{\sigma} \left(\frac{2}{MN} \right)^{\frac{1}{2}} b_\sigma \left\{ \frac{\sin}{\cos} \right\} (2\pi\sigma \cdot \mathbf{r}). \quad (32)$$

If the electron is at the point \mathbf{r}_e we have

$$\mathbf{D} = -\frac{e}{|\mathbf{r} - \mathbf{r}_e|^3}(\mathbf{r} - \mathbf{r}_e). \quad (33)$$

Introducing the new variables

$$\boldsymbol{\rho} \equiv \mathbf{r} - \mathbf{r}_e \quad (34)$$

and

$$\cos\theta \equiv \frac{\sigma \cdot (\mathbf{r} - \mathbf{r}_e)}{\sigma |\mathbf{r} - \mathbf{r}_e|} \quad (35)$$

we have

$$\Delta U = \frac{ee^*}{2a^3} \left(\frac{2}{MN} \right)^{\frac{1}{2}} b_\sigma \left\{ \frac{\sin}{\cos} \right\} 2\pi(\sigma \cdot \boldsymbol{\rho} + \sigma \cdot \mathbf{r}_e)(\cos\theta/\rho^2), \quad (36)$$

and the total interaction energy W_{σ, \mathbf{r}_e} becomes

$$W_{\sigma, \mathbf{r}_e} = \frac{ee^*}{2a^3} \left(\frac{2}{MN} \right)^{\frac{1}{2}} b_\sigma \int_0^\infty \int_0^\pi \left\{ \frac{\sin}{\cos} \right\} 2\pi(\sigma \cdot \boldsymbol{\rho} + \sigma \cdot \mathbf{r}_e) \times (\cos\theta/\rho^2) 2\pi\rho^2 \sin\theta d\theta d\rho. \quad (37)$$

The integral may be evaluated easily and gives

$$W_{\sigma, \mathbf{r}_e} = \frac{ee^*}{a^3\sigma} \left(\frac{2}{MN} \right)^{\frac{1}{2}} b_\sigma \left\{ \frac{-\cos}{\sin} \right\} (2\pi\sigma \cdot \mathbf{r}_e), \quad (38)$$

which reduces to Fröhlich's result² if one puts $e^* = e$.

V. TRANSITION PROBABILITIES

If the interaction energy between the vibrational modes and a conduction electron in the lattice is treated

as a perturbation (assuming so few conduction electrons that each can be treated independently), the unperturbed wave function is the product of a free electron wave function and $6N$ harmonic oscillator wave functions of quantum numbers n_{σ} :

$$\psi_{\mathbf{K}, n_1 \dots n_{\sigma} \dots} = V^{-\frac{1}{2}} e^{2\pi i \mathbf{K} \cdot \mathbf{r}} \prod_{\sigma} \psi_{n_{\sigma}}, \quad (39)$$

where V is the volume of the crystal and \mathbf{K} is the wave vector of the electron. The unperturbed energy is

$$E_{\mathbf{K}, n_1 \dots n_{\sigma} \dots} = \frac{\hbar^2 K^2}{2m^*} + \sum_{\sigma} (n_{\sigma} + \frac{1}{2}) \hbar \omega, \quad (40)$$

where m^* is the effective mass of the electron.

The probability per unit time of a transition in which the electron goes from state \mathbf{K} to state \mathbf{K}' and the longitudinal optical mode of wave-vector σ goes from state n_{σ} to state n_{σ}' is given by the time-dependent perturbation theory as

$$\Phi_{\sigma} = 1/\hbar^2 |M_{\mathbf{K}\mathbf{K}'\sigma}|^2 (\partial/\partial t) (\sin^2 \xi t / \xi^2), \quad (41)$$

where

$$\hbar \xi = \frac{1}{2} [(h^2/2m^*)(K'^2 - K^2) + (n_{\sigma}' - n_{\sigma}) \hbar \omega], \quad (42)$$

and the matrix element $M_{\mathbf{K}\mathbf{K}'\sigma}$ is

$$M_{\mathbf{K}\mathbf{K}'\sigma} = \int \int \int V^{-\frac{1}{2}} e^{-2\pi i \mathbf{K}' \cdot \mathbf{r}} \psi_{n_{\sigma}'}^* W_{\sigma, \mathbf{r}} V^{-\frac{1}{2}} \times e^{2\pi i \mathbf{K} \cdot \mathbf{r}} \psi_{n_{\sigma}} d\mathbf{r} db_{\sigma}. \quad (43)$$

Inserting the values of $\psi_{n_{\sigma}}$ and $W_{\sigma, \mathbf{r}}$ and using the orthogonality and recursion properties of the Hermite polynomials, one obtains

$$\Phi_{\sigma} = \left(\frac{ee^*}{2a^3 \sigma} \right)^2 \frac{1}{NM \hbar \omega} \delta(\mathbf{K} - \mathbf{K}' \pm \sigma, 0) \times [n_{\sigma} \delta(n_{\sigma}', n_{\sigma} - 1) + (n_{\sigma} + 1) \delta(n_{\sigma}', n_{\sigma} + 1)] \times (\partial/\partial t) (\sin^2 \xi t / \xi^2). \quad (44)$$

The delta-function $\delta(\mathbf{K} - \mathbf{K}' \pm \sigma, 0)$ may be taken as the requirement of conservation of momentum in the transition. The factor $(\partial/\partial t) (\sin^2 \xi t / \xi^2)$ has an appreciable value only in the vicinity of $\xi = 0$, or if energy is approximately conserved.

The delta-functions $\delta(n_{\sigma}', n_{\sigma} - 1)$ and $\delta(n_{\sigma}', n_{\sigma} + 1)$ require that the quantum number of the vibrational mode change only by unity in the transition. The ratio of the probabilities of the transitions $n_{\sigma} \rightarrow n_{\sigma} + 1$ and $n_{\sigma} \rightarrow n_{\sigma} - 1$ is seen to be $(n_{\sigma} + 1)/n_{\sigma}$, so that the electrons tend to lose energy to the vibrational modes.*

The simultaneous conservation of energy and momentum determines the angle between the wave vectors of an electron and a mode with which it can interact. The conservation of momentum gives

$$\mathbf{K}' = \mathbf{K} \pm \sigma \quad (45)$$

and the approximate conservation of energy gives

$$(h^2 K'^2 / 2m^*) = (h^2 K^2 / 2m^*) \pm \hbar \omega + 2\hbar \xi \begin{cases} + \text{ for absorption by electron} \\ - \text{ for emission by electron,} \end{cases} \quad (46)$$

where $\xi \approx 0$.

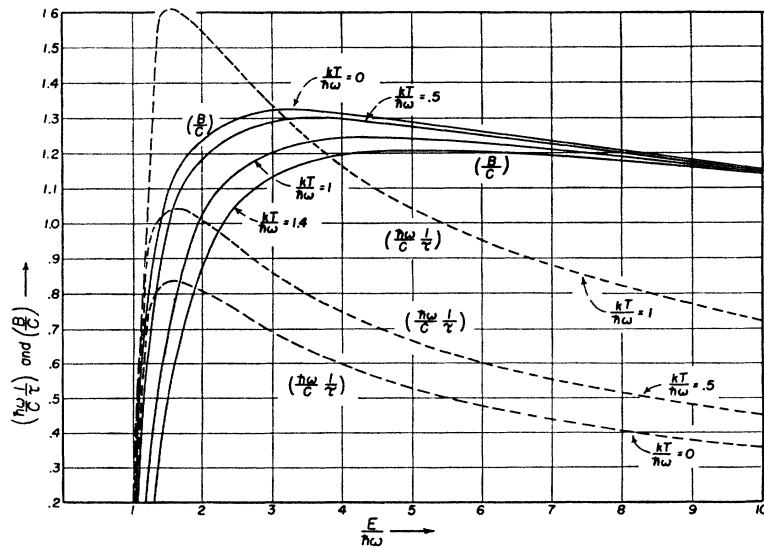
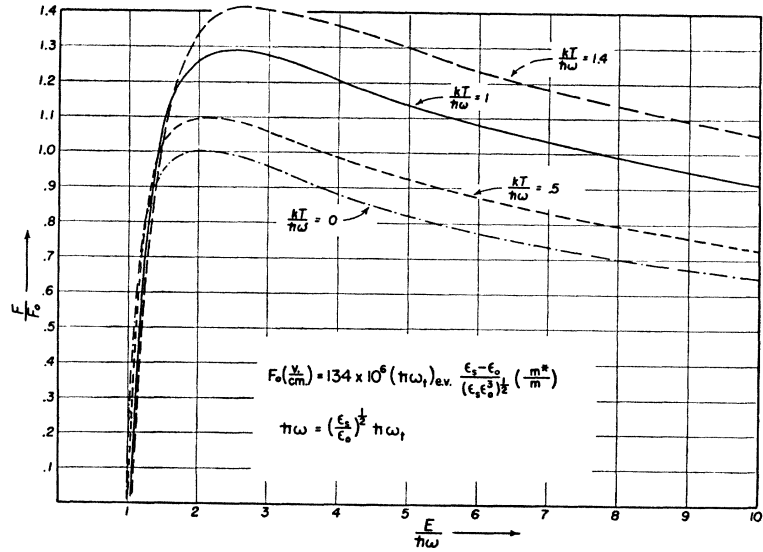


FIG. 2. Dependence of rate of energy loss and of relaxation time on energy and temperature.

* If the electron originally has an energy less than $\hbar \omega$, however, the emission process is impossible and it will gain energy from the lattice.

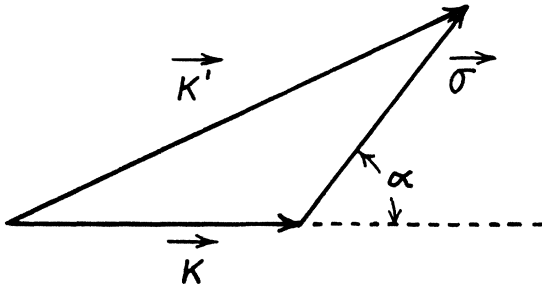
FIG. 3. Dependence of accelerating field on energy and temperature.



If α is the angle between \mathbf{K} and σ one easily finds

$$\cos\alpha = -(\sigma/2K) + (2m^*/h^2)[(2\hbar\xi \pm \hbar\omega)/2K\sigma] \quad (47)$$

$\left\{ \begin{array}{l} + \text{ for absorption.} \\ - \text{ for emission.} \end{array} \right.$



For a given K the electron can only interact with modes having wave vectors such that the right-hand member of Eq. (47) is less than unity in absolute value. Putting $\xi \simeq 0$, and introducing the notation

$$K_v \equiv 2m^*v/h \quad (48)$$

so that K_v is the wave vector of an electron with energy $h\nu$, we thus find as the limiting values* of σ which can interact with a given K :

$$\sigma_{\max} = K[1 + (1 \pm K_v^2/K^2)^{1/2}] \quad \left\{ \begin{array}{l} + \text{ for absorption} \\ - \text{ for emission,} \end{array} \right. \quad (49)$$

$$\sigma_{\min} = \pm K[-1 + (1 \pm K_v^2/K^2)^{1/2}] \quad \left\{ \begin{array}{l} + \text{ for absorption} \\ - \text{ for emission.} \end{array} \right. \quad (50)$$

In using Eq. (44) to calculate the probability of scattering of an electron we take for n_σ the average quantum number of a mode at the temperature T . This average

* For sufficiently large K the value of σ_{\max} given by Eq. (49) exceeds the maximum σ which can exist in the lattice—i.e., that at the furthest boundary of the Brillouin zone. Such fast electrons do not play a role in our low energy theory.

value \bar{n} is independent of σ and is given by

$$\bar{n} = \frac{\sum_n n \exp[-(n + \frac{1}{2})\hbar\omega/kT]}{\sum_n \exp[-(n + \frac{1}{2})\hbar\omega/kT]} = \frac{1}{\exp(\hbar\omega/kT) - 1} \quad (51)$$

VI. THE RATE OF LOSS OF ENERGY TO THE LATTICE

We have seen that, for an electron with energy greater than $\hbar\omega$, the probability of emission of a vibrational quantum exceeds the probability of absorption, and the electron tends to lose energy to the lattice. Following Fröhlich we now calculate the average rate of energy loss, which we denote by B . If Φ_{σ^a} is the probability of absorption and Φ_{σ^e} is the probability of emission we have, by Eqs. (44) and (51),

$$\Phi_{\sigma^a} = \left(\frac{ee^*}{2a^3\sigma} \right)^2 \frac{\bar{n}}{NM\hbar\omega} \delta(\mathbf{K} - \mathbf{K}' \pm \boldsymbol{\sigma}, 0) \frac{\partial \sin^2 \xi t}{\partial t \xi^2}, \quad (52)$$

$$\Phi_{\sigma^e} = \left(\frac{ee^*}{2a^3\sigma} \right)^2 \frac{\bar{n} + 1}{NM\hbar\omega} \delta(\mathbf{K} - \mathbf{K}' \pm \boldsymbol{\sigma}, 0) \frac{\partial \sin^2 \xi t}{\partial t \xi^2}, \quad (53)$$

and

$$B = \hbar\omega \sum_{\sigma} \Phi_{\sigma^e} - \hbar\omega \sum_{\sigma} \Phi_{\sigma^a}, \quad (54)$$

where the limits on the first summation are appropriate to the emission process and those on the second summation are appropriate to the absorption process, as given by Eqs. (49) and (50). The summations over σ can be replaced by integrations in "wave vector space." Since there is one value of σ for each volume of $1/2Na^3$ in wave vector space we have

$$\begin{aligned} \sum_{\sigma} () &\rightarrow 2Na^3 \int \int \int () d\sigma \\ &= 2Na^3 \int \int \int () 2\pi\sigma^2 \sin\alpha d\alpha d\sigma \quad (55) \end{aligned}$$

where we have taken spherical coordinates in wave vector space, with polar axis along \mathbf{K} , with radius vector σ , and with polar angle α . To carry out the evaluation of the summations in Eq. (54) it is convenient to make a further change of variable from α to ξ , using Eq. (47). Thus one obtains

$$B = C \left(\frac{\hbar\omega}{E} \right)^{\frac{1}{2}} \left[(\bar{n} + 1) \ln \frac{1 + (1 - \hbar\omega/E)^{\frac{1}{2}}}{1 - (1 - \hbar\omega/E)^{\frac{1}{2}}} - \bar{n} \ln \frac{1 + (1 + \hbar\omega/E)^{\frac{1}{2}}}{-1 + (1 + \hbar\omega/E)^{\frac{1}{2}}} \right], \quad (56)$$

where

$$C = \frac{\pi(2m^*)^{\frac{1}{2}}(ee^*)^2}{Ma^3(\hbar\omega)^{\frac{1}{2}}}, \quad (57)$$

and where E is the energy of the electron. It should be recalled that this equation is valid only if σ_{\max} , as given by Eq. (49), lies inside the first Brillouin zone. This requires that

$$E \lesssim \hbar^2/32m^*a^2, \quad (58)$$

or that the electron energy be less than about one to three electron volts for the various alkali halide crystals.

We have also assumed that the emission process is possible, so that we must have

$$E > \hbar\omega. \quad (59)$$

The quantity B/C is plotted against the "reduced energy" $E/\hbar\omega$ for various values of the "reduced temperature" $kT/\hbar\omega$ in Fig. 2.

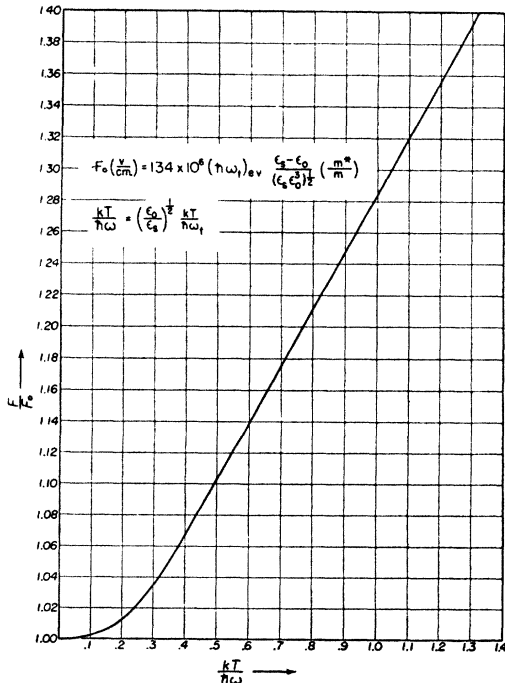


FIG. 4. Temperature dependence of breakdown field-strength.

VII. THE RELAXATION TIME

The field required to accelerate an average electron of given energy is obtained by equating the average rate of energy loss from the electron to the lattice, B , to the average rate of transfer of energy from the field to the electron, A . This latter rate of energy transfer is

$$A = eFv_d, \quad (60)$$

where F is the electric field strength and v_d is the drift velocity (which is a function of the energy and of F). The drift velocity may be expressed in terms of the relaxation time τ , defined by

$$v_d \equiv (e\tau/m^*)F, \quad (61)$$

whence

$$A = e^2F^2\tau/m^*. \quad (62)$$

The drift velocity, and thus also the relaxation time, is determined by the equilibrium between the tendency of the field to increase the z -directed velocity (assume the field along the z axis) and the tendency of the collisions to scatter the electrons away from the z axis and thus to decrease their z -directed velocity. Thus the drift velocity is determined by the equation

$$d\bar{v}_z/dt|_{\text{collisions}} = -d\bar{v}_z/dt|_{\text{field}} = -eF/m^*. \quad (63)$$

We consider the average effect of collisions on the electrons of energy E . Let an electron have its velocity \mathbf{v} at an angle β with respect to the z -axis, so that its z -directed velocity v_z is $v\cos\beta$. Let a collision with a vibrational mode occur, after which the electron is deviated through the angle γ and has a velocity \mathbf{v}' . The probability of such a collision is clearly independent of the azimuthal angle of \mathbf{v}' around \mathbf{v} . If we average over this azimuthal angle the final average z -directed velocity is $v'\cos\gamma\cos\beta$ and, on such a collision, the average change in v_z is

$$\Delta v_z = v'\cos\gamma\cos\beta - v\cos\beta = v_z[(v'/v)\cos\gamma - 1]. \quad (64)$$

Maintaining v constant, and averaging both sides of the equation over the angle β , or over v_z ;

$$\langle \Delta v_z \rangle = v_d[(v'/v)\cos\gamma - 1], \quad (65)$$

where the drift velocity v_d is the average of v_z for all orientations of the electron. To find $d\bar{v}_z/dt|_{\text{collisions}}$ we must now average $\langle \Delta v_z \rangle$ over the angle γ , weighting each value of γ with the probability per unit time of a collision which scatters the electron through the angle γ . Indicating this averaging process by the notation $\langle \rangle_\gamma$, we have

$$d\bar{v}_z/dt|_{\text{collisions}} = v_d \langle (v'\cos\gamma - v)/v \rangle_\gamma \quad (66)$$

or, using Eqs. (62) and (60), and recalling that \mathbf{v} is proportional to the wave vector \mathbf{K} ;

$$1/\tau = \langle (K - K'\cos\gamma)/K \rangle_\gamma. \quad (67)$$

If α is the angle between the wave vector σ and the electronic wave vector \mathbf{K} (see figure below Eq. (47)), we

TABLE I. Alkali halide data.

	ϵ_s	ϵ_0	$(\hbar\omega)_e.v.$	$a(10^{-8} \text{ cm})$	$M(10^{-24} \text{ gms})$	e^*/e	Theor. $F_0(10^6 \text{ v/cm})$ ($m^*/m=1$)	Theor. $F_{15^\circ}(10^6 \text{ v/cm})$ ($m^*/m=1$)	Exp't. $F_{15^\circ}(10^6 \text{ v/cm})$	$F_{15^\circ}(\text{Theor.})$ $F_{15^\circ}(\text{Exp't.})$
LiF	9.27	1.92	0.072	2.07	8.46	1.11	8.75	8.80	3.1	2.8
NaF	6.0	1.74	0.033	2.31	17.27	0.72	3.34	3.57	2.4	1.5
NaCl	5.62	2.25	0.024	2.81	23.2	0.56	1.35	1.57	1.5	1.1
NaBr	5.99	2.62	0.018	2.97	29.6	0.44	0.78	0.98	0.81	1.2
KF	6.05	1.85	0.03	2.66	21.2	0.84	2.72	2.96	1.9	1.6
KCl	4.68	2.13	0.019	3.14	30.8	0.55	0.965	1.20	1.0	1.2
KBr	4.78	2.33	0.015	3.29	43.6	0.50	0.63	0.85	0.70	1.2
KI	4.94	2.69	0.013	3.53	49.5	0.43	0.40	0.57	0.57	1.0
RbCl	5.0	2.19	0.017	3.27	41.6	0.63	0.88	1.12	0.83	1.3
RbBr	5.0	2.33	0.011	3.42	68.5	0.51	0.49	0.73	0.63	1.2
RbI	5.0	2.63	0.01	3.66	84.6	0.48	0.33	0.52	0.49	1.1

have

$$K' \cos\gamma = K + \sigma \cos\alpha \quad (68)$$

whence

$$1/\tau = \langle -\sigma \cos\alpha / K \rangle_{\sigma, \alpha}, \quad (69)$$

where we now average over σ and α , weighting each value with the probability per unit time of an appropriate collision. Thus

$$1/\tau = \sum_{\sigma} [-(\sigma/K) \cos\alpha \Phi_{\sigma^a}] + \sum_{\sigma} [-(\sigma/K) \cos\alpha \Phi_{\sigma^e}], \quad (70)$$

and transforming to integrals as in Eq. (55), we obtain

$$1/\tau = (B/2\hbar\omega)(\hbar\omega/E) + (C/\hbar\omega)(\hbar\omega/E)^{\frac{1}{2}} \times \{ (\bar{n}+1)(1-\hbar\omega/E)^{\frac{1}{2}} + \bar{n}(1+\hbar\omega/E)^{\frac{1}{2}} \}. \quad (71)$$

The quantity $\hbar\omega/C\tau$ like B/C , depends only on the reduced energy $E/\hbar\omega$ and the reduced temperature $kT/\hbar\omega$, and is plotted against $E/\hbar\omega$ for various values of $kT/\hbar\omega$ in Fig. 2.

VIII. THE BREAKDOWN FIELD-STRENGTH

For a given electronic energy the average rate of energy loss B is independent of the applied field, but the average rate of energy gain from the field increases quadratically with the field intensity (Eq. (62)). There exists a certain field intensity for which the energy gain is just compensated by the energy loss, and any field strength greater than this value will, on the average, accelerate the electrons of the given energy. This "acceleration field strength" is determined by the equality

$$A = B \quad (72)$$

or, by Eq. (68),

$$F = ((m^*)^{\frac{1}{2}}/e)(B/\tau)^{\frac{1}{2}} \quad (73)$$

which may be written

$$F = F_0 [((\hbar\omega/C)(1/\tau))(B/C)]^{\frac{1}{2}}, \quad (74)$$

where

$$F_0 = \frac{\sqrt{2}\pi m^* e e^{*2}}{M a^3 \hbar\omega}. \quad (75)$$

If e^* is expressed in terms of ω_t by Eq. (28) and ω is expressed in terms of ω_t by Eq. (29) we obtain

$$F_0 = \frac{2^{\frac{1}{2}}\pi^2 m^* e}{\hbar^2} \frac{\epsilon_s - \epsilon_0}{\hbar\omega_t (\epsilon_s \epsilon_0^3)^{\frac{1}{2}}} \quad (76)$$

or

$$F_0(\text{volts/cm}) = 134 \times 10^6 (\hbar\omega_t)_{e.v.} \frac{\epsilon_s - \epsilon_0}{(\epsilon_s \epsilon_0^3)^{\frac{1}{2}}} \left(\frac{m^*}{m} \right) \quad (77)$$

where F_0 is in volts/cm and $(\hbar\omega_t)_{e.v.}$ is in electron-volts.

The quantity F/F_0 , as given by Eq. (74), is easily obtained as a function of $E/\hbar\omega$ and $kT/\hbar\omega$ from Fig. 2. In Fig. 3 we plot F/F_0 against $E/\hbar\omega$ for various values of $kT/\hbar\omega$.

In accordance with the low energy criterion we adopt as the breakdown field at a given temperature the maximum of the corresponding curve in Fig. 3. We note that at $T=0$ the maximum occurs at $F/F_0=1$. Thus F_0 is the breakdown field strength at $T=0$. The maxima of the curves of Fig. 3 are plotted against the reduced temperature in Fig. 4, which therefore gives the temperature dependence of the breakdown strength.

The breakdown strength of a diatomic ionic crystal is obtained at $T=0$ from Eq. (77), and at other temperatures from Fig. 4. The breakdown strength depends only on the reststrahl frequency, the static and optical values of the dielectric constant, the effective mass, and the temperature.

In Table I we give the pertinent data for those alkali halides for which the reststrahl frequency is known, and the computed values of the breakdown strength assuming $m^*=m$.

IX. CONCLUSION—DIRECTIONAL EFFECTS

The theoretical values (assuming $m^*/m=1$) are compared with the experimental breakdown strengths in Table I. It is seen that the agreement is quite fair, the only notable exception being LiF.*

* Burstein, Oberly, and Plyler (Proc. Ind. Acad. Sci. 28, 388 (1948)) have presented evidence which indicates that there is an abnormally large amount of homopolar binding in LiF, and it should be noted that the presence of homopolar binding should tend to decrease the breakdown strength below the theoretical

It should be mentioned here that fluctuation effects, which have been neglected, may alter the breakdown criterion. Thus, although the field necessary to accelerate, on the *average*, an electron of given energy is as indicated in Fig. 3, there exists an appreciable probability that an electron will reach fairly high energies even without the benefit of the applied field, due to the statistical fluctuations in the interaction between the electron and the thermal vibrations of the lattice. Calculations of the effect of the fluctuations would involve a knowledge of the length of time an electron can afford to wait in the conduction band for a propitious fluctuation, before decaying into the lower almost-full band; that is, the treatment would require a knowledge of recombination probabilities, about which very little is known. Fortunately the curves of Fig. 3 are seen to be very flat in the neighborhood of their maxima, which tends to minimize the effect of fluctuations. Fluctuation effects may, however, be partially responsible for the fact that the theoretical breakdown strengths of Table I exceed the observed breakdown strengths and may perhaps be significant in the high-temperature region in which the temperature coefficient of the breakdown strength is observed to become negative.

The validity of the perturbation method also deserves some comment here. If the change in energy of an electron during a collision is $\hbar\omega$, and the mean time between collisions is Δt , a condition for the validity of the perturbation method is that $\Delta E \cdot \Delta t \gtrsim \hbar$. If we compute the mean time between collisions for electrons in NaCl at $T=0^\circ$ we find that for electrons of energy $\sim 3\hbar\omega$ (for which Δt is minimum) we obtain

$$\Delta E \cdot \Delta t \simeq 0.74\hbar.$$

Thus the condition for validity of the perturbation method is not strictly satisfied, but the extrapolation is not so drastic that we may expect to obtain qualitatively incorrect results. The perturbation method is

predictions. The goodness of the correlation between the deviation of theory and experiment, and the amount of homopolar binding found by Burstein *et al.*, seems to us to actually increase the confidence which one may place in the fundamental assumptions of the present theory.

commonly found to be remarkably trustworthy, even when cruelly abused.

Finally, we wish to point out that the directional effects observed in breakdown experiments can be at least qualitatively understood in terms of the present calculation. It is experimentally observed¹¹ that the breakdown strength of alkali halide crystals is independent of the orientation of the applied field relative to the crystallographic axes, but that the breakdown paths tend to lie in definite crystallographic axes. We have seen that the conservation rules for the collision between an electron and a vibrational mode restrict the range of wave vectors of the modes with which an electron of given energy can interact (see Eqs. (49) and (50)), and the maximum allowable σ increases with increasing electron energy. The slow electrons are thus insensitive to direction because the conservation rules permit them to interact only with modes near the origin of wave vector space, whereas the fast electrons are direction-sensitive because the conservation rules cause them to interact with modes at the zone boundaries. According to the low-energy criterion it is the slow electrons which determine the breakdown strength, but these electrons, once accelerated past a few tenths of an electron volt, travel relatively long distances through the crystal while being further accelerated to the ionization energy (~ 7 electron-volts). It is in this latter phase of their flight that they become direction sensitive* and form the direction-sensitive breakdown paths. It thus appears that the directional effects are associated with the symmetry of the Brillouin zones of the vibrational modes, and indeed Davisson¹¹ has shown that the directional properties of the breakdown paths are governed completely by the lattice symmetry, and not by the ionic characteristics or type of crystalline bonding. The directional effects seem to provide a potent argument in favor of the low energy criterion

¹¹ See A. von Hippel, *Zeits. f. Physik* **67**, 707 (1931); **68**, 309 (1931); A. von Hippel and J. Davisson, *Phys. Rev.* **57**, 156 (1940); J. W. Davisson, *Phys. Rev.* **70**, 685 (1946); **73**, 1194 (1948).

* Von Hippel (see reference 1) has suggested that the directional sensitivity of the fast electrons may arise from the symmetry properties of the forbidden and allowed energy bands, and this may also contribute to the effect.