

$$\begin{aligned}
B_{31}=B_{13}= & -\{3c/4a\}\{\beta'(C_2-C_{12}-C_{23}+C_{123})-\gamma'S_1S_3-i[\beta'(S_2-S_{12}-S_{23}+S_{123})-\gamma'S_1(1-C_3)]\} \\
& - (3c/28a)\epsilon'\{(1-C_3)(C_{12}-C_2)+S_3(S_2-S_{12})+3[C_1(C_2-C_{23})+S_1(S_2-S_{23})-C_{212}+C_{2123}] \\
& +2(-C_{2122}+C_{21223}+C_{22}-C_{223})\}-i(3c/28a)\epsilon'\{S_3(C_{12}-C_2)+(S_{12}-S_2)(1-C_3) \\
& +3[S_1(C_2-C_{23})+C_1(S_{23}-S_2)+S_{212}-S_{2123}]+2(S_{2122}-S_{21223}-S_{22}+S_{223})\},
\end{aligned}$$

and

$$\begin{aligned}
B_{23}=B_{32}= & -(\sqrt{3}c/2a)\{\beta'[1-C_3+\frac{1}{2}(-C_2-C_{12}+C_{23}+C_{123})]+\frac{1}{2}\gamma'[C_{1223}-C_{122}+C_1(1-C_3)]\} \\
& -i(\sqrt{3}c/2a)\{\beta'[S_3+\frac{1}{2}(S_2+S_{12}-S_{23}-S_{123})]+\frac{1}{2}\gamma'(S_{122}-S_{1223}+C_1S_3)\}-\epsilon'(\sqrt{3}/28)(c/a)\{5[(1-C_3)(C_2+C_{12}) \\
& -S_3(S_2+S_{12})]+C_1(C_{23}-C_2)+S_1(S_{23}-S_2)-C_{212}+C_{2123}+4(-C_{22}+C_{223}-C_{2122}+C_{21223})\} \\
& -i(\sqrt{3}/28)(c/a)\epsilon'\{5[(1-C_3)(S_2+S_{12})+S_3(C_2+C_{12})]+S_1(C_{23}-C_2)+C_1(S_2-S_{23})+S_{212}-S_{2123} \\
& +4(S_{22}-S_{223}+S_{2122}-S_{21223})\}.
\end{aligned}$$

The notation

$$\begin{aligned}
C_i &= \cos 2\pi k_i, \\
C_{ij} &= \cos 2\pi(k_i+k_j), \\
C_{122} &= \cos 2\pi(k_1+2k_2), \\
C_{123} &= \cos 2\pi(k_1+k_2+k_3), \\
C_{1223} &= \cos 2\pi(k_1+2k_2+k_3),
\end{aligned}$$

and

$$C_{21223} = \cos 2\pi(2k_1+2k_2+k_3)$$

has been used, and the S 's refer to the corresponding sines.

Corrections to the third-neighbor terms in the original model include changes of the coefficient of γ' for the elastic constant C_{44} in Eq. (8) and the coefficient of γ' in the equations for the terms A_{33} , B_{33} , B_{13} , and B_{23} .

Charged Dislocations in Ionic Crystals*

J. S. KOEHLER, D. LANGRETH, AND B. VON TURKOVICH
Department of Physics, University of Illinois, Urbana, Illinois
 (Received March 1, 1962)

The paper aims to show that the charge clouds around dislocations are important for the mechanical properties of ionic crystals. The previous work of Eshelby, Newey, Pratt, and Lidiard is extended by solving the nonlinear equation giving the potential distribution and by obtaining the boundary condition appropriate at the dislocation core. Three typical examples are worked out in detail. Finally, a series of experimental phenomena are discussed and it is shown how the charge cloud model can be used to understand the experimental behavior. In particular, the minimum in the yield stress versus annealing temperature of NaCl doped with a known concentration of PbCl_2 is used to obtain the energy of formation of a positive ion vacancy in NaCl. One finds that $E_F^+ = 0.53$ eV.

I. INTRODUCTION

IN this paper we shall try to show that the idea of charged dislocations screened by a cloud of charged lattice defects enables a number of mechanical and electrical properties of ionic crystals to be understood. This idea was first discussed by Eshelby, Newey, Pratt, and Lidiard¹ who used the theory of the charge cloud in the static case to understand the temperature dependence of the yield stress of NaCl crystals.

In Sec. II the general principles appropriate for static dislocations will be described. The equations obtained will be useful for pure and for crystals containing di-

valent positive impurity ions. Two essential additions to the theory will be described. First, Eshelby and co-workers simplified the problem by linearizing it. We have solved the nonlinear equations. Second, Eshelby and co-workers were not able to treat the region near the core of the dislocations; in fact, they did not establish what boundary condition the potential should satisfy at the dislocation core. We have attempted to deal with this region with considerable care. Applications of the theory to various experimental observations are described in Sec. III.

II. GENERAL THEORY FOR STATIC DISLOCATIONS

Qualitatively the charge cloud arises as follows: consider a dislocation which has some edge type character. Suppose that the energy E_F^+ required to form a posi-

* This research supported in part by the National Science Foundation.

¹ J. D. Eshelby, C. W. A. Newey, P. L. Pratt, and A. B. Lidiard, *Phil. Mag.* **3**, 75 (1958).

tive-ion vacancy differs from the energy E_F^- required to form a negative-ion vacancy. To be specific, suppose $E_F^+ < E_F^-$; then for a pure crystal in equilibrium at high temperature one would at first expect that the fractional concentration C_+ of positive-ion vacancies would exceed the fractional concentration C_- of negative-ion vacancies. However, this would result in a large Coulomb energy since the dislocation would become positively charged whereas the surroundings would have a negative space charge. The actual result is a compromise in which the dislocation is charged and an excess of positive-ion vacancies does exist near the dislocation, screening it; but far from the dislocation there are equal concentrations of positive and negative ions.

There are two conditions which must be satisfied. First, the distribution must be one which satisfies Poisson's equation. Second, the free energy of the system must be a minimum. Then, according to Lidiard,²

$$n_+ n_- = N^2 \exp[-(E_F^+ + E_F^-)/kT]. \quad (1)$$

The separate concentrations at a given position are given by the Boltzmann distribution, i.e.,¹

$$n_+ = N \exp[-(E_F^+ - ev)/kT], \quad (2)$$

$$n_- = N \exp[-(E_F^- + ev)/kT]. \quad (3)$$

Here n_+ and n_- are the number of positive- and negative-ion vacancies per unit volume, N is the number of positive ions per unit volume, and v is the electrostatic potential at the given position. If the divalent impurities can diffuse at the temperature under consideration, they will also be distributed according to Boltzmann distribution. Then

$$n_i = \gamma N \exp(-ev/kT), \quad (4)$$

where n_i is the number of divalent impurities per unit volume at a place where the potential is v . Poisson's equation is

$$\nabla^2 v = -4\pi\rho/\epsilon = -(4\pi e/\epsilon)(n_i + n_- - n_+), \quad (5)$$

where ρ is the charge density and ϵ is the static dielectric constant. Eshelby and co-workers solved Poisson's equation for the case $ev \ll kT$. It will be shown that, in fact, in most cases of interest $ev \gg kT$.

Far from the dislocation the crystal is neutral. Let us set the impurity concentration there equal to C . If we introduce a dimensionless potential $p(r)$, where

$$p(r) = ev(r)/kT, \quad (6)$$

then since the divalent impurities are distributed in accordance with the Boltzmann distribution one has

$$C = \gamma e^{-p(R)}, \quad (7)$$

where R will be half the distance between neighboring dislocations. In addition, the crystal must be neutral at

$r=R$ so that

$$C + \exp\{-[E_F^-/kT + p(R)]\} - \exp\{-[E_F^+/kT - p(R)]\} = 0. \quad (8)$$

Solving (8), Lidiard² obtains

$$e^{p(R)} = \exp(+E_F^+/kT) \left\{ \frac{1}{2}C + \left[\frac{1}{4}C^2 + \exp[-(E_F^+ + E_F^-)/kT] \right]^{1/2} \right\}. \quad (9)$$

In the above equations, C is the fractional divalent positive ion concentration. In the case of NaCl, $E_F^+ + E_F^- = 2.02$ eV. Suppose C is 10^{-6} which is a reasonably pure crystal, then the first term inside the square root is ten times larger than the second for temperatures below 472.8°C. Hence in most cases one can set

$$e^{p(R)} = C \exp(E_F^+/kT), \quad \frac{1}{2}C \gg \exp[-(E_F^+ + E_F^-)/2kT]. \quad (10)$$

If we define

$$z(r) = p(r) - p(R), \quad (11)$$

then Poisson's equation can be written³

$$\nabla^2 z = (8\pi Ne^2 C / \epsilon kT) \sinh z. \quad (12)$$

The boundary conditions at points far from the dislocation are

$$dz/dr = 0 \quad \text{at} \quad r=R; \quad (13)$$

i.e., the electric field is zero midway between dislocations. This occurs because each dislocation constitutes an electrically neutral system. In addition, z is so defined that it is zero at $r=R$. The double layer of charge at the surface of the crystal and around the dislocation gives rise to a potential difference between a point outside the crystal and one completely inside the crystal.⁴ Now a point on the dislocation axis is from this point of view outside the crystal and hence has potential zero. In Appendix I it is proved that if only electrical interactions are important the free energy of the crystal is minimum when the potential at the dislocation is zero; i.e., a point on the dislocation core is equivalent to a point outside the crystal. Thus, at the dislocation core,

$$z(a) = -ev(R)/kT = -p(R), \quad (14)$$

where $p(R)$ is given by either Eq. (7) or (8) and a is the dislocation core radius.

There is one situation not described by the above equations. At moderately low average impurity concentrations (i.e., about 3×10^{-6} at room temperature) the impurity concentration at the core saturates. Since the impurity term dominates the charge density, Poisson's equation becomes

$$\nabla^2 p = -4\pi Ne^2 / \epsilon kT. \quad (15)$$

³ Equation (12) is approximate. A more accurate version is: $\nabla^2 z = K^2 \sinh z / (1 + ce^{-z})$, where c is the average divalent ion concentration and K is the screening radius given in Eq. (18). The right side differs from Eq. (12) when the divalent ion concentration is nearly saturated.

⁴ K. Lehovec, J. Chem. Phys. **21**, 1123 (1953).

² A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 259.

The solution associated with zero core potential in the saturated region is

$$p = b \ln(r/a) - (\pi N e^2 / \epsilon k T)(r^2 - a^2), \quad (16)$$

where a is the core radius and b must be determined.

Outside the saturation region the type of solution used depends on whether z is large or small in comparison with unity. Let us first suppose that z is of order one. Equation (12) becomes

$$\nabla^2 z = K^2 z \left(1 + \frac{z^2}{6} + \frac{z^4}{120} \right). \quad (17)$$

where the screening constant K is given by

$$K^2 = 8\pi N e^2 C / \epsilon k T. \quad (18)$$

If z at the interface between the large z region and the small z region is z_0 , which is of order unity, we can define an effective screening constant,

$$K_e^2 = K^2 \left(1 + \frac{z_0^2}{6} + \frac{z_0^4}{120} + \dots \right). \quad (19)$$

The solution in this outer small z region is

$$z(K_e r) = -AK_0(K_e r), \quad (20)$$

where K_0 is the modified Bessel's function of zeroth order and A is a constant. This function will satisfy the outer boundary conditions.

There exists, however, a third region between the saturated region at small radius and the linear solution at large radius. This can be seen as follows. The impurity concentration at r is:

$$C_i = \gamma e^{-p(r)} = C^2 \exp(+E_F^+ / kT) e^{-p(r)} = C e^{-z(r)}. \quad (21)$$

Consider as a specific example $C = 10^{-5}$, $E_F^+ = 0.66$ eV, and $T = 300^\circ\text{K}$. At the outer edge of the saturation region $C^2 \exp(+E_F^+ / kT) = 12.280 = e^{p(r_s)}$. Hence, according to Eq. (21) if this radius is r_s , one must have $p(r_s) = 2.5080$ and $z(r_s) = 11.5129$.

Thus, at the outer edge of the saturation region $|z|$ is large compared with unity. In this intermediate region Eq. (12) becomes

$$\nabla^2 z = \frac{d^2 z}{ds^2} + \frac{1}{s} \frac{dz}{ds} = -\frac{1}{2} e^{-z}, \quad (22)$$

where $s = Kr$. This equation has a solution

$$e^{-z} = \frac{H}{s^2 \sin^2[\frac{1}{2} H^{1/2} \ln(s/s_0)]}. \quad (23)$$

This gives

$$\frac{dz}{ds} = -\frac{2}{s} \left\{ 1 + \frac{1}{2} H^{1/2} \cot[\frac{1}{2} H^{1/2} \ln(s/s_0)] \right\}. \quad (24)$$

If the dislocation core radius is a and the outer radius of the saturated region is na , then from (16) and (21) the

equation determining n is

$$C_i(r_s) = 1 = M e^{B a^2 (n^2 - 1) / n^b}, \quad (25)$$

where $B = \pi N e^2 / \epsilon k T$ and $M = C^2 \exp(+E_F^+ / kT)$. On matching slopes at r_s one finds

$$\left(\frac{dp}{dr} \right)_{r_s} = K \frac{dz}{ds} = \frac{2}{r_s} \left[1 + \frac{H^{1/2}}{2} \cot \left(\frac{H^{1/2}}{2} \ln \frac{Kna}{s_0} \right) \right] = \frac{b}{r_s} \left(1 - \frac{2Br_s^2}{b} \right).$$

If the argument of the cotangent is small at r_s it can be given a series expansion which yields

$$\ln \left(\frac{Kna}{s_0} \right) = \frac{1}{\frac{1}{2}b - 1 - Ba^2 n^2}. \quad (26)$$

If n is approximately unity, then (25) and (26) give

$$(n-1) = \frac{\ln M}{[2Ba^2(4+\ln M)]^{1/2}} \quad (27)$$

and

$$b = 2Ba^2 + [2Ba^2(4+\ln M)]^{1/2}, \quad (28)$$

where we have assumed that $(n-1) \ll 1$ and that $(b - Ba^2) \gg 1$. If $C = 10^{-5}$ and $T = 300^\circ\text{K}$, these assumptions are valid and $(n-1) = 0.03288$, while $b = 9.70207 \times 10^2$. The charge q per unit length of dislocation is

$$q = -\frac{1}{2} \epsilon b k T + \frac{1}{2} \pi N e a^2. \quad (29)$$

For the example considered this is 0.1268 esu per cm or 7.43 negative electronic charges per ionic length. This charge is so large that the dislocation core structure will be seriously disturbed. At 500°K there is no saturated region if $C = 10^{-5}$. In this case one fits the boundary condition at the core using Eq. (23) and then matches large z and small z solutions in the manner described below.

The intermediate and outer solutions must now be fitted together. This is done at $z = 1.5$ since the smallest extra terms appear in the differential equation if the fit is done there. The extra terms on the right side of Eq. (12) of λ are 14.5% of the terms retained. Thus,

$$e^{1.5} = 4.482 = \frac{H}{s^2 \sin^2[\frac{1}{2} H^{1/2} \ln(s/s_0)]} = e^{AK_0(K_e r)}, \quad (30)$$

and matching slopes

$$(2/s) \left\{ 1 + \frac{1}{2} H^{1/2} \cot[\frac{1}{2} H^{1/2} \ln(s/s_0)] \right\} = AK_1(K_e r) = AK_1(s/1.190). \quad (31)$$

Since $s_0 = 0.18957$ and since $\frac{1}{2} H^{1/2} \ln(s/s_0) = \frac{1}{2} \pi + \Delta$, where Δ is small compared with $\pi/2$, one obtains from Eqs. (30) and (31)

$$K_1(s/1.190)/K_0(s/1.190) = 4/3s. \quad (32)$$

TABLE I. The concentration and temperature dependence of the screening radius for rock salt. Values of $1/K$ are given in cm.

C	$T=300^\circ\text{K}$	$T=500^\circ\text{K}$	$T=700^\circ\text{K}$
10^{-3}	4.22×10^{-8}	5.45×10^{-8}	6.44×10^{-8}
10^{-4}	1.34×10^{-7}	1.73×10^{-7}	2.04×10^{-7}
10^{-5}	4.22×10^{-7}	5.45×10^{-7}	6.44×10^{-7}
10^{-6}	1.34×10^{-6}	1.73×10^{-6}	2.04×10^{-6}
10^{-7}	4.22×10^{-6}	5.45×10^{-6}	6.44×10^{-6}

Thus, the value of s at which the fit between intermediate and outer solutions is made is $s=0.844$. Hence, the charge cloud is quite compact.

Thus, for NaCl at 300°K , one finds that z has gone from -12.28 at the core to -1.5 while r goes from 8×10^{-8} cm to 3.62×10^{-7} cm. Thus, the cloud is very tightly bound to the dislocation. Note that the radius of the cloud is approximately the reciprocal of K . Table I gives values for $1/K$ for various impurity concentrations and temperatures in the case of rock salt. Note that in all of the above cases the screening radius is so small that the charge cloud size is below the limit of resolution of the ordinary optical microscope.

Consider two other illustrative examples. First, let us describe the case in which $C=10^{-5}$ and $T=500^\circ\text{K}$. In this situation the impurity concentration does not saturate at the core. The inner solution satisfies Eq. (22) and is

$$e^{-z} = \frac{H}{s^2 \sinh^2[\frac{1}{2}H^{1/2} \ln(s/s_0)]}, \quad (33)$$

so that

$$\frac{dz}{ds} = -\frac{2}{s} \{1 + \frac{1}{2}H \coth[\frac{1}{2}H^{1/2} \ln(s/s_0)]\}. \quad (34)$$

This solution is appropriate for smaller core potentials than those described in the first example. The boundary conditions are: First, at the core,

$$e^{-z(a)} = e^{p(R)} = e^{+3.80740} = \frac{H}{(0.14679)^2 \sinh^2[\frac{1}{2}H^{1/2} \ln(0.14679/s_0)]}.$$

Second, matching values and slopes at $z = -1.5$, one has

$$e^{1.5} = \frac{H}{s^2 \sinh^2[\frac{1}{2}H^{1/2} \ln(s/s_0)]} = e^{AK_0(K_0 r)} = e^{AK_0(s/1.190)} \quad (36)$$

and

$$\frac{2}{s} \{1 + \frac{1}{2}H \coth[\frac{1}{2}H^{1/2} \ln(s/s_0)]\} = AK_1 \left(\frac{s}{1.190} \right). \quad (37)$$

For the particular case in question, one finds that $s=0.3081$, $s_0=0.02466$, $H=0.7953$, and $A=0.9941$. From Eq. (34) evaluated at the core we can obtain the

charge per unit length on the dislocation. One finds

$$q = -(\epsilon k T / 2e) K a (\partial z / \partial s)_a. \quad (38)$$

In the present example, this gives $q = -1.0459 \times 10^{-3}$ esu per cm or -6.1202×10^{-2} electronic charges per ionic distance. Hence, the magnitude of the charge is much reduced. Note also that the charge cloud is even more compact than in the first case examined so that the cloud size is only roughly given by $1/K$.

Consider finally the case $C=10^{-5}$ and $T=700^\circ\text{K}$. One then finds that

$$e^{-z(a)} = e^{p(R)} = e^{-0.569835}. \quad (39)$$

Hence, in this case the Eshelby-type solution suffices, i.e.,

$$z(r) = AK_0(Kr), \quad (40)$$

where K_0 is the zero-order Bessel function. A is determined by the core condition which is

$$0.569835 = AK_0(0.1241) = 2.21578A.$$

Therefore, $A=0.2572$. The core charge is again given by Eq. (38) and $q = +5.553 \times 10^{-4}$ esu per cm = $+3.248 \times 10^{-2}$ electronic charges per ionic length. Note that the sign of the core charge has changed, i.e., the temperature is now above the value giving no charge cloud.

Thus, for a given average divalent ion concentration the magnitude of the charge on the core drops very rapidly as the temperature increases. The present calculations give the equilibrium arrangement. In practice one may not achieve equilibrium at low temperatures. It is, of course, possible to use the above methods to treat situations in which only one or two kinds of point defects can achieve their equilibrium arrangement.

The temperature at which the core becomes unsaturated increases as the divalent impurity concentration increases. For rock salt these temperatures are given in Table II.

If the charge on the core is very small then there will be large errors if the present continuum model is used. A model using discrete charges would then be more appropriate. The present calculation can be

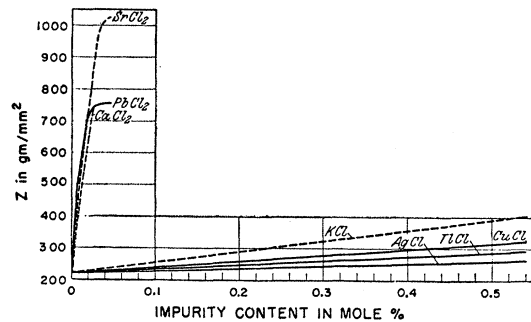


Fig. 1. The increase in tensile strength Z for fracture of NaCl produced by monovalent and divalent impurities. Note that all divalent impurities produce equal effects showing that ionic radius is not important (see reference 5).

TABLE II. Temperature at which divalent ion concentration at dislocation core drops below saturation ($E_F^+ = 0.66$ eV).

C	T_s (°K)
10^{-3}	554.5
10^{-4}	415.8
10^{-5}	332.7
10^{-6}	below 300

thought of as giving the defect concentrations averaged along the dislocation length.

Suppose one attempts to pull the dislocation out of its charge cloud using either an external applied shearing stress or an external electric field. At sufficiently high temperature the dislocation will drag the mobile defects along behind it. Consider the situation at very low temperature where the defects are immobile. The force F per unit length exerted by the charge cloud on the dislocation is

$$F = Eq = -q \left(\frac{\partial v}{\partial r} + \frac{2q}{er} \right), \quad (41)$$

where the field of the charge on the dislocation has been subtracted from the total field to give the force acting on the dislocation located at r . This force should go through a maximum which determines the yield stress. The maximum occurs at

$$\frac{\partial^2 v}{\partial r^2} - 2q/er^2 = 0 \quad (42)$$

or

$$\frac{\partial^2 z}{\partial s^2} = 2qe/\epsilon kTs^2.$$

If $C = 10^{-5}$ and $T = 300^\circ\text{K}$, then the maximum force occurs at 8.51 \AA and is very large, i.e., $F = 0.628 \times 10^5$ dyn/cm. This corresponds to a yield stress of 1.58×10^{11} dyn/cm². Actually the dimensions are so small that undoubtedly thermal fluctuations will occur which will materially lower the yield stress. Nevertheless, it is probably true that the charge cloud can produce very large yield stresses.

If $C = 10^{-5}$ and $T = 500^\circ\text{K}$, the maximum force occurs at the core radius. Here $F = 1.425$ dyn/cm and the corresponding yield stress is 3.586×10^7 dyn/cm². This is appreciable, but not outside the range of observed values.

Since the exact details of the distribution at and near the core are crucial for these yield stress calculations it is clear that no quantitative statements can be made as yet. However, it appears likely that the yield stress should depend strongly on the temperature.

III. EXPERIMENTAL PHENOMENA

There are already a large number of experimental phenomena in ionic crystals which are clearly influenced by the charge clouds around dislocations. In this section we describe several such observations together with a qualitative description of the role played by the cloud.

A. Yield Stress and Fracture

Metag⁵ has obtained data which shows that the yield stress and the tensile stress for fracture both depend sensitively on the divalent impurity concentration and on the annealing given to the specimen before testing. Figure 1 shows the large increase in tensile fracture strength resulting from divalent impurities. Note that monovalent impurities which do not produce a charge cloud are not very effective.

Eshelby, Newey, Pratt, and Lidiard¹ point out that at a given average divalent ion impurity concentration a temperature exists such that no charge cloud forms so the yield stress should be a minimum. If the average divalent impurity concentration is not too small this temperature is given by

$$\ln C + E_F^+/kT = 0. \quad (43)$$

If the temperature associated with minimum yield stress can be measured in a sample containing known impurity concentration then the energy of formation of positive ion vacancies can be determined. Figure 2 gives Metag's⁵ data for NaCl containing PbCl_2 such that the lead concentration is 1.04×10^{-4} . The yield stress and tensile strength measurements were made at room temperature after holding at the temperatures indicated for six hours. A minimum is seen at 400°C . If the above equation is used to calculate E_F^+ in NaCl using this data one finds $E_F^+ = 0.534$ eV. This implies that $E_F^- = 2.02 - 0.534 = 1.486$ eV. Burgsmüller⁶ measured the tensile strength of rock salt of higher purity. He observed a minimum at 40°C . Such a displacement of the minimum is in the appropriate direction but he probably did not achieve equilibrium at 40°C . Further experiments are being done to confirm the above value for E_F^+ .

It is interesting to speculate on the mechanism of fracture. It is possible that if the charged dislocation is pulled away from its charge cloud a crack is produced at the dislocation core. This crack arises as a result of the Coulomb repulsion of the core charge for itself. Moreover, there are already large tensile stresses present

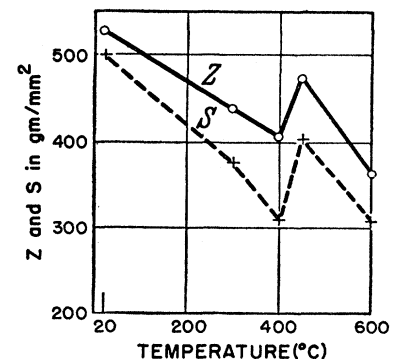


FIG. 2. The temperature dependence of the yield stress S and the tensile strength Z of NaCl containing 1.04×10^{-4} at. % of PbCl_2 (see reference 5).

⁵ W. Metag, Z. Physik 78, 363 (1932).

⁶ W. Burgsmüller, Z. Physik 80, 299 (1933).

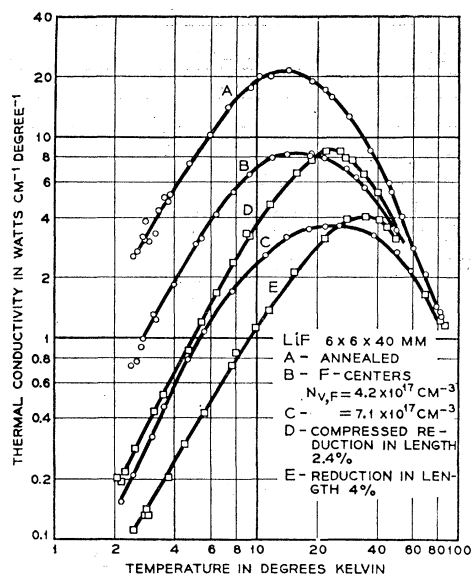


FIG. 3. The thermal conductivity of LiF containing known dislocation densities (see reference 9).

near the core of an edge dislocation. The crack presumably forms on the (100) plane because such a crack has lowest formation energy. Such a model for crack formation can only yield quantitative predictions if detailed calculations of the core structure are made when various core charges are present. This has not yet been done.

Recently Johnston, Stokes, and Li⁷ used impact tests to determine the temperature at which the transition from the high temperature ductile behavior to the low temperature brittle behavior occurs in various ionic crystals. At some temperature the materials became brittle, i.e., for tests made below that temperature practically no energy was absorbed before fracture occurred. The most interesting point about the results is that AgCl is ductile down to temperatures which are a much smaller fraction of its melting point than are NaCl or LiF. Johnston, Stokes, and Li did not state whether their experiments were done while the crystals were subjected to visible light. It would be of value to know whether the results differ when the crystals are kept in the dark throughout the experiment. With visible light photoelectrons are released which may help in establishing charge neutrality. It would also be of value to know whether the results are sensitive to the positive divalent ion concentration.

B. Low-Temperature Thermal Conductivity

The thermal conductivity of pure ionic crystals below a temperature of 10 to 50°K is proportional to T^2 . Klemens⁸ ascribed this behavior to the scattering of phonons by dislocations. The first quantitative measure-

⁷ R. J. Stokes, T. L. Johnston, and C. H. Li, *Phil. Mag.* **4**, 1316 (1959).

⁸ P. G. Klemens, *Proc. Phys. Soc. (London)* **A68**, 1113 (1955).

ments were made by Sproull, Moss, and Weinstock⁹ who determined the dislocation densities in LiF by counting etch pits. Their measurements give a thermal resistivity for dislocations which is a hundred times the value calculated by Klemens. In the calculation of Klemens the phonon scattering is produced by the strain field of the dislocation. It is our belief that the charge cloud is also important in the phonon scattering. The experimental results are shown in Fig. 3. Some care is required in using these results since the annealed crystal and also curve E (4% reduction in length) refer to crystals slowly cooled from 180°C after deformation so that the charge cloud probably has had time to form on all existing dislocations. The curve D (2.4% reduction in length) refers to a crystal deformed at room temperature where the charge cloud may not be fully formed. The dislocation densities for curves D and E differ by a factor of 2.5 whereas the thermal conductivities differ by a factor of about 3. The energy of motion of a positive ion vacancy in LiF is 0.65 eV so that it is conceivable that the charge cloud forms at least partially after deformation at room temperature. Further experiments are needed in which conductivity measurements are made immediately after deformation at room temperature and after various aging treatments at room temperature.

C. Slow Dislocation Velocities

Gilman and Johnston¹⁰ have recently measured the average dislocation velocity of single dislocations in LiF as a function of the temperature and the applied stress. For slow dislocation velocities their data is shown in Fig. 4. The interesting point is that for a given applied stress the dislocation velocity behaves as though it is controlled by a thermally activated process having an energy of motion of 0.7 eV. This is close to the energy of migration of a positive-ion vacancy $E_M^+ = 0.65$ eV.¹¹ It is, therefore, natural to suggest that for slowly moving dislocations the charge cloud forms at least partially, but always lags a bit behind the dislocation so that there is a back force on the dislocation. This would imply that a region containing large numbers of the appropriate point defects would be left behind a moving dislocation and indeed there is some evidence for this. Davidge and Whitworth¹² have shown that the debris can be revealed by etching in NaCl.

It would be of value to perform average velocity measurements on ionic crystals at the temperature at which the charge cloud disappears. If the suggestion made above is correct the stress dependence should be different.

⁹ R. Sproull, M. Moss, and H. Weinstock, *J. Appl. Phys.* **30**, 334 (1959).

¹⁰ J. J. Gilman and W. G. Johnston, *J. Appl. Phys.* **30**, 129 (1959).

¹¹ Y. Haven, *Rec. trav. chim.* **69**, 1471 (1950).

¹² R. W. Davidge and R. W. Whitworth, *Phil. Mag.* **6**, 217 (1961).

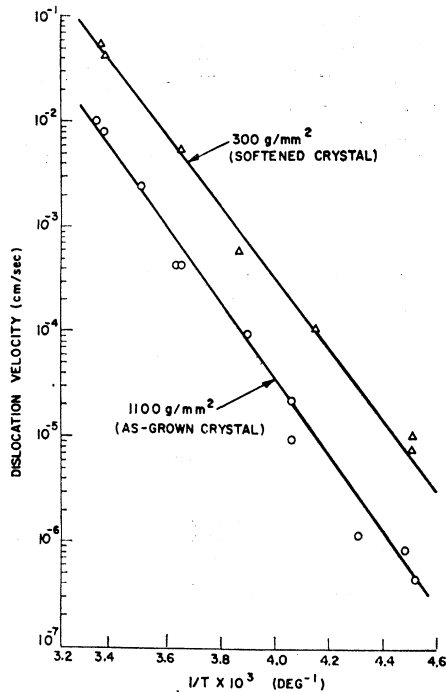


FIG. 4. The temperature dependence of the average dislocation velocity produced by a given applied shear stress (see reference 10).

Gilman and Johnston found that screw dislocations move about fifty times more slowly than edge dislocations if the measurements are made at the same stress and temperature. When point defects are generated at a screw dislocation it becomes a helical dislocation.¹³ It is possible that the slower velocity of screw dislocations occurs because, while a straight screw dislocation can move in any glide plane which contains the axis of the dislocation, a helical dislocation cannot move easily in any glide plane since it has some edge portions and moreover both positive and negative edge-type dislocations are present. Hence an applied stress, which urges one sign of edge dislocation in the direction of the motion appropriate for a straight screw dislocation, will urge the opposite sign edge in the reverse direction. Thus, it is not surprising that the screw dislocations are slow.

D. Direct Evidence for Charge Effects

Sproull¹⁴ has recently shown that a large electric field can produce dislocation motion in bent LiF crystals. He supposes that the motion of the charge cloud is small in comparison with the dislocation motion.

In addition, Remant and Vennik,¹⁵ and Rueda and Dekeyser¹⁶ have recently measured the converse effect, i.e., they bend a crystal and observe changes in the

potential of an electrode evaporated onto the surface of the ionic crystal.

Thus far these experiments are of a qualitative nature but undoubtedly more quantitative work will appear.

IV. SUMMARY

To summarize: We believe that the presence of charge clouds on dislocations and at the surface of ionic crystals are of great importance for their mechanical properties. In fact, it appears that the major difference in the behavior of dislocations in metals and in ionic crystals arises from the presence of the clouds in ionic crystals. It is clear that a great deal of additional research will be required to obtain a complete quantitative understanding, but the basic ideas seem to be reasonably clear.

APPENDIX. THE BOUNDARY CONDITION AT THE DISLOCATION CORE

In the past there has been some confusion as to what the appropriate boundary condition at the dislocation should be. It will be shown here that the correct boundary condition is that the electrostatic potential should vanish. This result is contingent upon the assumption that the energy involved is primarily electrostatic. We thus assume that the elastic energy necessary to form a jog on the dislocation is negligible compared with the electrostatic energy.

For simplicity we shall use for a calculational model a crystal with but a single dislocation. The result thus obtained can clearly be extended to a real crystal, since for all cases of practical interest the average spacing between the dislocations is much greater than $1/K$, the radius of the charge clouds of the dislocations, so that the dislocations do not interact electrically. Then we proceed in the usual fashion by minimizing the free energy $F = E - TS$ of the whole system with respect to the charge on the dislocation, where E is the total energy of the system, T the temperature, and S the configurational entropy. We have

$$E = \int_{V_1} (n_+ E_F^+ + n_- E_F^-) d^3x + E_e, \quad (A1)$$

where E_e is the total electrostatic energy. The symbol V_1 denotes that the integral extends over the entire crystal except the core of the dislocation. Furthermore, using the familiar formula of electrostatic theory, we have

$$E_e = \frac{1}{2} \int_V \rho v d^3x. \quad (A2)$$

The symbol V denotes that the integral extends over the entire crystal including the dislocation core. Here v is the potential and ρ is the charge density. Note that outside the dislocation core $\rho = e(n_- + n_i - n_+)$ and inside the core $\rho = \rho_D$, the charge on the dislocation. Thus, Eq. (A2) takes into account all the electrostatic energy,

¹³ F. Seitz, Phys. Rev. **79**, 1002 (1950).

¹⁴ R. L. Sproull, Phil. Mag. **5**, 815 (1960).

¹⁵ G. Remant and J. Vennik, Phil. Mag. **6**, 1 (1961).

¹⁶ F. Rueda and W. Dekeyser, Phil. Mag. **6**, 359 (1961).

including the energy entailed in charging the dislocation. Note that no particular assumption needs to be made about the distribution of charge on the dislocation.

Varying Eq. (A2) gives

$$\delta E_e = \frac{1}{2} \int_V (\rho \delta v + v \delta \rho) d^3x, \quad (\text{A3})$$

where δ represents a variation with respect to the charge on the dislocation. Now making use of Poisson's equation $\epsilon \nabla^2 v = -4\pi\rho$, and integrating by parts twice, we have for the first term of the right member of Eq. (A3),

$$\begin{aligned} \int_V \rho \delta v d^3x &= -\frac{\epsilon}{4\pi} \int_V \nabla^2 v \delta v d^3x \\ &= -\frac{\epsilon}{4\pi} \int_V v \delta \nabla^2 v d^3x = \int_V v \delta \rho. \end{aligned}$$

In setting the integrated parts equal to zero, we have used the fact that all fields vanish outside the crystal. Thus, Eq. (A3) can be written

$$\begin{aligned} \delta E_e &= \int_V v \delta \rho d^3x \\ &= \int_{V_1} ev (\delta n_- + \delta n_i - \delta n_+) d^3x + \int_{V_2} v \delta \rho_D d^3x, \end{aligned} \quad (\text{A4})$$

where V_2 denotes that the integral is to be taken only over the core of the dislocation.

For the configurational entropy we use Boltzmann's formula $S = k \ln W$, where W is the thermodynamic probability.¹⁷ Taking the variation, and using Stirling's formula for the factorials in W , we obtain in the usual

¹⁷ Here, if we consider a cell of unit volume, $W = (N!)^2 / n!(N-n_-)!n_+!n_i!(N-n_+-n_i)!$.

way

$$-T\delta S = \int_{V_1} kT \left(\ln \frac{n_+}{N} \delta n_+ + \ln \frac{n_-}{N} \delta n_- + \ln \frac{n_i}{N} \delta n_i \right) d^3x. \quad (\text{A5})$$

Then from Eqs. (A1), (A4), and (A5), we have

$$\begin{aligned} \delta F &= \delta E - T\delta S \\ &= \int_{V_1} \left[\left(E_F^+ - ev + kT \ln \frac{n_+}{N} \right) \delta n_+ \right. \\ &\quad \left. + \left(E_F^- - ev + kT \ln \frac{n_-}{N} \right) \delta n_- \right. \\ &\quad \left. + \left(ev + kT \ln \frac{n_i}{N} \right) \delta n_i \right] d^3x + \int_{V_2} v \delta \rho_D d^3x. \end{aligned} \quad (\text{A6})$$

Now making use of¹⁸ Eqs. (2), (3), and (4) and the fact that the total number of impurity ions in the crystal ($\int n_i d^3x$) is constant, we obtain

$$\delta F = \int_{V_2} v \delta \rho_D d^3x. \quad (\text{A7})$$

Now since $\delta \rho_D$ represents an arbitrary variation it is clear that $\delta F = 0$ only if the potential at the core of the dislocation vanishes.

¹⁸ Equations (2), (3), (4), and (A5) and, consequently, (A6) are valid only if $n_i, n_+, n_- \ll N$. We have seen that in practice the condition $n_i \ll N$ is often not satisfied near the dislocation. In this case Eqs. (2), (3), (4), (A5), and (A6) should be modified by replacing n_+/N by $n_+/(N-n_i)$ and n_i/N by $n_i/(N-n_i)$. Equation (A7) evidently then remains the same in either case. That the terms in the brackets in Eq. (A6) must cancel in all cases is made evident by their identity with those in the expression from which Eqs. (2), (3), and (4) are derived. The difference between the two expressions lies only in the meaning of the δn 's: in the former case they were independent variations, while in the present case they are essentially partial derivatives with respect to the charge on the dislocation.