Diffusion and Electrolytic Conduction in Crystals (Ionic Semiconductors)

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In the present paper a mechanism of diffusion and electrolytic conduction in solids is discussed, which is based on a formal treatment given by Frenkel. It is assumed that in a crystal in thermal equilibrium some of the atoms or ions are removed from their normal positions in the lattice to irregular ones in the interlattice space. Then diffusion and electrolytic conduction is possible by two processes; first by migration of the ions in the interlattice space, second by migration of the vacant places. The number of ions in the interlattice space can be calculated. If one considers the influence of polarization the result agrees in the order of magnitude with the observed data. It is also shown that the activation energy connected with the processes of movement is of the correct order of magnitude. Thus a satisfactory explanation of the exponential factor occuring in the empirical conductivity (or diffusion) formula is obtained. The constant factor multiplying the exponential can be explained at once for one group of cases; for the other group, where the constants apparently are too high, a tentative explanation is proposed.

THE experimental results[1] concerning diffusion and electrolytic conduction in crystals have led to the following conclusions: Diffusion and mobility of each kind of ions is represented by a term

$$Ae^{-B/T}. \tag{1}$$

This holds for ions in ionic crystals as well as for atoms in metals. Thus the (electrolytic) conductivity of binary compounds is generally given by

$$\kappa = A_1 e^{-B_1/T} + A_2 e^{-B_2/T}. \tag{2}$$ [2]

Often one term is negligible compared with the other. This means that practically only one kind of ion can move.

Now the most obvious explanation of this empirical formula, given by different authors is the following; the constant B, multiplied by Boltzmann's constant k represents the minimum energy that an ion needs to be able to leave its position, while A depends upon the mobility of a single ion, the ionic concentration, and in the case of conductivity the ionic charge. A more detailed discussion of the mechanism always involves these general ideas. If the theory is to be satisfactory it must at least yield the right order of magnitude of the constants involved, and at this point serious trouble arises.

One might expect for the work function $B \times k$ a value of the order of magnitude of the lattice energy of a single ion, about 5–10 electron-volts. Actually one finds values between about 1/20 and 2 volts. These values are so much smaller than the lattice energy that it has been suggested[3] that the process of motion would not occur in the lattice at all, but would be limited to inner and outer surfaces. This conception might remove the difficulties concerning the constant B, but it leads to quite impossible values for the constant A.[4] For instance, in some cases one would have to assume values for the ionic velocities in the neighborhood of that of light. So both from a theoretical and from an experimental point of view[4] this hypothesis must be abandoned, though a certain influence of the above mentioned surfaces on the conductivity is not necessarily excluded.

Using a model that certainly does not correspond to the actual conditions but which allows a calculation of the maximum value of the

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[1] A survey of the field of electrolytic conduction is given by A. Joffé, *The Physics of Crystals*, New York, 1928; G. v. Hevesy, Handbuch d. Physik **XIII**; C. Tubandt, Handbuch d. Exp. Physik **XIII**, 1 (1932); W. Jost, Müller-Pouillets Lehrbuch d. Physik **IV**, 4. In print.
[2] First observed experimentally by T. E. Phipps, W. D. Lansing and T. G. Cooke, J. Am. Chem. Soc. **48**, 112 (1926).

[3] A. Smekal, Phys. Zeits. **26**, 707 (1925).
[4] Discussion: see W. Jost, Zeits. f. physik. Chemie **B6**, 88, 210 (1929); **B7**, 234 (1930); A. Joffé, Zeits. f. Physik **62**, 730 (1930).

mobility, I have shown[5] that if one accepts the above interpretation of the exponential the maximum value of the constant A should be $A_{max} \sim 20 - 100$, if the conductivity κ is measured in ohm^{-1} cm^{-1}. For many cases the observed values are smaller than A_{max}, but in a number of cases A has values up to 10^6. As long as this discrepancy is not removed the interpretation of the exponential factor in Eq. (1) also remains in doubt. In the present article we will attempt to show that when one takes into account the polarization forces which come into play when an ion is moved from a regular to an irregular position in the lattice, one obtains B values of the observed order of magnitude. Furthermore, by means of a more refined treatment of the ionic diffusion process, the discrepancies in the A values can be formally removed. The most logical and detailed theoretical treatment of these problems that exists so far has been given by Frenkel.[6] He considers all possible processes, though his reasoning is rather formal and does not lead to numerical values of the exponential that could be compared with experiments. Nevertheless we can base our discussion on it.

Frenkel's treatment is based on the following considerations:

(1) An atom (or ion) with sufficient energy, for instance the atom a in Fig. 1, can be removed from its normal place to a metastable
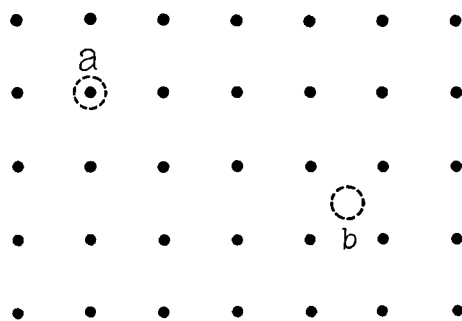

FIG. 1. Schematic representation of the diffusion and conduction process according to Frenkel: normal positions in the lattice and metastable positions in the interlattice space at b.

[5] W. Jost, Zeits. f. physik. Chemie B16, 129 (1932).
[6] I. Frenkel, Zeits. f. Physik 35, 652 (1926). Of other contributions to this field we mention: H. Braune, Zeits. f. physik. Chemie 110, 147 (1924); W. Braunbek, Zeits. f. Physik 44, 684 (1927). S. Dushman and I. Langmuir, Phys. Rev. 20, 113 (1922); 22, 357 (1923). A. van Liempt, Rec. Trav. Chim. 51, 114 (1932).

equilibrium position b in the "interlattice space," producing in this way a hole at a. In thermal equilibrium a certain number of atoms will be in the interlattice space and a corresponding number of holes will be left in the lattice.

(2) Two processes can cause diffusion or conductivity: (a) A neighboring ion with sufficient energy can jump over a potential barrier into one of the holes, and a second one can jump into the hole left by the first, etc. Frenkel calls this diffusion of the vacant places. (b) An ion in an irregular position b can jump over potential barriers to other irregular positions or to a vacant place, corresponding to a regular position.

Both processes, movement of the vacant places and movement of a particle in the inter-lattice space give diffusion and electrolytic conductivity. First we have to obtain an expression of the equilibrium concentration of the holes. One migh expect, if n is the number of holes per unit volume, N the number of regular places per unit volume and E the "hole energy," that this concentration would be proportional to $e^{-E/kT}$. Frenkel showed, however, by kinetic reasoning, that one gets instead

$$n \sim N e^{-E/2kT}, \qquad (3)$$

a rather important result.[7] As Frenkel explains, the involved process is analogous to the dissociation of a diatomic molecule. An atom in a regular position "dissociates" into an atom in an irregular position and a vacant place; later an atom in an irregular position can recombine with the vacant place to form an atom in a normal place. It seems worth while to show the validity of this result by a statistical treatment. We consider two sets, each of N cells, the one representing the regular places in the lattice, the other the irregular places in the interlattice space (their number can be different from that of the normal places, but this would not change the general form of the result). We distribute N particles among them. The number of particles in the normal places may be n_0 and in irregular places n_1, where $n_0 + n_1 = N$.

[7] It is remarkable, that in the theory of electronic semiconductors the same expression is obtained. See A. H. Wilson, Proc. Roy. Soc. A133, 458 (1931); 134, 277 (1931). R. Peierls, Ergebnisse der exakten Naturwissenschaften 11, 317 (1932).

Among the n_0 particles let there be $n_0{}^i$ with energy $\epsilon_0{}^i$, and among the n_1 particles, $n_1{}^i$ with energy $E + \epsilon_1{}^i$, where $i = 0, 1, 2 \cdots$ and

$$\sum n_0{}^i = n_0; \quad \sum n_1{}^i = n_1.$$

$$\sum n_0{}^i \epsilon_0{}^i + \sum n_1{}^i (E + \epsilon_1{}^i) = E_0.$$

Now the number of distributions of n_0 particles over N cells and n_1 particles over another N cells is

$$W = \frac{N!}{n_0!(N-n_0)!} \frac{N!}{n_1!(N-n_1)!} = \frac{(N!)^2}{(n_0!)^2(n_1!)^2},$$

if we put not more than one particle in each cell and if we do not distinguish between different particles. Should we distinguish between different atoms, this would have to be multiplied by $N!$, and this being a constant would not affect the following results. Then the number of ways of selecting $n_0{}^i$ particles out of n_0 and $n_1{}^i$ out of n_1, respectively, are (the particles are now distinguished by their positions in different cells)

$$W_0 = n_0! / \prod_i n_0{}^i!,$$

and

$$W_1 = n_1! / \prod_i n_1{}^i!,$$

and so the entire number of complexions

$$W_e = (N!)^2 / n_0! n_1! \prod n_0{}^i! \prod n_1{}^i!.$$

Determining the maximum of W_e under the above conditions, we obtain

$$n_0{}^i = (1/n_0)e^\alpha e^{-\beta \epsilon_0{}^i}; \quad n_1{}^i = (1/n_1)e^\alpha e^{-\beta(E+\epsilon_1{}^i)}$$

and

$$n_0 = \sum n_0{}^i = (1/n_0)e^\alpha \sum e^{-\beta \epsilon_0{}^i};$$

$$n_1 = \sum n_1{}^i = (1/n_1)e^\alpha e^{-\beta E} \sum e^{-\beta \epsilon_1{}^i};$$

thus

$$n_1{}^2 / n_0{}^2 = e^{-\beta E} (\sum e^{-\beta \epsilon_1{}^i} / \sum e^{-\beta \epsilon_0{}^i}).$$

Now for the first approximation we can assume $n_0 \sim N$ and $\epsilon_0{}^i \sim \epsilon_1{}^i$. This gives $n_1 \sim N e^{-E/2kT}$, $\beta = 1/kT$ in accordance with Frenkel's result (Eq. (3)).

So for comparison with experiment we need consider only $1/2$ of the calculated "hole energy." But this value $E/2$ generally will not be the only term in the exponent. For only a fraction of the ions in irregular positions or around holes can move because they have to surmount a potential barrier U. In both cases the total number of ions which move in diffusion and conduction processes is proportional to

$$e^{-(E/2+U)/kT}. \tag{4}$$

Before we derive values for E and U, we shall give an approximate expression for diffusion and electrolytic conductivity in case a and b.

The number of ions in the neighborhood of a hole depends on the lattice type, and is often between 4 and 8. Since the present calculations cannot give more than the correct order of magnitude, we shall assume the total number of ions around holes to be $6n_1$. We assume that the fraction $e^{-U/kT}$ of these ions can jump into holes. If the distance of an ion from the hole is d, and its average velocity is v, the mean thermal velocity, the diffusion constant is approximately $D = dv/2$. Our particles can move only in one direction, but the group of 6 particles around a hole is almost equivalent to one particle, capable of moving in every direction. Thus we obtain as the rate of diffusion near the holes

$$D_h = \tfrac{1}{6}(dv/2)e^{-U/kT}.$$

The average diffusion constant for all particles is given by this expression multiplied by the fraction of ions around holes, which is $6n_1/N$. So we obtain finally

$$D = \tfrac{1}{6}(dv/2)e^{-U/kT} \cdot 6 \cdot e^{-E/2kT}$$

$$= (dv/2)e^{-(E/2+U)/kT}.$$

Using as approximate numerical values $d = 3 \times 10^{-8}$ cm, $v = 5 \times 10^4$ cm sec.$^{-1}$, we obtain

$$A = dv/2 = 7.5 \times 10^{+4} \text{ cm}^2 \text{ sec.}^{+1} \sim 65 \text{ cm}^2 \text{ day}^{-1},$$

as maximum value for A in case of diffusion, in accordance with many of the experiments. To obtain the expression for electrolytic conductivity we may use Einstein's relation

$$D = BkT,$$

where B is the mobility of the ions, and the relation

$$\kappa = n(ze)^2 B,$$

where n is the number of ions per unit volume and ze the charge of one ion. The result is

$$\kappa = [n(ze)^2 \cdot d \cdot v / 2k \cdot T] e^{-(E/2+U)/kT}.$$

The factor before the exponential is practically identical with that derived by the classical electronic theory of metals, and has a numerical value of the same order of magnitude as D (when expressed in $cm^2 \ day^{-1}$), as can be shown by putting in reasonable numerical values. The value of κ is then of the order of magnitude

$$\kappa \sim (10-100)e^{-(E/2+U)/kT},$$

as mentioned above. For the motion in the interlattice space we would obtain practically the same expression. In regard to the application of Einstein's formula we refer to a paper of C. Wagner[8] and mention that our formula for κ could have been derived without Einstein's formula by using Braunbek's[9] method, which also would show that Ohm's law holds within rather wide limits. Of course one could easily obtain more accurate numerical factors by considering special crystal lattices. For instance if we consider particles which can move only in 3 mutually perpendicular directions, our above expression for D would be smaller by a factor $\frac{1}{3}$. Considering the uncertainty of any special assumptions a more accurate treatment is as yet not justified.

The next step is to obtain an expression for the energy E required to move an ion from a regular to an irregular position.[10] To do this we have to consider a special lattice type. As the first example we choose the NaCl-type of lattice. In this case we can obtain in a very simple way a rough value of the "hole energy" E. Suppose that an ion, say at 0, 0, 0 (Fig. 2) is removed to a point $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ in a distant cell. Suppose the new position is so far away from the original one that the potential of the displaced ion at that point can be neglected. This means that in the expression for the potential energy of the displaced ion we can neglect the
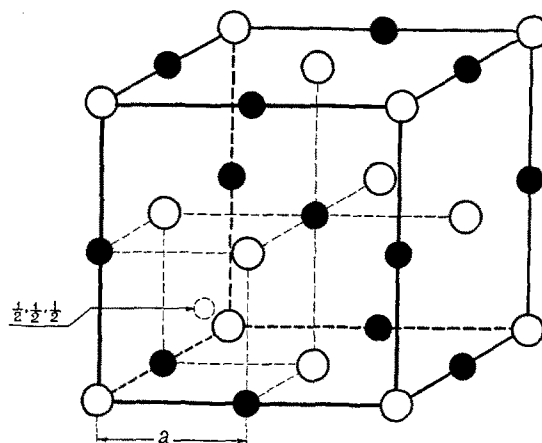
[8] C. Wagner, Zeits. f. physik. Chemie **B11**, 139 (1930).

[9] W. Braunbek, Zeits. f. Physik **44**, 684 (1927).

[10] Work functions, so called "Platzwechsel-energies" have been calculated before, by Rogowski (Arch. f. Elektrotechnik **18**, 123 (1927); and by Braunbek.[6] But both of them derived them for the displacement of the lattice of the positive ions as whole towards the negative ones. Though this calculation for Rogowski's purpose was justified—discussion of the electrical breakdown—its results cannot be used for the process of electrolytical conduction and diffusion which we consider.

Fig. 2. Sodium chloride lattice normal positions and positions in the interlattice space at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, etc.

presence of the hole and of ions in the interlattice space and obtain this energy merely by a summation over all ions in normal positions. The Coulomb part of the potential energy of the ion in its normal place is $-1.74e^2/a$, where a is the interionic distance. Its Coulomb energy in the interlattice space at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ is zero, because it is surrounded quite symmetrically by positive and negative ions; thus the work function would be $+1.74e^2/a$, this is about 8–10 electron-volts. If we should consider the repulsive forces this value would increase to about $2.27e^2/a$. Both values are much higher than the experimentally observed ones. $E/2 + U$, where U is the potential barrier, is about 1 volt for the cations of the alkali and silver halides.

Now it has been pointed out by Fajans[11] and Reis[12] that there is a correlation between electrolytic conductivity in crystals and polarizability and polarizing properties of the ions. Thus the work function for a small ion like Ag^+ would be smaller than that of ions of high polarizability, whereas that of anions with high polarizibility would be correspondingly larger. This gives an explanation of the fact that very often only one kind of ion is mobile. But quantitative calculations on this basis have never been carried through. It has even been concluded by some authors that such an influence could be important only for ions at surfaces, because only in asym-

[11] K. Fajans, Fortschr. d. physikal. Wissensch. (russ.) **V**, 294 (1926).

[12] A. Reis, Zeits. f. Physik **44**, 353 (1927).

metrical fields the polarization energy can reach considerable values. It is obvious that this conclusion is quite wrong. For it is quite unimportant if there exist any initial asymmetrical fields but it is only necessary that such fields be produced in the process of motion: and just this occurs in our case. In the final state we have asymmetrical fields both around the hole and around the ion in the interlattice space. In these fields the polarization energy can become very large, even great enough to compensate practically the whole work function computed only from the Coulomb forces.[13]

For this first estimate we use an expression for the polarization energy obtained by treating the crystal as a continuum* (more exact treatment below). If r_0 is the radius of an ion, considered as a sphere, its electrostatic energy in vacuum is $\frac{1}{2}e^2/r_0$; if we bring it into a medium of dielectric constant ϵ, its energy becomes $\frac{1}{2}e^2/r_0\epsilon$. The polarization energy is evidently the difference between the two

$$E_{pol} = -\frac{1}{2}e_2/r_0((\epsilon-1)/\epsilon).$$

Since a polarization arises around the hole as well as around the displaced ion (now a hole is equivalent to a charge of sign opposite to that of the displaced ion) this polarization energy occurs twice, we have

$$E_{pol} = -(e^2/r_0)((\epsilon-1)/\epsilon).$$

If we take $r_0 = a/2$ and $\epsilon = 6$[14] we obtain

$$E_{pol} = -1.67e^2/a,$$

an expression of the same order of magnitude as the Coulomb potential. Thus the final work function becomes

$$E \sim 0.6e^2/a \sim 2.5 \text{ volts}$$

which agrees quite well with observed values.

Of course, this can be considered only a rough approximation. But even this approximation is sufficient to account for the phenomenon of unipolar conductivity. In NaCl at low temperatures and* in silver halides generally only the cations can move. Now the radii of these cations are smaller than those of the anions; this gives a different value in the repulsive and polarization potential for anions and cations, favoring the mobility of the cations.

It is interesting to investigate a salt of high electrolytic conductivity, for example α-Ag_2S, stable above 179°C. We choose silver sulphide,[15] since it is one of the few salts (the α-modifications of Ag_2S, Cu_2S, AgJ, CuJ, $CuBr$) of extremely high electrolytic conductivity (conductivity as high or higher than that of the best aqueous electrolytes!) for which the lattice structure is known. It crystalizes in the fluorite type of lattice; from the density we take the distance between two silver ions as $a = 3.05A$.

First we compute the electrostatic energy necessary to produce a hole in the following way (see Fig. 3).[16] (A Cartesian coordinate system is placed with its origin at the center of the unit cell of our lattice having its axes parallel to the crystallographic axes.) Let a silver ion, say at

[13] M. Born (Zeits. f. Physik 79, 62 (1932)) has lately discussed in a similar case the "hole energy," in connection with the discrepancy between the theoretical value for the energy of the photographic primary process and the empirical value as determined by Pohl and coworkers. Although in this process the polarization energy in the neighborhood of two neutralized atoms is not quite negligible, it is not mentioned by Born. However, in this case the polarization energy is of a smaller order of magnitude than in ours, because the assymmetrical part of the field, produced by neutralizing two neighboring ions can be represented by a dipole field which decreases much more rapidly with the distance than the assymmetrical Coulomb fields around a hole and around a displaced ion at a distant point in the interlattice space. See, however, W. Klemm, Zeits. f. Physik 82, 529 (1933).

* See also M. Born's calculation of the heat of hydration of ions (Zeits. f. Physik 1, 45 (1920)) and K. F. Herzfeld's discussion Handb. d. Physik 22, 424, Berlin (1926).

[14] In the case of the silver halides ϵ is >10!

[15] Unfortunately the nature of the conductivity of silver sulphide is still under discussion (W. Jost u. H. Rüter, Zeits. f. physik. Chemie B21, 48 (1933). C. Wagner, Zeits. f. physik. Chemie B21, 25 (1933). We can, however, avoid any of these difficulties by basing our discussion on the rate of diffusion which has been measured for copper ions in small concentrations in silver sulphide (H. Braune, Zeits. f. physik. Chemie 112, 270 (1924); C. Tubandt, H. Reinhold, Z. anorg. Chem. 177, 253 (1928); W. Jost u. H. Rüter, Zeits. f. physik. Chemie B21, 48 (1933). From Braunes measurements we take the diffusion constant

$$D = 10 \times e^{-1610/T} \text{ cm}^2 \text{ day}^{-1}.$$

This velocity is as high or higher than that of salts in aqueous solutions!

[16] Holes can also be produced by removing ions to surfaces. But as long as only ions of one type are removed this would give an amount, depending on the size of the surface. Such a process, though it might occur, could not be identified with the generally observed conductivity.
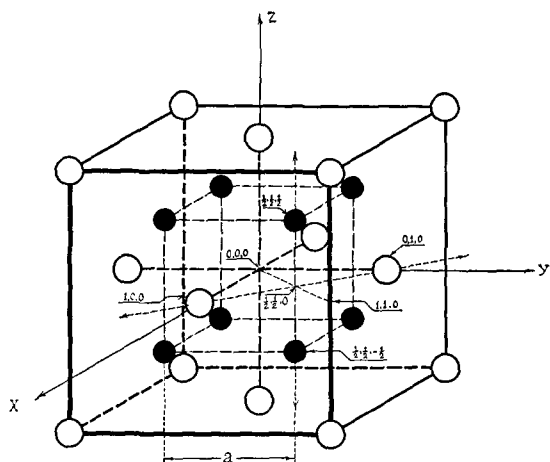
FIG. 3. Silver sulphide (fluorite type of lattice). Normal positions and positions in the interlattice space at 0, 0, 0, etc. Solid circle, silver ions; circle, sulphur ions.

$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ be displaced into the center of a distant complete unit cell, equivalent to the origin 0, 0, 0. Suppose again the new position is so far away from the original position, that we can obtain the potential energy by a summation over all ions in normal positions. The work function E is the difference between the normal lattice energy of a silver ion and the energy of the displaced silver ion in the irregular position 0, 0, 0 with all lattice points in the neighborhood regularly occupied. In the calculation of this energy difference we need only consider in the summation the groups of ions for which the potential at 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, is appreciably different. Although the two individual summations need not converge to the respective lattice energies their difference is independent of the mode of summation. Carrying through this summation for the first 38 negative and the first 55 and 56 positive ions respectively (since in the first case the potential of the ion $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ on itself has to be omitted) we obtain as electrostatic potential energies of an ion at

$$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \qquad\qquad 0, 0, 0,$$

$$-10.289\ e^2/a + \text{const.} \quad -7.981\ e^2/a + \text{const.}$$

$$\Delta E_{\text{Coul}} = +2.308\ e^2/a.$$

The separate contributions to Δ of the following positive and negative ions can be neglected as was tested by a further summation. By consideration of the repulsive forces this

energy would decrease slightly (see below), but still its value would be about 9 electron-volts, much higher than the experimental value, which in the case of silver sulphide must be of the order of magnitude of 0.1 volt.

Again the discrepancy can be removed by consideration of the polarization energy. The expression for the polarization energy is

$$E_{\text{pol}} = -\sum[(\alpha_-)/2(F_-{}^i)^2 + (\alpha_+)/2(F_+{}^i)^2]$$

where α_- and α_+ are the respective polarizabilities of anions and cations and F_+ and F_- are the field strengths at the positions of the respective ions. The summation must be extended over the neighborhood of the hole and over that of the ion in the interlattice space, where again the assumption is involved that the distance between the hole and the displaced ion is large. For the field strengths F besides those produced by the silver ion (in the neighborhood of the hole the field is equivalent to that of a negative charge in the original position of the removed silver ion; but because it appears in the square we can as well take the field of one silver ion) we have to consider those produced by the induced dipoles. It is almost impossible to do this exactly. Thus we computed first the polarization energy neglecting the fields of the induced dipoles. To take into account this effect and the fact, that the polarizability in the inhomogeneous fields in the neighborhood of ions would be smaller than that observed in homogeneous fields, we take only one-half of the above polarization energy. This assumption was tested by considering roughly the dipole fields; furthermore the value obtained in this way is almost identical with that obtained by treating the crystal as a homogeneous dielectric. Carrying through the summation in the neighborhood of a hole and of an ion in the interlattice space we obtain for the polarization energy

$$E_p = -(9.3\alpha_- + 16.2\alpha_+)e^2/a^4.$$

In addition we have to consider the potential of the repulsive forces. We use Born's expression for this potential between a silver and a sulphur ion, we have

$$E_{+-} = +1/9 \times 0.63(e^2 r_0{}^8/r^9)$$

where r_0 is the equilibrium distance in the lattice

and where the numerical factor is obtained by means of the equilibrium condition for the lattice (only repulsive forces between a sulphur ion and the nearest silver ions have been considered, which is allowable in the first approximation). For the repulsive potential between two silver ions we have a corresponding expression

$$E_{++} = 0.29e^2\sigma^8/9r^9,$$

where σ is the diameter of a silver ion, taken from Goldschmidt's data. The numerical factor is taken from the NaCl type of lattice; this means that we assume for the repulsion between two silver ions at a distance equal to the sum of their radii the same expression that holds for the forces between an alkali and a halogen ion.[17] We obtain for the increase of the repulsion potential for an ion, attending its removal from a normal place to a place in the interlattice space

$$\Delta E_{rep} = -0.11(e^2/a).$$

In the expression for the polarization energy we have to express α in units of a^3. With the data given by Van Vleck[18] and dividing the final expression by 2 we obtain $E_p = -2.15e^2/a$.[19]

Finally we obtain for the complete work function associated with the displacement of an ion from its normal position into the interlattice space

$$E = \Delta E_{Coul} + \Delta E_{rep} + E_p = (2.31 - 0.11 - 2.15)e^2/a$$
$$= +0.05e^2/a \sim 0.24 \text{ electron-volts,}$$

which is of the same order of magnitude as the observed value for $E/2 + U$ (U potential barrier) 0.14 volt. Of course this result is only an approximate value, but in any case it shows that the work function is small. One must not conclude that a small or even negative value of the work function would mean instability of the lattice, and therefore be physically impossible. For our main assumption was that in the neighborhood of a vacant place there was no other vacant place. This means that only a certain small fraction of ions can be removed with so little energy, for the succeeding ones more energy would be required. In any case we may conclude from our calculation that the work function is small compared with the lattice energy, and this is just what follows from the experiments.[20]

The last step that still remains is to find a value for the height of the potential barriers connected with the motion either of an ion near a hole or in the interlattice space. It can be shown that these values are also small compared with the lattice energy, though the accuracy of our calculations is not yet sufficient to give full agreement with the observed values in the case of Ag$_2$S. This is as much as we can expect for the present.

Let us first consider a vacant place, let as say at $-\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{1}{2}$ (see Fig. 3). Suppose that a silver ion at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ jumps in a straight line into this vacant place. On its way it has to pass two equal potential barriers whose height depends chiefly upon the repulsive forces of the surrounding negative ions. These maxima are

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[17] This approximation for the repulsive potentials may be not very good. But the inaccuracy certainly lies within the limits of other approximations we have made, and a more accurate treatment would be worth while only if a much better approximation could be obtained. This would require that besides considering van der Waals forces (M. Born and J. E. Meyer, Zeits. f. Physik **75**, 1 (1932)) one would have to abandon the simple expression for the repulsive forces consisting of an inverse power or an exponential function of the distance. Both assumptions are too rough for such a close approach of the ions though they allow one to calculate good values for the equilibrium energy of the lattice. And furthermore one would have to consider the displacement of ions in the neighborhood both of holes and of migrating ions. Moreover the polarizability may not be assumed to be constant. See also J. E. Meyer, J. Chem. Phys. **1**, 327 (1933).

[18] Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932.

[19] By using the expression for a continuous dielectric, as we did above, we should obtain for the polarization energy $\sim -2.4 \, e^2/a$, if we use Goldschmidt's data for the radius of the Ag-ion, and for the dielectric constant $\epsilon = 10$ (this corresponds about to the value for AgCl; the dielectric constant of Ag$_2$S has not been measured, but cannot be smaller than this value).

[20] In the case, where the work function is almost zero, we may assume for the present approximation that a certain fraction of ions is removed from regular places, depending only very little on temperature, whereas it would require much higher energy to remove more ions. It is noteworthy that this result is equivalent to a picture given by G. C. Schmidt (Ann. d. Physik **80**, 605 (1926)). He assumed for the explanation of the experimentally found unipolar conductivity, that the crystal is built up of complex molecules, from which only one ion can dissociate with little energy.

reached in the neighborhood of the points $\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{3}$ and $-\frac{1}{3}$, $-\frac{1}{3}$, $-\frac{1}{3}$, and have values of about $0.1e^2/a$. But this is not the maximum of the potential in the path of the ion. At the point 0, 0, 0 the potential energy has a higher value, which we can compute approximately. We have already calculated the difference in Coulomb potential for $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and 0, 0, 0 when all surrounding positions are occupied. This was $+2.3e^2/a$.

If we now consider repulsive forces and the fact that initially $-\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{1}{2}$ is unoccupied, and then during the displacement both this place and the position $+\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ are unoccupied, we obtain $\Delta E = \sim 0.45e^2/a$, where the change in polarization energy is neglected, which, as an approximate calculation showed, certainly would not decrease this value. Though this value is of the usually observed order of magnitude, about 2 volts, it is too high for the case of silver sulfide. Thus it seems more probable that motion in the interlattice space is the actual process occurring in the case of silver sulfide. However, our calculations do not exclude the first process. It is readily seen that they must yield a result which generally is too high. For we have regarded the surrounding ions as remaining fixed in the lattice, whereas indeed by any perturbation such as that produced by a displaced ion or a hole, they will tend to move to new equilibrium positions with lower potential energy.

Thus far we have considered only the motion of an ion from a normal position to another normal position which is vacant. Now we shall consider the migration of ions initially in abnormal lattice position at equilibrium. In this process the assumption that the neighboring ions are not displaced in the path of the migrating ion has to be abandoned. An ion in the interlattice space at 0, 0, 0 (see Fig. 3) may move to the equivalent point 1, 1, 0. Obviously it has to pass an energy maximum at $\frac{1}{2}$, $\frac{1}{2}$, 0 due to repulsive forces. If we should calculate the repulsive potential for this point we should obtain extremely high values, but these would not mean much because the applied formulae do not hold at such small distances. What really will happen if we bring a silver ion to $\frac{1}{2}$, $\frac{1}{2}$, 0 is that the silver ions at the neighboring points $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$ as well as the sulphur

ions at 1, 0, 0 and 0, 1, 0 will be pushed aside in the direction of the arrows (Fig. 3.) Since not only these neighboring ions but also those in the distant surrounding would be displaced it is practically impossible to give an exact treatment. We shall first try to get an approximation by assuming reasonable displacements of the immediate neighbors and then calculate the work required for this displacement and the potential between a silver ion and the nearest surrounding ions.

We choose the displacement of the neighboring ions so that the repulsive potential is the same as for the ion in 0, 0, 0. This displacement is not very different from that which makes the distance between the migrating Ag-ion at $\frac{1}{2}$, $\frac{1}{2}$, 0 and the lattice silver ions equal to twice the radius of a silver ion, and the distance to the next sulphur ions equal to the normal lattice distance $a/2 \cdot 3^{\frac{1}{2}}$. We do not need to know these distances more exactly because in our later computation of the Coulomb potential they enter only with the first power. The assumed displacements are the following; $0.24a$ for the silver ions and $0.16a$ for the sulphur ions. The Coulomb potential at $\frac{1}{2}$, $\frac{1}{2}$, 0, if one neglects the displacements of the surrounding ions, differs from that at 0, 0, 0 by an amount $+0.16e^2/a$. If we consider in the change of potential produced by shifting the neighboring ions only the contribution of the above mentioned 4 nearest ions, we obtain an additional contribution $-0.26e^2/a$. Thus for the first approximation the change in the Coulomb potential and repulsive potential (the latter is zero!) becomes $\Delta E_1 = -0.10e^2/a$.

It remains to calculate the work required for the displacement of the four neighboring ions. We take a one dimensional model, a chain of alternating positive and negative ions, of which we take into account 12 ions of charge $\pm e$ (see Fig. 4). We displace the ions symmetrically from the center so that the distance between the middle ions becomes 1.5 times the original distance a and that between each other pair of neighboring ions $0.95a$. We compute the change in potential energy assuming Coulomb and repulsive forces. Using Madelung's[21] potential and the inverse ninth power for the repulsive

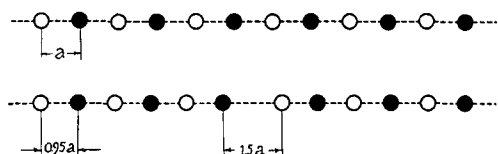[21] E. Madelung, Phys. Zeits. **19**, 524 (1918).

FIG. 4. One-dimensional model representing the deformation of the lattice by a migrating ion.

potential we find by means of the equilibrium condition for the latter $0.69e^2a^8/9r^9$.

Then we find for the change in potential energy for the above displacement, considering the Coulomb forces between every pair of the 12 ions and the repulsive forces between each pair of neighboring ions $\Delta E = 0.18e^2/a$. The compression could actually be distributed over a still longer chain of ions, which would decrease the required energy even more. We assume, that this value also gives the right order of magnitude for a three dimensional model, for which we assume as an approximate value $\Delta E_2 = 0.2e^2/a$. The sum of this energy and the Coulomb contribution ΔE_1 yields the following value for the potential barrier

$$U \sim 0.1e^2/a \sim 0.45 \text{ e.v.,}$$

as long as we neglect the change in the polarization energy, which could not be great. In the above we have arbitrarily determined the displacements in a way that allowed simple calculations, whereas they should be determined to give a minimum value of the barrier. Though this minimum problem cannot be solved without a prohibitive amount of labor, the result obtained with the assumed approximations makes it probable that the proposed mechanism accounts satisfactorily not only for the generally observed order of magnitude of the barrier but also gives fair agreement with the actual values in the case of silver sulfide. The observed value for $E/2 + U$ in this case is 0.14 e.v., our calculations give 0.6 volt. Better agreement than one of order of magnitude can not be expected.[22]

To show that the special properties of Ag_2S are necessary to obtain a work function of almost zero we give here the approximate value for Na_2S, which is isomorphous with Ag_2S, with an interionic distance of 3.26A. The main difference in the work function is caused by the difference in the polarization energy, which depends on the larger interionic distances and the smaller polarizability of the sodium ion compared with the silver ion.[23] For the polarization energy we obtain with the same assumptions as above $E = -1.42e^2/a$.

This is smaller (in its absolute value) than for the case of silver sulphide by about $0.7e^2/a$, and this difference accounts at once for the generally observed small conductivities of alkali compounds as compared with the analogous silver compounds (the conductivity of Na_2S has not yet been measured). By an approximate calculation of the work function for sulphur ions in case of silver sulphide we can easily account for the experimental fact of unipolar conduction.

The formal manner in which A-values higher than about 100 could be explained[24] may be mentioned at this point.* There seems to be

[22] We have not yet discussed the mechanism of transfer of an ion between normal positions and abnormal ones in the interlattice space. It may happen that the potential barrier, which an ion must cross is greater than the energy difference between its initial and final positions. Apparently this additional potential barrier is unimportant for electrolytic conduction, which depends only on the equilibrium concentration of ions in the interlattice space. However, for diffusion this barrier is quite important, because in the process of concentration equalization the exchange of ions in normal positions and in the interlattice space has to be considered. It is necessary, that the microscopic equalization occurs in a time interval very small compared to the time required for the propagation of ions over observable distances. For a detailed discussion one may refer to the treatment of an analogous problem given in a previous article (W. Jost, Zeits. f. physik. Chemie **B9**, 73 (1930)).

[23] Using the formula for a continuous dielectric to obtain approximate results, one would have to assume for r_0 in case of Na_2S a higher value than in the case of Ag_2S. For not the diameter of the cation is of importance, but the distance to the nearest surrounding ions.

[24] See also: W. Jost, Zeits. f. physik. Chemie **B16**, 129 (1932).

* *Note added in proof.* I am indebted to Professor K. F. Herzfeld for calling my attention to the fact that similar difficulties arise in the treatment of thermionic emission; the observed factor multiplying the exponential is sometimes of greater order of magnitude than the maximum theoretical value. This discrepancy has been attributed to the neglect of the temperature variation of the work function (see e.g., L. Brillouin, *Les Statistiques Quantiques*, Vol. II, p. 223, Paris, 1930). It is very probable that a similar situation exists in the case of electrolytic conduction since it is readily seen that the work function might vary considerably with temperature. In view of this fact one

only one possibility which is satisfactory, though it is not easily proved. If an ion, moving in the interlattice space, has enough energy to pass one energy barrier, then its energy is also sufficient to pass an infinite number of barriers as long as the energy is not used to excite lattice oscillations.[25] Thus one has to expect a variable free path, depending on this excitation function. If the expression for the mean free path λ were of the form

$$\lambda = f \cdot a \cdot e^{-U'/kT},$$

where f is a large number, then one would obtain a formula in agreement with the experiments without having unreasonable values for the actual free path as long as U' is large enough.

A second reason for a variable free path for the motion of a particle in the interlattice space if the following; because of the presence of "holes" and of ions in the interlattice space, which we neglected in the first approximation, the potential barriers will not all be of the same height, and a path which is short for an ion of low energy may be longer for an ion with higher energy. This suggests an exponential dependence on temperature of the sort already mentioned.

Of course one would also have to discuss the influence of holes and ions in the interlattice space on the work function, but a more detailed treatment does not seem to be justified as long as one cannot obtain much more accurate results. By the above calculations we have shown that for a model representing a motion of particles in the lattice one obtains reasonable values for the electrolytic conductivity and diffusion. For the present one cannot yet expect to obtain accurate numerical values. The agreement in order of magnitude seems to prove the correctness of our assumptions, and indicates that objections raised against a lattice process are not tenable. Of course our model as already mentioned by Schottky and Wagner[26] would permit an explanation of effects depending on perturbations of the lattice, if one assumes that at low temperatures thermal equilibrium is not always reached. For metals similar ideas would have to be assumed. Here holes in the crystal can be produced by removing particles to the surface, without transferring them into the interlattice space.[27] This process would also be possible with ionic crystals, but it is rather improbable; an effect not depending on the size of the surfaces could only be obtained by removing equal numbers of positive and negative ions, by building up new lattice structures outside the former surface.

is not justified in drawing general conclusions concerning the conduction mechanism from the observed deviations from a simple exponential relation.

[25] Compare A. v. Hippel, Zeits. f. Physik **75**, 145 (1932), who discusses the same question for electrons in the case of the electric breakdown of insulators.

[26] W. Schottky, H. Ulich u. C. Wagner, Thermodynamik S, 380 (1929); W. Schottky and C. Wagner, Zeits. f. physik. Chemie **B11**, 163 (1930); C. Wagner, Zeits. f. physik. Chemie. Bodenstein-Festband, S, 177 (1931).

[27] This means: extending the crystal beyond its original limits.