ON THE CRITERION FOR DIELECTRIC BREAKDOWN IN IONIC CRYSTALS

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Summary

Previous theories on the criterion for electronic breakdown in ionic crystals are reviewed, in particular those of Fröhlich and Heller. It is shown that the ideas proposed by Heller are based on insufficient examination of the physical picture of breakdown, and the validity of Fröhlich's criterion is vindicated so long as electron-lattice collisions determine the distribution function. However, for the relatively high densities of conduction electrons existing just before breakdown the effect of electron-electron collisions may well be more important than the effect of electron-lattice collisions in determining the distribution function. Accordingly a critical field strength is calculated for a Maxwellian distribution of conduction electrons by a method which is a modification of Fröhlich's work. Comparison with the somewhat inadequate experimental results existing at present suggests that the breakdown field should be identified with the critical field originally proposed by Fröhlich.

I. INTRODUCTION

The theory of the dielectric breakdown of ionic crystals has been dealt with in detail by Fröhlich (1937, 1939), who developed a criterion which could be applied for the calculation of the breakdown field strength at sufficiently low temperatures.

Recently Callen (1949), Heller (1951), and Franz (1952) have advanced criteria for dielectric breakdown in certain cases. The work of Callen is based on the so-called low energy criterion of von Hippel (1935) as opposed to Fröhlich's high energy criterion, and will not be discussed further since it has been dealt with in the literature and is, moreover, not required for the line of thought of the present work. Heller uses an idealized model of a non-polar crystal to calculate in detail the distribution function for the conduction electrons at high field strengths. The results of this calculation are then incorporated in his breakdown criterion to estimate the breakdown field strength. The actual numerical work is done for diamond, but Heller states that his criterion is also applicable to ionic crystals and compares the results of his criterion with those of Fröhlich. Franz likewise endeavours to calculate this distribution function but uses a method which is incorrect, since he assumes that the effect of the field is simply to shift the electron distribution function bodily in momentum space by an amount determined by some relaxation time constant. This has been shown to be in error for high fields in insulators by Fröhlich (1947b).

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In the present work breakdown criteria are re-examined and it is found that the original Fröhlich criterion is correct for the model to which it was applied. However, it is possible that the model is not in accord with reality on some points ; in particular, evidence will be advanced to show that electron-electron collisions may be much more frequent than electron-lattice collisions just before breakdown. A modification of Fröhlich's calculations (1937, 1947a) will be applied to determine a critical field strength for the instability of a Maxwellian distribution of conduction electrons.* Experimental evidence, though not convincing, will be found to be slightly in favour of the original Fröhlich theory.

II. BREAKDOWN CRITERIA
(a) *The Fröhlich Criterion*

Fröhlich (1939, 1947a) has distinguished two extreme cases for the establishment of equilibrium in electron distributions at high field strengths. In the first instance he has considered that collisions between conduction electrons and lattice vibrations maintain equilibrium together with the applied field, while collisions between conduction electrons themselves are of negligible consequence. This corresponds to the so called " low temperature " breakdown theory. Alternatively, it may be considered that collisions amongst conduction electrons themselves and between conduction electrons and electrons in shallow traps are much more frequent than collisions between conduction electrons and lattice vibrations. This assumption leads to the " high temperature " breakdown theory.†

In the case of the low temperature theory Fröhlich (1937) has calculated the mean rate of energy gain from the field as

$$A(F,E) = \frac{e^2 F^2}{m} \tau(E), \quad \dots \dots \dots \dots \dots \text{(1)}$$

where

$$\left. \begin{array}{l} \dfrac{1}{\tau(E)} = \dfrac{1}{\tau_0(E)} \left\{ 1 + \dfrac{2}{\exp(h\nu/kT_0) - 1} \right\}, \\[3mm] \dfrac{1}{\tau_0(E)} = \dfrac{2^{2/3}\pi}{16\sqrt{2}} \cdot \dfrac{e^4 h}{m^{\frac{1}{2}} Ma^5 \nu} E^{-3/2}, \end{array} \right\} \quad \dots \dots \dots \text{(2)}$$

and the mean rate of energy loss to the lattice vibrations by an electron of energy E as

$$B(E) = \frac{2^{\frac{1}{2}}\pi e^4 m^{\frac{1}{2}}}{Ma^3} \log \gamma \, E^{-\frac{1}{2}}, \quad \dots \dots \dots \dots \text{(3)}$$

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* Since this paper was written the author has been informed by Professor Fröhlich that he has carried out the calculation of the critical field strength for a Maxwellian distribution of conduction electrons. It appears that his work is quantitatively more exact than that presented here, so that he may be able to draw more definite conclusions in his comparison with experimental work than those drawn on the basis of the present calculations.

† This distinction concerns the mechanism by which the electron distribution function is stabilized. It will be found necessary to make a further distinction below based on the mechanisms of energy transfer from the electrons to the lattice. This will lead to yet another set of physical conditions for which an instability criterion can be given for the electron distribution function.

in which e and m are the electronic charge and mass respectively, F is the electric field strength, ν the reststrahlen frequency, M the reduced ionic mass, a the lattice constant, T_0 the lattice temperature, and log γ is a slowly varying function of E such that, for $E = I$ (ionization energy), $(\log \gamma)^{\frac{1}{2}} = 2 \cdot 6$ for most alkali halides. These formulae are valid for energies greater than a certain energy $(E_0 \sim 1 \text{ eV})$ and less than the ionization energy $(I \sim 5 \text{ eV})$.

Fröhlich's low temperature breakdown criterion is then

$$A(F, I) = B(I), \quad \dots\dots\dots\dots\dots\dots \quad (4)$$

which is used as a determining equation for the breakdown field strength F^*. The physical idea of this criterion can be explained with the aid of Figure 1.
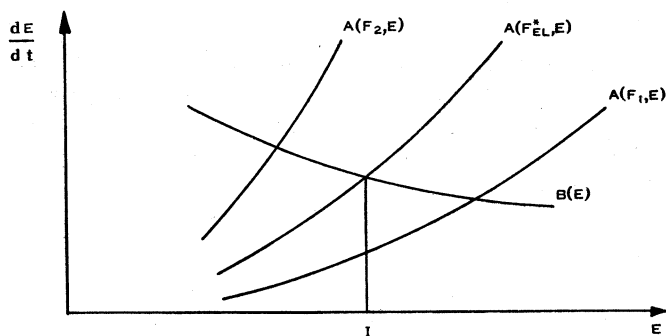

Fig. 1.—Average rate of energy gain from the field and energy loss to the lattice vibrations per electron.

For a field $F_1 < F^*$ the only electron which can, on the average, make a net energy gain from the field will be one whose energy is greater than the ionization energy ; while for a field $F_2 > F^*$ an electron of less than ionization energy will make a net average gain from the field. It is then argued that F^* is the breakdown strength, since it is at this field strength that the field is, on the average, first able to accelerate an electron of slightly lower energy up to the ionization energy.

(b) The Heller Criterion

Concentrating essentially on a low temperature model (in the sense explained above), Heller (1951) has modified Fröhlich's idea and produced a new breakdown criterion.   Remarking that Fröhlich has only considered the average behaviour of one electron, Heller rightly points out that high field strengths will change the electron distribution function from a Maxwellian one (as already shown by Fröhlich (1947b)) and then advances a breakdown criterion based on the idea that the field alters the ionization rate by altering the distribution function. He alleges that Fröhlich has ignored this by simply considering the change which the field produces in the average ionization process caused by one electron.

The essence of his work can most easily be seen by considering the kinetic equation derived by Fröhlich (1947b):

$$\left.\begin{aligned}\frac{\partial f_0}{\partial t} &= \frac{B(x)}{kT}\ \frac{\partial}{\partial x}\left[\{1+C^2(x)\}\frac{\partial f_0}{\partial x}+f_0\right],\\[2mm] f_1 &= -\sqrt{\frac{2}{mkT_0}}\ eF\tau(x)\ \frac{\partial f_0}{\partial x},\end{aligned}\right\} \quad \cdots\cdots\cdots\cdots \ (5)$$

in which we have defined a dimensionless variable $x=E/kT$, and expanded the electron distribution function in a series of Legendre polynomials

$$f(x,\theta,t)=f_0(x,t)+f_1(x,t)\cos\theta,$$

assuming that only these two terms are required. (θ is the angle between the applied field and the momentum direction and t is the time). The quantities $A(x)$, $B(x)$, and $\tau(x)$ are given by (1), (3), and (2) respectively, and

$$C^2(x)=\frac{2}{3}\ \cdot\ \frac{A(x)x}{B(x)}.$$

The equations (5) are valid only in the same energy range as equations (1), (2), and (3). The first equation of (5) can be written

$$\frac{\partial\rho}{\partial t}=\frac{\partial S}{\partial x}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \ (6)$$

where ρ is the density function

$$\rho(x,t)=4\pi\sqrt{x}\,f_0(x,t),$$

and S is a current density,

$$S(x,t)=\frac{4\pi\sqrt{x}\,B(x)}{kT}\ \cdot\ \left[\{1+C^2(x)\}\frac{\partial f_0}{\partial x}+f_0\right]. \quad \cdots\cdots \ (7)$$

For stationary conditions we have then from (6) that

$$S(x)=\text{const.} \quad \cdots\cdots\cdots\cdots\cdots\cdots \ (8)$$

Fröhlich has imposed the boundary condition that there can be no diffusion of electrons into or from the negative energy region and hence (8) becomes

$$S(x)=0. \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \ (8a)$$

This is simply a mathematical statement of the fact that, under the assumptions made, there are no electron removal or introduction processes.

However, it is clear that such processes will be important particularly at high field strengths. The ionization rate will depend on the field strength through the field dependence of both the distribution function and the total number of conduction electrons. If we denote the ionization rate by $S(F)$ then Heller replaces (8a) by

$$S(x)=S(F), \quad \cdots\cdots\cdots\cdots\cdots \ (8b)$$

alleging that, in the steady state, the ionization rate must be equal to the recombination and trapping rate. Since recombination and trapping occur mainly from amongst the low energy electrons, equation (7) will still determine the electron distribution function for energies between E_0 and I (the range of validity for equations (2) and (3)), in spite of the fact that electron-electron collisions are now being considered to be of importance in some energy ranges. Equation (7) then becomes

$$\{1+C^2(x)\}\frac{\partial f_0}{\partial x}+f_0=\frac{kT}{4\pi\sqrt{x}B(x)}S(F), \quad \ldots\ldots\ldots\ldots \text{(9)}$$

and we note from (3) that $\sqrt{x}B(x)$ is independent of x. The solution to (9) is easily obtained as

$$f_0=\frac{kT}{4\pi\sqrt{x}B(x)}S(F)+N\exp\left\{-\int_0^x\frac{dy}{1+C^2(y)}\right\}, \quad \ldots\ldots\ldots \text{(10)}$$

in which N and S are to be determined by the normalization condition and the details of the ionization process.

For low energies or very low field strengths the solution (10) becomes

$$f_0=\frac{kT}{4\pi\sqrt{x}B(x)}S(F)+N_1\exp(-x), \quad \ldots\ldots\ldots\ldots\ldots \text{(10a)}$$

while for higher field strengths and higher energies

$$f_0=\frac{kT}{4\pi\sqrt{x}B(x)}S(F)+N_2\exp(\Delta F^{-2}x^{-2}), \quad \ldots\ldots\ldots\ldots \text{(10b)}$$

where Δ is a constant containing various factors appearing in $C^2(x)$. This solution (10b) is identical with the solution given by Heller for the same energy region, apart from different lattice interaction parameters which lead to a different value of Δ. Heller has performed very detailed calculations to determine the electron distribution function in the ionization region, for which purpose he has made arbitrary assumptions concerning the cross section for ionizing collisions. He then states that

$$S(F)\equiv\alpha(F)N_C$$
$$=AN_C\{N_T(F)+N_H\}, \quad \ldots\ldots\ldots\ldots \text{(11)}$$

where N_C is the number of electrons in the conduction band, $N_T(F)$ the number of empty trapping centres at field F, N_H the number of holes in the valence band, and A must apparently be understood as some sort of combined recombination and trapping coefficient. For an insulator obviously

$$N_C=N_H+N_T(F)-N_T(0), \quad \ldots\ldots\ldots\ldots \text{(12)}$$

since conduction electrons can come only from the valence band or from traps. Combining (11) and (12) we have

$$\alpha(F)=A\{N_C+N_T(0)\}. \quad \ldots\ldots\ldots\ldots \text{(13)}$$

Heller then gives as his breakdown criterion

$$\alpha(F)\approx A\,.\,N_T(0), \quad \ldots\ldots\ldots\ldots\ldots \text{(14)}$$

on the ground that N_C begins to increase rapidly (proportionally to $\alpha(F)/A$) when $\alpha(F)$ exceeds $A \cdot N_T(0)$. This means that breakdown is to be considered as occurring when the ionization rate is so high that the trapping rate cannot keep pace with it, the equilibrium number of conduction electrons then being such a rapidly increasing function of field strength that no dielectric would carry the current involved.

(c) A Re-examination of the Breakdown Criteria

Although, at first sight, Heller's ideas would appear to be a logical extension of Fröhlich's work, nevertheless it seems that they are based on insufficient examination of the physical aspects of the problem. The main misconception in his treatment is that he assumes that the ionization rate will be balanced by the trapping and recombination rate when the conduction electrons have attained their equilibrium distribution in a given external field. This cannot be so ; for, if trapping and recombination were together responsible for balancing ionization from the valence band, then a net transfer of electrons from the valence band to traps would be continuously required. There could not then be any equilibrium no matter how weak the field. It is plain that, in the state of equilibrium, ionization from the valence band must be balanced by recombination to the valence band and ionization from traps must be balanced by trapping processes. (Ionization in both these cases may be due to thermal ionization, ionization by inelastic collision with conduction electrons, and field emission. In the case of traps all three processes will probably contribute, but ionization from the valence band will be mainly due to inelastic collisions.) It is now clear that it is incorrect to replace (8a) by (8b), since a given ionization rate $S(F)$ does not imply a current of electrons in energy space, as each high energy electron lost by an ionizing collision will be replaced by one from a recombining collision. Equations (9) and (10) will then be correct with $S(F)=0$ (as originally given by Fröhlich), and the breakdown field would logically be conceived as that field for which the recombination rate is unable to balance the ionization rate. However, this is exactly what Fröhlich has calculated in his original paper. It is easily seen that for fields $F \gg F^*$ the high energy electron from a recombining collision is not, on the average, able to lose its energy to the lattice, and in fact undergoes a further ionizing collision thus nullifying the effect of recombination in balancing ionization. Thus the Fröhlich criterion gives the field strength for which recombining collisions are unable to effect a net removal of electrons from the conduction levels.

(d) A New Approach to the Breakdown Criterion

It would seem that the breakdown field strength of ionic crystals in the low temperature region should be identified with that critical field strength given by Fröhlich, since at this field strength ionization would increase the number of conduction electrons indefinitely. However, it seems to have been overlooked that for large electron densities electron-electron collisions will be the dominating feature in determining the distribution, and not electron-lattice collisions as assumed by both Fröhlich and Heller in their derivation of the

distribution function.* Moreover, since the time taken for conduction electrons to establish a temperature under the influence of mutual collisions is many orders of magnitude less than the time required for breakdown to build up, the electron distribution can be expected to change back to Maxwellian under these conditions. This process decreases the number of electrons of high energy (of order of the ionization energy) to such an extent that, while the ionization rate is not actually zero, it is of such infinitesimal proportions that it could scarcely be conceived as being responsible for breakdown (cf. (**10a**) and (**10b**)).

The critical field strength is then that field strength for which a Maxwellian distribution of conduction electrons cannot attain any finite temperature for which equilibrium will exist between the energy gain from the field and the energy loss to the lattice by the conduction electrons. This picture, which is at first sight similar to the model on which Fröhlich (1947a) calculates his high temperature breakdown, differs from it in very important respects :

(i) In the low temperature case the number of conduction electrons will be independent of their temperature T for any given lattice temperature T_0. The number will in fact be that for which the electron-electron collision relaxation time has just superseded the electron-lattice collision relaxation time as being the chief factor determining the distribution function. In the high temperature case, on the other hand, the number of conduction electrons is a very sensitive function of T, due to excitation from the large numbers of shallow traps which exist at the higher temperatures.

(ii) In the low temperature case the transfer of energy from the electrons to the lattice is almost entirely due to collisions between conduction electrons and lattice vibrations, while in the high temperature case practically all the energy lost to the lattice is by transitions of electrons in shallow traps.

III. The Critical Field Strength

The low temperature critical field strength will thus be determined from

$$A(F,T,T_0) = B(T,T_0), \quad \dots\dots\dots\dots\dots\dots \quad (15)$$

as the lowest value of F for which (**15**) yields no finite solution for T. (That this is, in fact, possible is evident from the analysis below.) Since the number of conduction electrons is not a function of T we have

$$A(F,T,T_0) = \frac{e^2 F^2}{m} \tau(T,T_0), \quad \dots\dots\dots\dots\dots \quad (16)$$

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* Heller has estimated the relative importance of electron-electron collisions by asserting that 10^{12} conduction electrons per c.c. give evidence of breakdown. This estimate seems unreasonably low, particularly since it is implicit in his breakdown criterion that the density of conduction electrons just before breakdown is of the same order of magnitude as the number of electron acceptor impurity atoms, which figure he estimates at 10^{17} per c.c. This latter figure is more in agreement with the order of magnitude obtained experimentally on mica by Kawamura, Onuki, and Okura (1952) who found that avalanches contained about 10^8 electrons just before breakdown. Since their specimens were 5×10^{-4} cm thick, any reasonable estimate of the " avalanche cross section " will give a figure more of order 10^{17} than 10^{12} for the electron density. It is for just such densities that electron-electron collisions would be expected to achieve the same degree of importance as electron-lattice collisions.

in which $\tau(T,T_0)$ is the average relaxation time given by

$$\tau(T,T_0)=\frac{\int\tau(E,T,T_0)\sqrt{E}\exp(-E/kT)\mathrm{d}E}{\int\sqrt{E}\exp(-E/kT)\mathrm{d}E}. \quad \dots\dots\dots (17)$$

The quantity $\tau(E,T,T_0)$ represents the average relaxation time of an electron of energy E in a Maxwellian distribution of temperature T with lattice temperature T_0. It can be derived easily from Fröhlich's (1937) calculations as

$$\frac{\exp(-E/kT)}{\tau(E,T,T_0)}=\frac{2a^3N}{(2\pi)^3}\int_0^{2\pi}\mathrm{d}\varphi\int_{-\pi}^{\pi}\sin\theta\,\mathrm{d}\theta$$

$$\times\int_0^{w_0}\frac{w^2}{2k^2}\left[\Phi_w^e\exp\{-(E+h\nu)/kT\}+\Phi_w^a\exp(-E/kT)\right]w^2\mathrm{d}w,$$

$$\dots\dots\dots\dots\dots (18)$$

in which a is the lattice constant, w is the wave number of the lattice wave, k is the wave number of the electron, and Φ_w^a, Φ_w^e are the probabilities per second that an electron makes a transition into or from the state considered by emission or absorption respectively. The integrations (representing the sum over all processes) have been performed by Fröhlich and give

$$\frac{1}{\tau(E,T,T_0)}=\frac{1}{\tau_0(E)}\cdot\frac{\exp(h\nu/kT_0-h\nu/kT)+1}{\exp(h\nu/kT_0)-1}, \quad \dots\dots (19)$$

in which

$$\frac{1}{\tau_0(E)}=\frac{2\pi e^4m^{\frac{1}{2}}}{2^{\frac{1}{2}}hMa^3\nu E^{\frac{1}{2}}} \quad \dots\dots\dots\dots (20)$$

replaces the expression for $\tau_0(E)$ given in (2) since we are now dealing with energies less than the critical energy stipulated. Substituting (19) and (20) in (17) and introducing the result into (16) gives

$$A(F,T,T_0)=\left(\frac{2}{m}\right)^{3/2}\frac{Ma^3h\nu}{2e^2(\pi)^{3/2}}\,F^2\sqrt{kT}\,\frac{\exp(h\nu/kT_0)-1}{\exp(h\nu/kT_0-h\nu/kT)+1}. \quad \dots\dots (21)$$

Similarly the average loss to the lattice can be found from*

$$B(T,T_0)=\frac{\int B(E,T,T_0)\sqrt{E}\exp(-E/kT)\mathrm{d}E}{\int\sqrt{E}\exp(-E/kT)\mathrm{d}E}. \quad \dots\dots\dots\dots (22)$$

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* The averaging in (17) and (22) is not strictly correct. Fröhlich (personal communication) has pointed out that (17) should read

$$\tau(T,T_0)=\frac{-\int\tau(E,T,T_0)E^{3/2}\{\partial\exp(-E/kT)/\partial E\}\mathrm{d}E}{\int E^{1/2}\exp(-E/kT)\mathrm{d}E}.$$

This will alter the result for $\tau(T,T_0)$ by the numerical factor 2, and, as no conclusions are drawn from the absolute magnitude of the critical field, the error will not affect the conclusions of this work.

The integrations of (17) and (22) have been taken from 0 to ∞. Those in (17) should be from 0 to I and the form of the integrand should change for the critical energy ~ 1 eV. However, contributions from such relatively high energies will be small due to the form of the distribution function. The lower limit of the integrations in (22) should be $h\nu$ as electrons with energy less than $h\nu$ cannot lose energy to the lattice. This will probably be a more serious source of error.

Using Fröhlich's (1937) calculations we find similarly

$$B(E,T,T_0)=\frac{h\nu}{\tau_0(E)}\log \Gamma \frac{\exp (h\nu/kT_0-h\nu/kT)-1}{\exp(h\nu/kT_0)-1}. \qquad \ldots \ldots \ldots (23)$$

Substituting (23) in (22) and making use of (20) gives then

$$B(T,T_0)=\left(\frac{2m}{\pi}\right)^{\frac{1}{2}} \frac{2\pi e^4}{Ma^3} \frac{\log \Gamma}{(kT)^{\frac{1}{2}}} \frac{\exp (h\nu/kT_0-h\nu/kT)-1}{\exp (h\nu/kT_0)-1}, \qquad \ldots (24)$$

in which $\log \Gamma$ has been assumed to be independent of E (actually it is a slowly varying function of E of order of magnitude unity). The quantities $A(F,T,T_0)$ and $B(T,T_0)$ are plotted diagrammatically in Figure 2 from which it appears
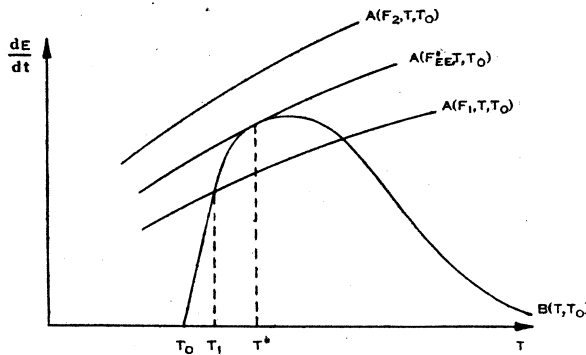

Fig. 2.—Average rate of energy gain from the field and energy loss to the lattice vibrations per electron of a Maxwellian distribution.

that for a field $F_1 < F^*$ an equilibrium temperature T_1 will be attained, while for a field $F_2 > F^*$ no equilibrium temperature for the conduction electrons will be possible. Hence F^* is the critical field strength for which the Maxwellian distribution of conduction electrons becomes unstable, the corresponding electronic temperature being T^*. An approximate analytic expression for F^* can be obtained subject to certain simplifying assumptions. Since the curves $A(F,T,T_0)$ are reasonably flat in the vicinity of $T=T^*$, we may take T^* to be that value which maximizes $B(T,T_0)$ with respect to T. The condition for a maximum is

$$(1-h\nu/kT) \exp (h\nu/kT_0-h\nu/kT)=1, \qquad \ldots \ldots \ldots (25)$$

and, if we assume $h\nu \ll kT_0$ (a condition which is satisfied for many of the alkali halides between about -100 °C and room temperature), then $(h\nu/kT_0-h\nu/kT)<1$, and on expanding the exponential we find

$$T^* \simeq 2T_0. \qquad \ldots \ldots \ldots \ldots \ldots (26)$$

Substitution of this value of T in the instability criterion (15) gives with the help of (21) and (24)

$$F_{EE}^* \simeq \frac{m\pi e^3}{Ma^3h\nu} (\log \Gamma)^{\frac{1}{2}} \frac{[h\nu/kT_0\{\exp (h\nu/kT_0)+1\}]^{\frac{1}{2}}}{\exp (h\nu/kT_0)-1}, \qquad \ldots (27)$$

as an approximate expression for the critical field strength which causes instability when electron-electron collisions determine the distribution function of the conduction electrons. This will be compared with the value

$$F_{EL}^* = \frac{2^{1/3} m^{1/2} \pi h e^3}{4 M a^4 I (h\nu)^{\frac{1}{2}}} (\log \gamma)^{\frac{1}{2}} \left\{ 1 + \frac{2}{\exp (h\nu/kT_0) - 1} \right\}^{\frac{1}{2}}, \quad \cdot \cdot \ (28)$$

obtained originally by Fröhlich (1937) for the critical field strength which causes instability when electron-lattice collisions determine the distribution function of the conduction electrons.

IV. Discussion

(a) Identification of the Breakdown Field

The question as to the identification of the breakdown field strength immediately arises, and it seems that breakdown will occur for that field strength which is the higher of F_{EE}^* or F_{EL}^* in any given instance.

For suppose $F_{EE}^* < F_{EL}^*$; then not until $F = F_{EL}^*$ would there be any mechanism by which the number of conduction electrons could be sufficiently increased to make electron-electron collisions predominate in determining the distribution function. However, when $F = F_{EL}^*$ the number of conduction electrons increases rapidly till the distribution becomes Maxwellian, and since $F_{EL}^* > F_{EE}^*$ breakdown should then occur.

If on the other hand $F_{EL}^* < F_{EE}^*$, it may reasonably be supposed that a field $F = F_{EL}^*$ simply changes the conduction electron distribution to a Maxwellian one whose temperature is about twice the lattice temperature (cf. equation (26)). For alkali halides with $I \gtrsim 5$ eV there would then be an almost negligible ionization rate. It is then reasonable to suppose that breakdown would not occur until $F = F_{EE}^*$.

(b) The Magnitude of the Breakdown Field

Quantitative calculations show that F_{EE}^* and F_{EL}^* are of the same order of magnitude for most of the alkali halides, and as given by (27) and (28) respectively are of the order of half the measured breakdown strengths given by von Hippel (1935). This is not as serious as would seem at first sight since many factors may be considered, some of which cause effects of considerable magnitude and all of which would tend to improve the agreement between theory and experiment.

Firstly, from the experimental point of view the results of von Hippel must be subject to some doubt. Recent careful work by Calderwood and Cooper (1953), in which the specimens were annealed so as to be as free as possible from mechanical strain, has shown that some of von Hippel's results are probably too high. Unfortunately, however, they have not tested a sufficiently full range of substances to make adequate comparison.

Secondly, from the theoretical point of view several comments arise. In the derivation of (27) the results of a perturbation calculation have been extended to regions of doubtful validity ; also log Γ has been put as unity. Thus, granted

the model, less quantitative significance applies to the value of F_{EE}^* than to that of F_{EL}^*. Further, if the Born lattice theory of the dielectric constant of ionic crystals be accepted, then the reststrahlen frequency and several of the crystal constants appearing in the final results for F_{EE}^* and F_{EL}^* can be replaced by the experimentally measured dielectric constants, and the calculated breakdown strengths increased by factors of the order of 50 per cent. This has been done by Fröhlich (1939) for F_{EL}^*, but is not repeated for the present calculations, since no significance will be attached to the absolute magnitude of F_{EE}^*.

It is evident that in the present state of the theory an examination of the magnitudes of breakdown strengths will be of little use in determining which critical field strength is to be identified with the breakdown field strength.

(c) Dependence of Breakdown Strength on Temperature

Omitting universal constants and writing $z = h\nu/kT_0$ we have for the critical field strengths

$$F_{EE}^* \propto \frac{1}{Ma^3h\nu} \cdot \frac{[z\{\exp(z)+1\}]^{\frac{1}{2}}}{\exp(z)-1}, \quad \cdots\cdots\cdots\cdots (29)$$

$$F_{EL}^* \propto \frac{1}{Ma^4I(h\nu)^{\frac{1}{2}}} \left\{1 + \frac{2}{\exp(z)-1}\right\}^{\frac{1}{2}}. \quad \cdots\cdots\cdots (30)$$

The temperature dependences are then contained entirely in the functions of z. The ratio of these temperature dependent terms is given by

$$\left\{\frac{z}{\exp(z)-1}\right\}^{\frac{1}{2}} \simeq 1, \quad \cdots\cdots\cdots\cdots\cdots (31)$$

the approximation being subject to the restriction imposed in the derivation of (27), namely, $z \leqslant 1$. It cannot be expected, then, that measurements of the temperature dependence will show which is the critical field strength to be identified with the breakdown field, since both criteria give approximately the same temperature dependence.

Calderwood and Cooper (1953), working on sodium chloride and potassium chloride in the temperature range −100 to 50 °C, have found that the breakdown strength increases with increasing temperature more rapidly than predicted by the functions of (29) and (30). This is also understandable on the basis of Fröhlich's calculation of the temperature dependence of the relaxation time, since in this temperature range an increasing number of thermal defects (not taken into account in the calculations) would reduce the relaxation time at a faster rate than that predicted.

(d) Dependence of Breakdown Strength on Physical Parameters

The variation of breakdown strength at room temperature over a series of alkali halides is given in Table 1. The quantities listed are the experimental breakdown strength F_{EX}^* according to von Hippel (1935), the critical field F_{EL}^* according to Fröhlich (1937), and the critical field F_{EE}^* from equation (27).

Units have been adjusted so that all values given are relative to the corresponding value for sodium chloride. This is easily achieved for the theoretical results since from (27) and (28) we have immediately

$$\frac{F^*_{EE}}{F^*_{EL}} \propto \frac{aI}{(h\nu)^{\frac{1}{2}}} \cdot \left\{ \frac{z}{\exp(z)-1} \right\}^{\frac{1}{2}} \cdot \qquad \ldots\ldots\ldots\ldots (32)$$

An examination of these results shows clearly that the breakdown strength varies from crystal to crystal in a manner which agrees much more closely with the critical field F^*_{EL} than with F^*_{EE}. Although it is possible that breakdown occurs at a field strength F^*_{EL} for some alkali halides and F^*_{EE} for others, and, although the accuracy of the experimental results quoted is dubious, it seems most likely on the basis of these experimental results that F^*_{EE} is less than F^*_{EL} for these substances, and that F^*_{EL} of Fröhlich's original work should be identified with the breakdown field strength.

TABLE 1

RELATIVE VALUES OF BREAKDOWN FIELD STRENGTHS AND CRITICAL FIELD STRENGTHS
FOR A SERIES OF IONIC CRYSTALS AT ROOM TEMPERATURE

Substance	F^*_{EX}	F^*_{EL}	F^*_{EE}
Sodium chloride ..	1·00	1·00	1·00
Sodium bromide ..	0·66	0·99	1·15
Sodium iodide ..	0·53	0·87	1·01
Potassium chloride ..	0·66	0·62	0·86
Potassium bromide ..	0·47	0·52	0·77
Potassium iodide ..	0·40	0·48	0·70
Rubidium chloride ..	0·53	0·45	0·69
Rubidium bromide ..	0·40	0·39	0·68
Rubidium iodide ..	0·33	0·29	0·50

Heller has criticized Fröhlich's theory on the ground that it predicts that breakdown strength should vary inversely with internal ionization energy, and he suggests that two crystals with similar lattice parameters but different internal ionization energies be used to test the validity of his criticism. However, it is obvious that this criticism is quite invalid since the breakdown strength is a function of many other physical constants apart from the ionization energy which is contained implicitly in a knowledge of those constants together with the laws governing the formation of crystals. In other words, the best that any theory can do is to give a correct manner of variation from crystal to crystal, since in the nature of things it is not possible to vary one physical constant while keeping the others fixed.

V. ACKNOWLEDGMENTS

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