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On the Electrical Breakdown of the Alkali Halides

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A theoretical justification is given for the mechanism proposed by von Hippel to account for the electrical breakdown of the alkali halides. Values of the breakdown field calculated on the basis of the theory are found to compare favorably with those obtained experimentally. A critical comparison is made with another explanation of the breakdown proposed by Fröhlich.

INTRODUCTION

THE experimental investigations of von Hippel[1] concerning the electrical breakdown of the alkali halides have shown marked regularities. One of these is the fact that the breakdown decreases with the atomic weight of both the anion and the cation (from 4.9×10^5 volts per cm for RbI to 31×10^5 volts per cm for LiF). He has proposed the following mechanism to account for the breakdown. The few free electrons, which are always accidentally present in such a crystal, on the one hand, are accelerated by the field; and, on the other hand, are slowed down by collisions with the ions of the lattice. It is assumed that every time an electron of appropriate speed collides with an ion there will be a considerable probability of excitation of a vibration of the lattice. Neither very slow, nor very fast electrons will be slowed down appreciably; the former because they lack sufficient energy to excite a quantum of vibrational energy, the latter because they lack sufficient time to do so. If the external field becomes strong enough to produce a net acceleration even for electrons of medium speed, which are retarded most strongly by the lattice vibrations, then each of these will be accelerated until it has sufficient energy to produce a second free electron by collision with a halogen ion. Thus there will be built up an avalanche of electrons; a breakdown will occur.

Von Hippel finds that this picture gives satisfactory agreement with his experimental material if it is assumed that the electrons which lose most energy excite one optical, or "reststrahl," vibration as they cross 0.5 to 0.9 of a lattice cell. Such a mean free path for free electrons is in marked contrast with the value of several hundred lattice distances which is found in the theory of metals. Calculations by Fröhlich,[2] however, show that the mean free path in these crystals is of the very order of magnitude given by von Hippel. For some speeds, indeed, it appears to be even shorter.

The difference in behavior between free electrons in insulators and those in metals is due primarily to the fact that in metals their number is comparable with the number of atoms in the lattice. This fact has several consequences that all work in the same direction. (1) The interaction of an electron in a metal with all the ions except the few neighboring ones is negligible because of the shielding effect of the other free electrons. (2) The free electrons in a metal, obeying the Fermi-Dirac statistics, occupy all different orbits so that the highest orbit has a kinetic energy far greater than the thermal energy $3kT/2$, and all the lower orbits are completely occupied. Since the kinetic energy of an electron changes little upon collision with the lattice, only the electrons on the surface of the Fermi-Dirac distribution can make transitions by such collisions, and then only to a limited number of free final states. (3) The great kinetic energy and high speeds of the metallic electrons result in less likelihood of a transfer of energy to an ion.

Fröhlich proposes that the breakdown occurs when all the electrons which have sufficient energy to produce additional free electrons by collisions (i.e., energy equal to the ionization potential) can be accelerated by the field. Clearly this process does not give rise to an electronic avalanche, inasmuch as the breakdown field is not great enough to accelerate the new free

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[1] A. von Hippel, J. App. Phys. **8**, 815 (1937).

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

electrons, nor even the original electrons that have lost energy by this ionization. From his view it is only by thermal excitation that the electrons will attain sufficiently high energy for such further acceleration, a process which is too improbable to account for the breakdown phenomenon.

In the numerical work of Fröhlich there appears an assumption that the force of interaction between a free electron and a lattice ion is of the form e^2/r^2, where e is the elementary charge on each of them and r is the distance between them. This has to be modified, however, in accordance with the dielectrical and optical properties of alkali halide crystals. Accordingly the force is smaller than e^2/r^2, and consequently the mean free path greater than that obtained by Fröhlich. If this modification is made, the breakdown field turns out to be sufficiently strong to accelerate all free electrons affected, i.e., even those which have energies only slightly greater than the quantum of lattice-vibrational energy, and which, therefore, lose most energy in collisions with the vibrating ions. Hence, what follows in this paper may be considered as a theoretical justification of the breakdown mechanism proposed by von Hippel.

Energy Loss in a Lattice Field

The slowing down of electrons in a lattice field has been treated by Fröhlich with the help of Born's quantum mechanical perturbation theory. We prefer to discuss the problem in a way analogous to Bohr's calculation[3] of the energy loss of alpha-particles as they pass through a gas. This method has the advantage of showing the physical process more clearly. Moreover, the application of Born's approximation in this problem cannot be considered more rigorous, as we shall discuss later. Both methods, it is true, yield similar results.

Let the force between a free electron and an ion be given by

$$\epsilon e^2/r^2, \tag{1}$$

where ϵ is a dimensionless constant which accounts for the fact that an ion displaced in a dielectric medium will act, in effect, with a modified electric charge. Leaving ϵ to be determined in the following section, we integrate this force over the time of the electron's passage near the ion. Thus we obtain for the total momentum (P_b) transferred to the ion during this time

$$P_b = 2\epsilon e^2/vb,$$

where v is the speed of the electron (assumed to be constant) and b is the distance of nearest approach of the electron to the ion. The kinetic energy (W_b) which any one ion receives in this encounter will then be

$$W_b = P_b^2/2M,$$

where M may be either M_+, the mass of the positive ion or M_-, the mass of the negative ion. Taking the sum of the above expression for both ions, we may write the result in terms of the reduced mass μ, where $1/\mu = 1/M_+ + 1/M_-$. Thus

$$W_b = 2\epsilon^2 e^4/\mu b^2 v^2.$$

Within the limits of b and $b+\Delta b$ the number of ions receiving energy when the electron has gone unit distance is

$$\pi b \Delta b/a^3,$$

where a is the distance between two neighboring ions. (This simple expression can be used instead of a summation over the lattice points because of the predominant influence of the distant ions.) Hence, the average energy ($\Delta W_b/\Delta s$) lost by an electron along unit path in a lattice of the NaCl type, for ions between b and $b+\Delta b$, is

$$\frac{\Delta W_b}{\Delta s} = \frac{\pi b \Delta b}{a^3} \cdot \frac{2\epsilon^2 e^4}{\mu b^2 v^2}.$$

Integrating this expression over all the ions in the lattice, we obtain for the space rate of energy loss of the electron

$$\frac{dW}{ds} = \int \frac{2\pi\epsilon^2 e^4}{\mu a^3 v^2} \cdot \frac{db}{b}.$$

This integral diverges if taken over all the values of the variable b. The physical limitations, however, do not justify integration over the range of values as b approaches either zero or infinity. Up to this point our calculation has been carried out on the assumption that the ions behave as if they were free. This is a good

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[3] N. Bohr, Phil. Mag. **24**, 10 (1913).

approximation only if the time of the electron's passage is short as compared with the period of vibration of the ions in the lattice, specifically if

$$2b/v \ll 1/\omega,$$

where ω is given by $2\pi\nu$, and ν is the frequency of the lattice vibration. The normal modes of vibration of such a lattice are of two kinds, *viz.*, the acoustic ones in which ions of opposite charges vibrate with small phase-differences and the optical ones in which they vibrate with large phase-differences. The electron, repelling the negative ions and attracting the positive ions, will excite primarily the optical vibrations. Because of the importance of distant ions in the process described, those vibrations will contribute most to the slowing down of the electron that have ions of the same charge vibrating nearly in phase. These vibrations have frequencies close to the so-called "reststrahl" frequency so that we may choose the value of this as the approximate frequency of the lattice vibration. Now if the time of passage becomes longer than the period of this vibration, the lattice can follow the motion of the electron in an adiabatic way so that the resulting energy-loss is zero. From these considerations we take as the upper limit of our integral the value of b given by

$$b_{\text{upper}} = v/2\omega.$$

The lower values of b are limited by our use of the particle concept of classical theory. This cannot be applied without quantum modification for distances smaller than $\lambdabar$, i.e., the wave-length of the particle divided by 2π. Hence, we choose

$$b_{\text{lower}} = \lambdabar.$$

(This choice corresponds in Born's approximation to the fact that an electron wave cannot excite a lattice vibration which has a wave-length short compared to its own wave-length.) Introducing these limits into the integral, we obtain

$$\left(\frac{dW}{ds}\right)_c = \frac{2\pi\epsilon^2 e^4}{\mu a^3 v^2} \cdot \ln\left(\frac{\frac{1}{2}mv^2}{h\nu}\right). \tag{2a}$$

We note that the space rate of loss of energy is zero when the kinetic energy of the electron is equal to the quantum of *reststrahl* vibration.

Formula (2a) agrees with a similar one given by Fröhlich (Cf. No. 17 in reference 2) except for the logarithmic factor. Fröhlich's expression can also be obtained by the use of Bohr's method, however, if the lower limit of b is chosen as $2^{4/3}\pi a$ instead of $\lambdabar$. Now for high speed electrons $2^{4/3}\pi a$ is greater than $\lambdabar$ so that this limit is justifiable. But for slow electrons, which are important in our theory, $2^{4/3}\pi a$ is less than $\lambdabar$ so that the expression (2a) is the better approximation. Modifying Fröhlich's calculations so as to include electrons of low energy, we obtain the following quantum formula

$$\left(\frac{dW}{ds}\right)_q = \frac{\pi\epsilon^2 e^4}{\mu a^3 v^2} \cdot \ln\left(\frac{p^2 - mh\nu + (p^4 - 2mh\nu)^{\frac{1}{2}}}{p^2 - mh\nu - (p^4 - 2mh\nu)^{\frac{1}{2}}}\right), \tag{2b}$$

where p represents the momentum of the electron. Expression (2b) agrees with the classical one (2a) when p^2 is large compared with $mh\nu$ (except for an additive term, i.e., ln 4). The applicability of Born's approximation used in obtaining (2b), however, is questionable in this problem.

Born's approximation can be employed only if less than one transition occurs, on the average, during the longer one of the following two times: the period of the lattice vibration, or the time during which an electron moves a distance equal to its own wave-length. In our problem the first of these is the longer time. Yet, according to Fröhlich's work, several quanta are emitted during this time. Thus Born's method is not valid here.

In the case of metals, although the transition probability is much smaller, there is also doubt as to the validity of this same perturbation theory being applied. Peterson and Nordheim[4] have shown that if coupling between the electronic motions and the lattice vibrations becomes strong, it is more correct to start with an electronic wave function that represents the motion of the electron in the lattice distorted by the vibration. This treatment leads to results similar to those obtained by the use of Born's

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

approximation. In Bohr's classical method, however, the lattice vibrations need not be quantized; hence, there is no difference between it and the procedure of Peterson and Nordheim.

In our present problem even the time required for an electron to move through the distance of its wave-length will be shorter than the time for the occurrence of one transition. In the use of Bohr's correspondence principle the speed of the electron, then, cannot be considered constant because of the retarding influence of the lattice. Fortunately, only those electronic speeds are important in determining an electrical breakdown for which there is a balance between the acceleration due to the external field and the retardation due to the ionic lattice. For these reasons we believe that the results obtained by the correspondence method give a fairly accurate picture of the actual behavior of the electrons. Indeed, the agreement with the results of Fröhlich help to justify the use of Born's approximation.

Modified Ionic Charge

In a real crystal the energy density due to an electric displacement D is given by

$$D^2/8\pi\kappa,$$

where κ is the dielectric constant. Let us imagine, however, a fictitious crystal in which the ions are fixed. The energy density in this case would be

$$D^2/8\pi\kappa',$$

where κ' is the dielectric constant under this condition. (κ' can be obtained by extrapolation of the square of the refractive index n to infinite wave-length with the omission, however, of the infra-red terms in the dispersion formula.) Now the difference between the energy density of the real crystal and that of the fictitious crystal, namely,

$$D^2/8\pi\kappa' - D^2/8\pi\kappa$$

is just the energy density due to the displacement of the ions. It can be obtained also by considering directly the energy of vibration of two neighboring ions in terms of their force of interaction F. We obtain the value

$$F^2/8\pi^2\mu\nu^2.$$

Multiplying this by $1/2a^3$, which is the number of such dipoles in unit volume, we have for the energy density due to ionic displacements

$$F^2/16\pi^2\mu\nu^2a^3.$$

Equating the two expressions for the energy density, we find

$$F=\left[2\pi\mu\nu^2a^3\left(\frac{1}{\kappa'}-\frac{1}{\kappa}\right)\right]^{\frac{1}{2}}D.$$

The interaction of an electron with an ion results in an electric displacement equal to e/r^2. Therefore, we may now identify our expression for the force of interaction with our assumption (1). Thus we obtain

$$\epsilon=\frac{1}{e}\left[2\pi\mu\nu^2a^3\left(\frac{1}{\kappa'}-\frac{1}{\kappa}\right)\right]^{\frac{1}{2}}. \qquad (3)$$

Breakdown Field

Electrical breakdown will occur if the electric field causes a net acceleration of all free electrons, even though their speed is such that the space rate of their energy loss is a maximum. If this condition is fulfilled, an avalanche is produced. We choose the following equation, therefore, for the determination of the breakdown field (E_B):

$$E_B=(dW/ds)_{\max}. \qquad (4)$$

In order to find $(dW/ds)_{\max}$ we rewrite Eqs. (2a) and (2b), respectively, as

$$\left(\frac{dW}{ds}\right)_c=\frac{\pi m\epsilon^2e^4}{h\nu\mu a^3}\left(\frac{1}{x}\ln x\right), \qquad (5a)$$

where x represents $mv^2/2h\nu$; and

$$\left(\frac{dW}{ds}\right)_q=\frac{\pi m\epsilon^2e^4}{h\nu\mu a^3}\left[\frac{1}{y}\ln\frac{y-1+(y^2-2y)^{\frac{1}{2}}}{y-1-(y^2-2y)^{\frac{1}{2}}}\right], \qquad (5b)$$

where y represents $mv^2/h\nu$. Now $(dW/ds)_c$ becomes a maximum when x is equal to 2.7; hence, $(1/x)\cdot\ln x$ has a maximum value of 0.37. On the other hand, $(dW/ds)_q$ becomes a maximum when y is equal to 3.4; hence,

$$\frac{1}{y}\cdot\ln\frac{y-1+(y^2-2y)^{\frac{1}{2}}}{y-1-(y^2-2y)^{\frac{1}{2}}}$$

has a maximum value of 0.91. Substituting these

TABLE I. *Comparison of calculated values of breakdown field with experimental values. Ratio of effective to ordinary mass of the electron which produces agreement between theory and experiment.*

CRYSTAL	h (10^{-2} VOLT)	κ	n	E_{Bq} (Calc)* (10^5 VOLT/CM)	E_B (Exp)[1] (10^5 VOLT/CM)	m/m_0
LiF	7.2	10.0	1.39	26	31	1.2
NaF	3.3	6.0	1.32	12	24	2.0
NaCl	2.4	5.9	1.48	6.1	15	2.5
NaBr	1.8	6.39	1.63	3.5	8.1	2.3
KCl	1.9	4.7	1.48	6.0	10.0	1.7
KBr	1.5	4.87	1.41	3.9	7.0	1.8
KI	1.3	5.58	1.55	3.2	5.7	1.8
RbCl	1.7	4.8	1.49	3.6	8.3	2.3
RbBr	1.15	5.0	1.55	2.2	6.3	2.9
RbI	1.05	5.2	1.69	1.5	4.9	3.3

* These calculated values have not been corrected for preferential directions as was done by Fröhlich. Such a correction seems to us to be inadvisable at present, as long as the theory for breakdown in different directions has not yet been discussed.

values, respectively, in (5a) and in (5b), we have

$$\left(\frac{dW}{ds}\right)_{c-\max}=\frac{0.37\pi m\epsilon^2e^4}{h\nu\mu a^3} \tag{6a}$$

and

$$\left(\frac{dW}{ds}\right)_{q-\max}=\frac{0.91m^2e^4}{h\nu\mu a^3}. \tag{6b}$$

Now substituting these expressions and (3) in our condition (4), we obtain for the breakdown field

$$E_{Bc}=\frac{0.74\pi^2me\nu}{h}\left(\frac{1}{\kappa'}-\frac{1}{\kappa}\right) \tag{7a}$$

by the use of the classical picture, and

$$E_{Bq}=\frac{1.82\pi^2me\nu}{h}\left(\frac{1}{\kappa'}-\frac{1}{\kappa}\right) \tag{7b}$$

by the use of the quantum mechanics.

In order to compare these formulae with the experimental values of von Hippel we need to know ν, κ, κ', and m. We have used the values of ν listed by von Hippel. For κ we have taken an average of the values given in Landolt-Bornstein's *Tabellen* (1936). For κ' we computed the square of the index of refraction for wave-lengths just beyond the infra-red region, thus eliminating the effect of the infra-red lattice vibrations. The mass of the electron (m), however, presents a problem. For one cannot use the real mass; one must insert the so-called "effective mass,"[5] which describes the motion of an electron in a periodic field. This mass, in general, will be greater than the ordinary mass (m_0) of the electron because of the smaller speed with which an electron of a given energy is propagated through the potential barrier of a periodic field. Because the calculation of the "effective mass" is complex, we have preferred to compute the breakdown field for m_0 and then to determine the ratio m/m_0 necessary for absolute agreement between the theoretical value and the experimental one in each case. In Table I we list only the quantum mechanical values E_{Bq} (7b), which are approximately twice the classical ones E_{Bc} (7a).

ANALYSIS OF RESULTS

The values obtained for m/m_0 are in a range not unreasonable for alkali halide crystals. We believe, however, that the theoretical values are not very accurate and that the theory ought to be revised in several respects. For example, the breakdown field may be actually lower than the one calculated and the ratio m/m_0, consequently, higher. For, even though all the electrons cannot be accelerated by the field, electrons of sufficiently high speeds may be produced by thermal fluctuations. In this way any small field could produce a breakdown in a long enough time unless a mechanism for reabsorption into the lattice were designed. Nevertheless, our result would probably not be modified much. For the breakdown field calculated by us would have to be corrected only by a quantity varying logarithmically with the time necessary for the electron to be reabsorbed. In connection with this process, however, the dependence of the breakdown field upon temperature might be explained. Another important effect which is probably related to the behavior of electrons at high speeds is the breakdown in preferential directions that has been found by von Hippel. In spite of the incompleteness of the theory presented here we believe that it does indicate the properties of the crystal upon which the magnitude of the breakdown field depends.

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[5] F. Bloch, Zeits. f. Physik **52**, 555 (1928).