CONDUCTION IN POLAR CRYSTALS.
I. ELECTROLYTIC CONDUCTION IN SOLID SALTS.

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1.

The electrolytic conductivity of solid polar salts was first discussed from a theoretical point of view by Frenkel.[1] Frenkel's ideas have more recently been developed by Jost.[2] According to Jost, in any polar lattice in thermal equilibrium at temperature T a number of ions will leave their proper positions, such as (a) in Fig. 1, and occupy "interlattice" positions such as (b). If E is the work required to remove an ion from a position (a) to a position (b) at an infinite distance, then these authors show that the proportion of the total number of ions of the lattice which are in "interlattice" positions is
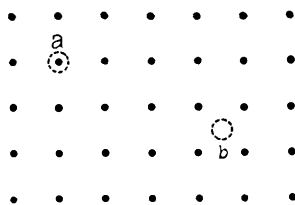

Fig. 1.

$$e^{-\frac{1}{2}E/kT}.$$

The quantity E will in general be different for the several kinds of ion of which the lattice is built up.

Both the holes left by the displaced ions, and the displaced ions themselves, will be mobile, and may be assumed to have a mobility of the form

$$\text{const. } e^{-U/kT},$$

U being, in the case of the ion in an interlattice position, the work required to move the ion half-way to its next metastable position. The conductivity σ will thus be of the form

$$\sigma = \text{const. } e^{-(\frac{1}{2}E + U)/kT}.$$

[1] Frenkel, *Z. Physik*, 1926, **35,** 652.
[2] Jost, *J. Chem. Physics*, 1933, **1,** 466 ; *Z. physik. Chem., A*, 1934, **169,** 129 ; B, 1936, **32,** 1 ; *Diffusion und Chemische Reaktion in festen Stoffen*, Leipzig, 1937.
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Schottky [3] has proposed an alternative mechanism.   According to him, in the alkali-halide crystals the work required to pack even the small metal ion into an interlattice space will be so great that at ordinary temperatures the number of such ions will be insignificant.   But even in this case it is possible to remove a positive *and* a negative ion from their lattice points, and to place them on the outside of the crystal. The work necessary for this process is

$$W = W^+ + W^- - W_L$$

where W^+ is the work required to remove a positive ion out of the crystal, W^- the work required to remove a negative ion, and W_L the lattice energy of the crystal per ion pair.   Schottky shows that in a crystal in thermal equilibrium at temperature T the number of such pairs of vacant places is proportional to

$$e^{-\frac{1}{2}W/kT}.$$

The conductivity will be due to the motion of the vacant lattice points through the crystal, a certain activation energy being again necessary.

Schottky and Jost have estimated the energies E, U, W etc., by treating the vacant lattice points as holes in a medium of uniform dielectric constant, and also by estimating the energy due to the exchange repulsive forces between the ions.   They show on energetic grounds that for the alkali halides the conductivity will be mainly of the Schottky type, while for the silver halides it is of the Jost type, a conclusion which is supported by experiments due to Wagner and Beyer.[4]

It is the purpose of the present paper to attempt a detailed calculation of the energies E, U, W etc., for alkali-halide crystals on the basis of the Born theory of polar lattices.   For this purpose we develop a mathematical method for calculating the polarisation of a crystal round a vacant lattice point.   This method may be applied to a number of similar problems, for example the optical absorption spectra of polar salts ; this is done in the following papers.

In § 2 we discuss the theory of the dielectric constant of polar salts, which is important for our calculation.   In § 3 we show how to find the field round a point charge placed at any lattice point of a simple cubic crystal, of which the atoms are polarisable but are not free to move. In § 4 we extend these calculations to the case of a polar salt in which the ions are free to move in the field.   In § 5 we use these calculations to obtain the energies referred to above.

2. The Dielectric Constant.

We must distinguish between the dielectric constant κ for static fields and κ_0 for alternating fields of frequency great compared with that of the residual rays ($5 \cdot 10^{12}$ sec.$^{-1}$). $\sqrt{\kappa_0}$ is the refractive index in the near infrared.   We may take κ_0 to be given by

$$\frac{\kappa_0 - 1}{\kappa_0 + 2} = \frac{4\pi}{3} \frac{1}{a^3} \frac{\alpha_1 + \alpha_2}{2} \qquad . \qquad . \qquad . \quad (2.1)$$

where a is the interionic distance and α_1, α_2 are the polarisabilities of the ions.

The polarisation of the crystal in static fields is due to the displacement of the positive and negative ions in opposite directions by the applied field,

[3] Schottky, *Z. physik. Chem.*, B, 1935, **29**, 335.
[4] *Ibid.*, 1936, **32**, 113.

as well as to their polarisability. This displacement may be calculated in the following way for crystals with the sodium-chloride structure.

The potential energy of a pair of ions of unlike sign at a distance r from one another may be written

$$- \frac{e^2}{r} + w(r),$$

where $w(r)$ is called the " overlap " energy.[5]

Consider now a displacement in which the positive ions are displaced a distance x to the right, the negative ions a distance x to the left. Let the restoring force *due to the " overlap " repulsion between the ions* be $- px$ on each ion. To find p we note that when the ions are displaced the change in the energy per ion pair is

$$w(a + 2x) + w(a - 2x) + 4w(\sqrt{a^2 + 4x^2}) - 6w(a) \qquad . \qquad (2 \cdot 2)$$

This includes the interaction between nearest and next nearest neighbours, the latter being zero. Expanding and differentiating with respect to x, we obtain for p

$$p = 4[w''(a) + 2w'(a)/a] \qquad . \qquad . \qquad . \qquad (2 \cdot 3)$$

Following Born and Mayer,[6] we set for $w(r)$

$$w(r) = Ae^{-r/\rho}, \qquad . \qquad . \qquad . \qquad . \qquad (2.4)$$

and thus obtain for p,

$$p = 4A \left(\frac{1}{\rho^2} - \frac{2}{a\rho} \right) e^{-a/\rho}. \qquad . \qquad . \qquad . \qquad (2.5)$$

We estimate A by making use of the condition that the crystal is in equilibrium, namely

$$\alpha_M e^2/a^2 = 6A \rho^{-1} e^{-a/\rho} \qquad \alpha_M = 1 \cdot 7476$$

which gives

$$p = \frac{2\alpha_M e^2}{3a^2} \left[\frac{1}{\rho} - \frac{2}{a} \right] \qquad . \qquad . \qquad . \qquad . \qquad (2 \cdot 6)$$

Thus p is given in terms of the repulsive exponent ρ, which has been deduced by Born and Mayer,[6] from the compressibility of the alkali-halides.

To calculate the dielectric constant, then, we need only to know the electrostatic force on each ion. If there were no overlap between the ions we could take this to be

$$E + \frac{4\pi}{3} P \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2 \cdot 7)$$

where E is the field in the dielectric and P the polarisation. This assumption gives, in the usual way,

$$\frac{\kappa - 1}{\kappa + 2} - \frac{\kappa_0 - 1}{\kappa_0 + 2} = \frac{4\pi}{3} \frac{e^2}{pa^3}. \qquad . \qquad . \qquad (2 \cdot 8)$$

From (2.6) and (2.8), together with observed values of κ, κ_0, we may calculate ρ, but obtain values which differ considerably from those deduced from the compressibility, as is shown in Table I ; the first column shows Mayer's values, and the second (marked $\gamma = 1$) from the dielectric constant using (2.8).

The disagreement between theory and experiment is probably due to the term $4\pi P/3$ in (2.7), which is accurate only if the induced dipoles may be treated as points. We therefore modify the theory as follows : We divide the polarisation of the crystal into two terms

$$P = P_0 + P_1.$$

[5] Cf. Fowler, *Statistical Mechanics*, 2nd ed., p. 320
[6] *Z. Physik*, 1932, **75,** 1.

where P_0 is the polarisation due to the induced dipoles on the ions and P_1 ($= ex/a^3$) is the polarisation due to the displacement of the ions. Following a paper due to Heckmann,[7] we then assume that the field effective in polarising each ion is

$$E + \frac{4\pi}{3}(P_0 + \gamma P_1),$$

and the field effective in displacing each ion is

$$E + \frac{4\pi}{3}(P_1 + \gamma P_0),$$

where γ is a numerical constant. The physical basis of such an assumption will be given below.

TABLE I.—VALUES OF THE CONSTANT ρ IN THE OVERLAP ENERGY ; THOSE DEDUCED FROM THE DIELECTRIC CONSTANT USE THE EXPERIMENTAL VALUES OF κ, κ_0 GIVEN IN TABLE II.

Crystal.	$\rho(\times 10^8$ cm.)		
	from compressibility (Born and Mayer).	from dielectric constant	
		$\gamma = 1$ formula 2·8.	$\gamma = 0$.
NaF .	—	0·20	0·26
NaCl .	0·326	0·20	0·32
NaBr .	0·334	0·19	0·34
NaI .	0·384	0·20	0·38
KCl .	0·316	0·21	0·32
KBr .	0·326	0·20	0·33
KI .	0·351	0·19	0·34
RbCl .	0·356	0·22	0·33₅
RbBr .	0·340	0·20	0·34
RbI .	0·351	0·18	0·33

The dielectric constant may then be found as follows : for P_1 we have

$$P_1 = \frac{e^2}{pa^3}\left[E + \frac{4\pi}{3}(P_0 + \gamma P_1)\right],$$

where p is the restoring force per unit displacement defined above. For P_0 we have

$$P_0 = \frac{\alpha}{a^3}\left[E + \frac{4\pi}{3}(P_0 + \gamma P_1)\right],$$

where $\alpha = \frac{1}{2}(\alpha_1 + \alpha_2)$. Writing $\beta_0 = \alpha/a^3$, $\beta = e^2/pa^3$ we obtain

$$\frac{\kappa - 1}{4\pi} = \frac{P}{E} = \frac{8\pi\beta\beta_0(\gamma - 1)/3 + (\beta + \beta_0)}{1 - 4\pi(\beta + \beta_0)/3 + 16\pi^2\beta\beta_0(1 - \gamma^2)/9} \qquad . \quad (2 \cdot 9)$$

For $\gamma = 0$ this reduces to

$$\kappa - \kappa_0 = \frac{4\pi\beta}{1 - 4\pi\beta/3} \cdot \qquad . \qquad . \qquad . \qquad (2 \cdot 10)$$

using formula (2.1) for κ_0. For $\gamma = 1$ formula (2.8) is obtained.

The values of ρ calculated from (2.10) and (2.6) are shown also in Table I, marked $\gamma = 0$. It will be seen that the values obtained agree much better with Born's values from the compressibility than those obtained before (i.e. with $\gamma = 1$). We may deduce that $|\gamma|$ is small compared with unity, or, in other words, that, in calculating the interaction between induced dipoles in the ions and the displacements of the ions, the term $4\pi P/3$ is to be neglected.

Additional evidence that γ is small compared with unity may be obtained from the relation between the dielectric constant and the residual rays. Consider a crystal in which the positive ions are vibrating in one direction, the negative in the opposite. Let the displacements of the ions at any moment be

$$x_1 = M_2\xi/(M_1 + M_2), \quad x_2 = M_1\xi/(M_1 + M_2),$$

[7] Z. Krystall., 1925, **61**, 250 ; Z. Physik, 1925, **33**, 646.

where M_1, M_2 are their masses. If $- q\xi$ is the restoring force on any ion, then the frequency of the vibration is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{q}{M}} \qquad M = \frac{M_1 M_2}{M_1 + M_2}.$$

This restoring force is actually made up of the term px already discussed, and a term due to the interaction of the dipoles. We do not, however, need to discuss the latter in detail.

If now the crystal is placed in a static field E (E is the field within the crystal), the displacement ξ of the ions is given by

$$q\xi = e\left(E + \frac{4\pi}{3}\gamma P_0'\right)$$

where P_0' is the additional polarisation of the ions due to the field E, and γ the factor already introduced. Since

$$P_0' = (\kappa_0 - 1)E/4\pi,$$

this gives

$$q\xi = eE[1 + \tfrac{1}{3}\gamma(\kappa_0 - 1)],$$

and hence

$$P_1 = \frac{e^2 E}{qa^3}[1 + \tfrac{1}{3}\gamma(\kappa_0 - 1)]. \qquad . \qquad . \qquad . \quad (2.11)$$

If, as before, α_1, α_2 are the polarisabilities of the ions, we have

$$P_0 = \frac{\alpha_1 + \alpha_2}{2a^3}\left[E + \frac{4\pi}{3}(P_0 + \gamma P_1)\right]. \qquad . \qquad . \quad (2.12)$$

Making use of the equation (2.1) to eliminate $\alpha_1 + \alpha_2$, we obtain from (2.12)

$$P_0 = \frac{\kappa_0 - 1}{4\pi}\left[E + \frac{4\pi}{3}\gamma P_1\right]. \qquad . \qquad . \qquad . \quad (2.13)$$

From (2.13) and (2.11) we obtain P_0, P_1 in terms of E; since

$$\kappa - 1 = 4\pi P/E,$$

we obtain finally

$$\frac{\kappa - \kappa_0}{[1 + \tfrac{1}{3}\gamma(\kappa_0 - 1)]^2} = \frac{4\pi e^2}{qa^3} = \frac{Ne^2}{\pi M \nu^2}. \qquad . \qquad . \quad (2.14)$$

This formula was first given by Heckmann.[7] In Born and Göppert-Mayer's article [6] the term $4\pi P/3$ is neglected, and thus the formula is derived with $\gamma = 0$.

TABLE II.

	$\dfrac{Ne^2}{\pi M \nu^2}$.	κ.	κ_0.	γ.
LiF . .	6·20	$9·27^{a,\ b}$	1·92	0·29
NaF . .	3·10	$4·9^b$	1·74	0·04
NaCl . .	2·94	$5·62^a$	2·33	0·13
NaBr . .	1·95	$6·0_0{}^b$	2·70	0·53
NaI . .	2·72	$6·6^b$	2·96	0·24
KCl . .	2·12	$4·8^{b,c}$	2·17	0·29
KBr . .	2·03	$4·7_8{}^b$	2·35	0·21
KI . .	1·94	$4·94^b$	2·65	0·16
RbCl . .	1·95	$4·78^c$	2·18	0·39
RbBr . .	1·65	$4·7^b - (5·1)^c$	2·34	$0·44 - (0·66)$
RbI . .	1·62	$4·51^c$	2·59	0·17

[a] Büchner and Eucken, *Z. physik. Chem. B*, 1934, **27**, 321.
[b] Errera, *Physik. Z. Sov. Union*, 1933, **3**, 443; *Z. Electrochemie*, 1930, **36**, 18.
[c] Højendahl, *Z. physik. Chem. B*, 1933, **20**, 54.

In Table II we show the values of γ deduced from experimental values of κ, κ_0, ν. It will be seen that γ is in general nearer to zero than unity. This is in agreement with our conclusions deduced above from the attempt to calculate κ using an overlap energy deduced from the compressibility.

We must now discuss the physical meaning of the factor γ. The fact that γ is not equal to unity must be connected with the fact that the ions overlap. In all these crystals the negative ions are much more polarisable than the positive ; the quantity κ_0 is mainly due to the negative ions ; and since the latter do not overlap very much, it is reasonable to include the term $4\pi P/3$ in calculating κ_0.
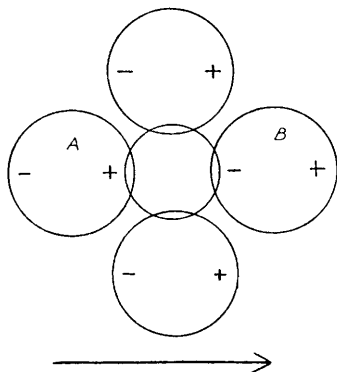
But consider now the force tending to displace a positive ion due to dipoles μ induced on the negative ions. In Fig. 2 the small sphere represents a positive ion and the large spheres negative ions. The arrow shows the direction of the external field. The induced dipoles on the negative ions are not, of course, at the centres of these ions, but the excess positive and negative charge will be mainly near the edge of the ion. If there is any considerable overlap between the positive ion and the adjacent ions A and B the force on the positive ions due to the dipoles on the latter will be considerably less than $4\mu/a^3$, and may be even reversed in sign.

FIG. 2.

The field at the central ion is

$$E + \frac{4}{3}\pi\gamma\mu/a^3,$$

while, if we subtract the contributions from A and B we obtain a field

$$E + \left(\frac{4}{3}\pi - 4\right)\mu/a^3.$$

Thus the contribution from this pair of dipoles must be taken to be

$$\left[\frac{4}{3}\pi(\gamma - 1) + 4\right]\mu/\gamma^3.$$

If $\gamma = 0$ this is equal to $0.2\ \mu/a^3$, and we see that the contribution of these dipoles is approximately zero.

A similar argument may be applied to the dipoles induced on a negative ion by the displacement of the positive ion ; if the positive ion has penetrated inside it, its displacement will have the opposite effect to what it would have if it were outside.

Eucken and Büchner [8] have discussed the dielectric constant of semipolar crystals of high dielectric constant, and assume that the relative motion of the positive and negative ions affects the charge on either ion. We shall neglect any such effect for the alkali-halides.

3. Polarisation Round a Point Charge in a Lattice with the Ions Fixed.

We discuss first the problem of a *rigid* lattice, in which the ions are not allowed to move away from their mean positions, but in which they have polarisabilities α_1, α_2. Suppose a charge Q is placed at a definite point of the lattice, referred to as the point Q. Then dipoles are induced on all

[8] *Z. physik. Chem.*, B, 1934, **27**, 321.

the other ions. Our first problem is to find the potential V at the point Q due to these dipoles.

The difficulty of the problem lies in the fact that the dipole on any one ion is due, not only to the charge Q but to the dipoles at all the other lattice points as well.

Denote as before by κ_0 the dielectric constant of the medium (for undisplaced ions) ; κ_0 is given in terms of α_1, α_2 by (2.1). Then at a large distance r from Q the polarisation of the medium is

$$P = \frac{Q}{r^2}\,\frac{1}{4\pi}\left(1 - \frac{1}{\kappa_0}\right),$$

and so the dipoles induced on the ions are

$$M_1 a^3 Q/r^2, \quad M_2 a^3 Q/r^2 \qquad . \qquad . \qquad . \qquad . \qquad (3.1)$$

where

$$M_1 = \frac{2\alpha_1}{\alpha_1 + \alpha_2}\,\frac{1}{4\pi}\left(1 - \frac{1}{\kappa_0}\right) \qquad . \qquad . \qquad . \qquad (3.2)$$

with a similar expression for ions of type 2.

Our zero order approximation is to assume that (3.1) holds for *all* the ions of the lattice. Then, since a dipole μ at a given lattice point gives a potential $-\mu/r^2$ at Q, we can obtain the potential V by direct summation

$$V = - Qa^3\left[M_1 \sum_1 \frac{1}{r^4} + M_2 \sum_2 \frac{1}{r^4}\right].$$

Here r denotes the distance of any lattice point from Q, and the summations are over the lattice points of types 1 and 2.

In the applications of this paper Q will be taken at some simple lattice position. Consider, for instance, a sodium chloride lattice and take Q at a lattice point of type 2. Then the summations are those carried out by Jones and Ingham,[9] and we obtain

$$V = - \frac{Q}{a}(6.3346\,M_2 + 10.1977\,M_1). \qquad . \qquad . \qquad (3.3)$$

As our approximation of first order, we take as unknown the dipoles μ on the six nearest neighbours to Q, *viz.*, those at the (100) lattice points. We assume (3.1) to be valid for all the other ions. The field at a (100) lattice point due to the dipoles on all the ions outside it we found by direct summation [10] to be

$$E_1 = - \frac{Q}{a^2}(0.388\,M_1 + 1.965\,M_2), \qquad . \qquad . \qquad (3.4)$$

and that due to the other five (100) ions is

$$E_2 = - 2.371\,\mu/a^3,$$

the minus sign denoting that the field is in the opposite direction to that due to Q. The equation for μ is then

$$\mu = \alpha_1\left[\frac{Q}{a^2} + E_1 + E_2\right],$$

giving, if we write $\mu = Qam$, $\beta_1 = \alpha_1/a^3$, $\beta_2 = \alpha_2/a^3$,

$$m = \frac{\beta_1(1 - 0.388\,M_1 - 1.965\,M_2)}{1 + 2.371\,\beta_1}. \qquad . \qquad . \qquad (3.5)$$

The potential at the centre is then, to the *first* order

$$V = - \frac{Q}{a}[4.1977\,M_1 + 6.3346\,M_2] - \frac{6\mu}{a^2}. \qquad . \qquad . \qquad (3.6)$$

[9] *Proc. Roy. Soc.*, A, 1925, **107,** 636.
[10] In the summation the potentials due to 23 rings of lattice points were included. The contribution of each ring after the fourteenth was less than $0.001\,M/a^2$.

The process may be carried to any desired degree of approximation, we have taken it to the fourth, the dipoles at the points (100), (110), (111), (200) being taken as unknowns and written Qam, Qam', etc.; m, m', m'', m''' are then found to be given by

$$m = \beta_1(1 - 2{\cdot}3713\, m - 4{\cdot}5749\, m' - 1{\cdot}2879\, m'' \\ + 1{\cdot}4966\ m''' + 0{\cdot}041_2\, M_1 - 0{\cdot}0519\, M_2),$$

$$m' = \beta_2(0{\cdot}5 - 2{\cdot}2874\, m - 2{\cdot}7074\, m' - 2{\cdot}2999\, m'' - 0{\cdot}8087\, m''' \\ + 0{\cdot}0365\, M_1 - 0{\cdot}0444\, M_2),$$

$$m'' = \beta_1(0{\cdot}\dot{3} - 0{\cdot}9659\, m - 3{\cdot}4499\, m' - 0{\cdot}7691\, m'' - 0{\cdot}8134\, m''' \\ - 0{\cdot}49_0{}^2\, M_1 - 0{\cdot}019\, M_2),$$

$$m''' = \beta_2(0{\cdot}25 + 1{\cdot}4966\, m - 1{\cdot}6174\, m' - 1{\cdot}0845\, m'' \\ - 0{\cdot}2964\, m''' - 0{\cdot}846\, M_1 - 0{\cdot}379\, M_2).$$

These equations were then solved for m, m', m'', m'''. The poteianl is then

$$V = - \frac{Q}{a}[3{\cdot}309 M_1 + 2{\cdot}9596 M_2 + 6(m + m') + 2{\cdot}\dot{6} m'' + 1{\cdot}5 m'''] \quad (3.8)$$

We have evaluated V for a crystal with $\alpha_1 = \alpha_2$ and $\kappa_0 = 4$. We have also evaluated it for certain real crystals; for these we assumed α_1/α_2 to be the same as for the free ions, using values tabulated by Pauling.[11] The absolute values were deduced from κ_0 using formula (3.1). The results are shown in Table III; V_0 denotes the quantity

$$V_0 = \frac{Q}{4\pi a}\left(1 - \frac{1}{\kappa_0}\right).$$

In view of these results we believe that the first approximation is a satisfactory one, and it will be used in the more complicated calculations where the ions are allowed to move.

TABLE III.—POTENTIAL AT A POSITIVE LATTICE POINT DUE TO DIPOLES INDUCED BY A CHARGE Q PLACED AT THAT POINT.

Crystal.			NaCl.	KCl.	RbCl.
Dielectric constant κ_0	4		2·33	2·17	2·18
α_1/α_2	1		20·3	4·4	2·6
	Order of Approx.				
$- V/V_0$	0	16·53	20·03	18·96	18·25
	1	18·57	21·88	20·60₅	19·82
	2	18·15	21·83	20·44	19·59₄
	3	18·03	21·62	20·27	19·46
	4	18·5	21·69	—	—

We also show in Table IV the potentials, to the first order, when the charge Q is placed at a *negative* lattice point.

TABLE IV.

	NaCl.	KCl.	KBr.
$- V/V_0$	13·21	14·69	14·35

In the calculations of Schottky and Jost on the energies of holes in crystals, it has been usual to treat the crystal as a uniform dielectric with a hole in it of radius R. The potential at the centre due to the polarised

[11] *Proc. Roy. Soc.*, A, 1927, **114**, 181.

medium is then

$$- \left(\mathrm{I} - \frac{\mathrm{I}}{\kappa_0} \right) \frac{Q}{R}.$$

It is interesting to compare this method with ours. We treat first a crystal with $\alpha_1 = \alpha_2$.

If $\kappa_0 - \mathrm{I} \ll \mathrm{I}$ the zero order approximation is correct and the potential at the centre is, by (3.3)

$$- \mathrm{I6 \cdot 53} \frac{Q}{a} \frac{\mathrm{I}}{4\pi} \left(\mathrm{I} - \frac{\mathrm{I}}{\kappa_0} \right).$$

Hence we must take

$$R = 4\pi a / \mathrm{I6 \cdot 53} = \mathrm{o \cdot 76} a.$$

The volume of this sphere is $\mathrm{I \cdot 84}\ a^3$, considerably greater than the atomic volume a^3.

For $\kappa_0 = 4$ we have from Table III

$R = 4\pi / \mathrm{I8 \cdot 5} = \mathrm{o \cdot 68} a$

and the volume of the sphere is $\mathrm{I \cdot 32}\ a^3$.

For the other salts the results may be obtained in the same way and are shown opposite.

The calculations of this section may be used to find the energy of an electron located on one of the metal ions, or a positive hole in one of the halogen ions, due to the polarisation of the

Crystal.		R/a.	
$\alpha_1 = \alpha_2,\ \ \kappa_0 - \mathrm{I} \ll \mathrm{I}$		0·76	
$\alpha_1 = \alpha_2\ \ \ \ \kappa_0 = 4$		0·68	
		Positive Ion.	Negative Ion.
NaCl	. . .	0·58	0·95
KCl	. . .	0·61	0·85₅
RbCl	. . .	0·635	—
KBr	. . .	—	0·88

surrounding medium. The ions are supposed not to be displaced. The energy in either case is $- \frac{1}{2}|eV|$. For a number of crystals the energies are (in e.V.)

These results are used in Paper II for a discussion of the absorption

	NaCl.	KCl.	KBr.	RbCl.
Electron in metal ion	− 2·50	− 2·02	—	− 1·86
Hole in halogen ion	− 1·52₅	− 1·44	− 1·43	—

spectrum of these crystals. Similar calculations have been made for other positions of the charge Q, as follows :—

I. Charge at Centre of Face, *i.e.* at the Point $(\tfrac{1}{2}a, \tfrac{1}{2}a, 0)$.

In the approximation of zero order, the potential at the centre, corresponding to (3.3) is, using the summations of Jones and Ingham

$$V = - \mathrm{I4 \cdot I368}\ Q(M_1 + M_2)/a. \qquad . \qquad . \qquad (3.9)$$

To the first approximation, we take unknown dipoles μ_1, μ_2 at the four nearest neighbours of type (1), (2) and assume (3.1) to be true for everything more distant. Then the field E_1 acting on an ion of type (1) is found to be

$$E_1 = \frac{2Q}{a^2} - \mathrm{o \cdot 7071} \frac{\mu_1}{a^3} - \frac{3\mu_2}{a^3} - \mathrm{I \cdot 35_6} \frac{M_1 Q}{a^2} - \mathrm{o \cdot 7}^{20}_{19} \frac{M_2 Q}{a^2} \quad . \quad (3 \cdot \mathrm{Io})$$

The field E_2 is obtained by interchanging (1) and (2) in this equation. The simultaneous equations for μ_1, μ_2 are

$$\mu_1 = \alpha_1 E_1,\ \mu_2 = \alpha_2 E_2 . \qquad . \qquad . \qquad . \qquad (3.11)$$

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and the potential is

$$V = - 6 \cdot 1368 \frac{Q(M_1 + M_2)}{a} - \frac{4(\mu_1 + \mu_2)}{a^2} \qquad . \qquad . \qquad (3.12)$$

II. Charge at Centre of Cube, *i.e.* at the Point $(\tfrac{1}{2}a, \tfrac{1}{2}a, \tfrac{1}{2}a)$.

The corresponding formulæ are :

Approximation of zero order

$$V = - 11 \cdot 8571 \frac{Q(M_1 + M_2)}{a}. \qquad . \qquad . \qquad . \qquad (3.13)$$

Approximation of first order.—We take dipoles μ_1, μ_2 on the nearest neighbours. Then the field acting on an ion of type (1) is

$$E_1 = \frac{4Q}{3a^2} - 1 \cdot 7678 \frac{\mu_1}{a^3} - 4 \cdot 3849 \frac{\mu_2}{a^3} - 0 \cdot 592 \frac{M_1 Q}{a^2} + 0 \cdot 122 \frac{M_2 Q}{a^2} \quad (3.14)$$

with a similar expression for E_2. The simultaneous equations for μ_1, μ_2 are again given by (3.11), and

$$V = - 4 \cdot 7460 \, Q(M_1 + M_2)/a - 5 \cdot 3333 \, (\mu_1 + \mu_2)/a^2. \qquad . \qquad (3.15)$$

TABLE V.

Crystal.	NaCl.	KCl.	RbCl.
Centre of cube (0)	23·714	23·714	23·714
(1)	26·67	25·705	25·356
Centre of face (0)	28·27	28·27	—
(1)	33·79	32·35	—

The values of $- V/V_0$ obtained, to the first and second orders, are shown in Table V.

4. Potentials when the Ions are Displaceable.

We now pass on to the case of an actual crystal in equilibrium in a static field, so that the ions are displaced into new positions. As before, we place a charge Q at a given point of the lattice, let the crystal settle down into equilibrium in its field, and attempt to find the potential at Q due to the polarisation of the medium.

At large distances from Q the polarisation of the medium is

$$P = \frac{Q}{4\pi r^2}\Big(1 - \frac{1}{\kappa}\Big). \qquad . \qquad . \qquad . \qquad (4.1)$$

We shall need to know the relative contributions made to (4.1) by the two kinds of ion. As before, let $- px$ be the restoring force, due to overlap forces, on any ion in a uniformly polarised medium where each ion is displaced a distance $\pm x$. Then the dipoles induced at the lattice points of types 1 and 2 are

$$\mu_1 = \alpha_1\Big[E + \frac{4\pi}{3}(P_0 + \gamma P_1)\Big] + \frac{e^2}{p}\Big[E + \frac{4\pi}{3}(P_1 + \gamma P_0)\Big],$$

with a similar expression for μ_2.

Making use of the notation

$$\beta_1 = \alpha_1/a^3, \quad \beta_2 = \alpha_2/a^3,$$

$$\beta = \frac{e^2}{pa^3}\Big\{\frac{E + 4\pi(P_0 + \gamma P_1)/3}{E + 4\pi(P_1 + \gamma P_0)/3}\Big\}, \qquad . \qquad . \qquad (4.2)$$

we see that the two dipoles are in the ratio

$$(\beta + \beta_1)/(\beta + \beta_2) \qquad . \qquad . \qquad . \qquad . \qquad (4.3)$$

Actually our final results turned out to be very insensitive to β (we tried several values). We have therefore set the expression in the curly brackets in (4.2) equal to unity. β may then be calculated from (2.6), using Born

and Mayer's values of ρ, or from (2.10) from the dielectric constant. In our calculations we have used (2.10).

It follows from (4.1) and (4.3) that the dipoles induced at each lattice point of types 1 and 2 are respectively

$$M_1' a^3 Q / r^2, \quad M_2' a^3 Q / r^2 \qquad . \qquad . \qquad . \qquad (4.4)$$

where

$$M_1' = \frac{1}{4\pi}\left(1 - \frac{1}{\kappa}\right) \frac{\beta + \beta_1}{\frac{1}{2}(\beta_1 + \beta_2) + \beta},$$

with a similar expression for M_2'.

The displacement x of the ions is

$$x = M'a^3 Q / er^2 \qquad . \qquad . \qquad . \qquad . \qquad (4.5)$$

where

$$M' = \frac{1}{4\pi}\left(1 - \frac{1}{\kappa}\right) \frac{\beta}{\frac{1}{2}(\beta_1 + \beta_2) + \beta}.$$

Our *zero* order approximation can then be found by summing the potentials at the point Q as before. In our *first* order approximation, we take the dipole μ and the displacement x of the nearest neighbours to Q as unknowns ; those of all more distant ions are taken as given by (4.4).

We apply these methods first to calculate the potential round a lattice point from which a positive ion has been removed. Q is thus $- |e|$. Each adjacent negative ion is in equilibrium in the field of all the dipoles and of Q, and under the repulsive overlap forces of five positive ions. Consider first the latter. The displacements of the positive ions, measured outwards from Q, are

$$\begin{array}{ll} (200) & -\frac{1}{4}M'a, \\ (110) & -\frac{1}{2}M'a. \end{array}$$

The energy of one of the (100) ions is thus

$$w(a - x - \tfrac{1}{4}M'a) + 4w[\{(a - M'a/2\sqrt{2})^2 + (x + aM'/2\sqrt{2})^2\}^{\frac{1}{2}}].$$

The repulsive *force* on one of the (100) ions outwards, was found to be, substituting for $w(r)$,

$$F_r = \frac{A}{\rho}\Big[-\exp\Big\{\frac{-a + \tfrac{1}{4}M'a + x}{\rho}\Big\} + \frac{4}{d}\Big(x + \frac{M'a}{2\sqrt{2}}\Big)e^{-d/\rho} \Big]$$

$$= \frac{\alpha_M e^2}{a^2}\Big[-\tfrac{1}{6}\exp\Big\{\frac{\tfrac{1}{4}M'a + x}{\rho}\Big\} + \frac{2}{3d}\Big(x + \frac{M'a}{2\sqrt{2}}\Big)e^{-(a-d)/\rho} \Big],$$

where

$$d^2 = (a - M'a/2\sqrt{2})^2 + \tfrac{1}{6}(x + M'a)^2.$$

The electrostatic force, writing $\mu = -mea$, $x = \xi a$, was found to be

$$F_e = \frac{e^2}{a^2}\Big[\frac{1 + \sqrt{2} + 0.25}{(1 + \xi)^2} - \frac{4(1 + \xi)}{(1 + 2\xi + \xi^2)^{3/2}} - \frac{1}{(2 + \xi)^2} - \frac{2.3713\,m}{(1 + \xi)^3} - 0.388\,M'_1 - 1.965\,M'_2 \Big]$$

The equations determining m and ξ are

$$\begin{aligned} F_r + F_e &= 0 \\ me^2/\beta_1 a^2 &= F_e \end{aligned} \qquad . \qquad . \qquad . \qquad (4.6)$$

ξ was found by estimating the solution $\xi = \xi'$, putting $\xi = \xi' + \Delta\xi$, and expanding in terms of $\Delta\xi$. V is then given by

$$V = \frac{e}{a}\Big[4.1977\,M_1' + 6.3346\,M_2' + \frac{6\xi}{1 + \xi} + \frac{6m}{(1 + \xi)^2} \Big]. \quad . \quad (4.7)$$

In obtaining these formulæ we have assumed that there is no overlap between the ions, so that the constant γ of § 2 is unity. In view, however,

of the considerations of § 2, we ought to assume that the dipole ex due to the displacement of the ion (200) makes no contribution to the field polaris-ing the negative ion (100). The calculation was carried out with this modification ; the energies were only very slightly changed as shown in Table VI.

5. The Energy Required to Remove an Ion.

In order to obtain the energies discussed in § 1, we require the work necessary to remove a positive or negative ion out of the crystal. As before we assume that when the ion has been removed the potential at that lattice point changes from $\alpha_M e/a$ to $\alpha_M e/a - V$, and the ions initi-ally in contact with the displaced ion move a distance outwards x ; V and x are given by formulæ (4.6) and (4.7).

Then the work necessary to remove an ion consists of the following terms :
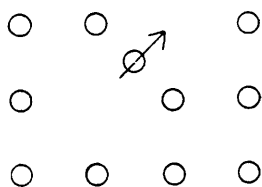
(1) that due to the electrostatic forces, namely

$$\alpha_M e^2/a - \tfrac{1}{2}eV ;$$

(2) that due to the overlap forces ; consider the work done to bring back the ion into the hole ; if we keep the ions displaced the work done is

$$6w(a + x).$$

We then move the ions back to their original positions, the force opposing this motion is initially $w'(a + x)$, so the total work is, per neighbour,

$$\tfrac{1}{2}xw'(a + x).$$

Thus the contribution of the overlap forces to the work to remove an ion is

$$- 6[w(a + x) - \tfrac{1}{2}xw'(a + x)] . \quad (4.8)$$

By the same methods we calculated the work to remove a negative ion, the work to place a positive ion in the centre of the cube and in the centre of the face. Also, in order to obtain the activation energy for the motion of a " hole " we calculated the energy of the configuration shown in Fig. 3, in which a " hole " is moving from one lattice point to another in the (110) direction.[12]

FIG. 3.—Illustrating the motion of an ion from a neighbouring lattice point into a "hole."

6. Results and Discussion.

The experimental values of κ_0, κ, a, W_L used in these calculations are those given by Born and Göppert-Mayer.[13]

Work to Remove Positive or Negative Ion out of the Lattice.

We denote the energies required by W_0^+ and W_0^- and show how they are made up below. We also give V, the potential, and x, the displacement *outwards* of the nearest neighbours. The work to form a pair of vacant lattice points is $W_0^+ + W_0^- - W_L$ where W_L is the lattice energy per ion pair. We give the results in detail for NaCl in

[12] Details of this calculation will be published later.
[13] *Handb. Physik.*, 1933, **24/2**, pp. 647, 724, 726.

Table VI. The values shown in bold faced type are obtained with the dipoles at (200) neglected, as explained above. The change in the energy is small.

TABLE VII shows $W_0{}^+$, $W_0{}^-$ calculated for a number of crystals, and also W_L, the lattice energy per ion pair given

TABLE VI.

	Positive Ion Removed.		Negative Ion Removed.	
x/a . . .	·071	**0·065**	0·078	**0·072**
$-Va/e$ . .	1·39	**1·35**	1·19	**1·16**
$\alpha_M e^2/a$.	1·748	**1·748**	1·748	**1·748**
$\frac{1}{2}eV$ . . $\left.\right\} \times \dfrac{a}{e^2}$	$-0·69$	**$-0·67$**	$-0·585$	**$-0·58$**
$-6w + 3xw'$.	$-0·15$	**$-0·15$**	$-0·14$	**$-0·145$**
W_0 . .	0·91	**0·93**	1·02	**1·03**

by Born and Göppert-Mayer. The quantity E defined by

$$E = (W_0{}^+ + W_0{}^- - W_L)$$

is of importance, since the number of pairs of holes is proportional to $e^{-\frac{1}{2}E/kT}$.

We believe our calculated energies E to have an accuracy of the order of 5 to 10 per cent., since in Paper III of this series they are used to calculate the energy of an F-centre, with results in very good agreement with experiment.

TABLE VII.—ENERGIES IN E.V.

	NaCl.	KCl.	KBr.
Work $W_0{}^+$ to remove positive ion	4·62	4·47	4·23
Work $W_0{}^-$ to remove negative ion	5·18	4·79	4·60
Lattice energy per ion-pair W_L .	7·94	7·18	6·91
$\frac{1}{2}E = \frac{1}{2}(W_+ + W_- - W_L)$.	0·93	1·04	0·96

At 600° C., $e^{-\frac{1}{2}E/kT}$ is equal to 10^{-5}, there are thus about 10^{17} pairs of holes per cubic centimetre.

Electrolytic Conductivity According to the Mechanism of Schottky.

According to Schottky, electrolytic conductivity may be due to the motion of vacant lattice points of either sign, since a neighbouring ion can move into the " hole " and fill it up. If $W_1{}^+$, $W_1{}^-$ are the energies of the configuration shown in Fig. 3 for absent positive and negative ions respectively, then the activation energies $U_1{}^+$ and $U_1{}^-$ are given by

$$U_1{}^+ = W_1{}^+ - W_0{}^+, \text{ etc.}$$

We have confined our calculations to the case of NaCl. In Table VIII we give also the displacements x of the neighbouring ions.

TABLE VIII.

	Positive Ion Absent.	Negative Ion Absent.
x/a . . .	0·12₈	0·13₁
$W_1 \left.\right\} \dfrac{e^2}{a}$ . .	1·01	1·13
W_0 . .	0·91	1·02
U_1 . .	0·10	0·11
U_1 (e.V.) . .	0·51	0·56
$\frac{1}{2}E$ (e.V.) . .	0·93	0·93
$A = U_1 + \frac{1}{2}E$ (e.V.)	1·44	1·49

Since the number of positive and negative holes is proportional to $e^{-\frac{1}{2}E/kT}$, we have finally that the conductivity is proportional to exp.

$(- A^+/kT)$, exp. $(- A^-/kT)$ for the motion of positive and negative ions respectively, where

$$A^+ = \tfrac{1}{2}E + U_1^+$$
$$A^- = \tfrac{1}{2}E + U_1^-.$$

Comparison with Experiment.

We shall not expect so great an accuracy here as in calculating the energies of vacant lattice points, as the value assumed for ρ is important, and may well vary with distance for such large displacements of the ions.

Smekal [14] gives for NaCl, as the observed values

$$A^+ = 2\cdot 0 \text{ e.V.}$$
$$A^- = 2\cdot 2 \text{ e.V.}$$

Lehfeldt [15] gives a table of mean values of A found by different observers; for NaCl these are, in e.V.,

$$1\cdot 9, \quad 1\cdot 7, \quad 2\cdot 6, \quad 2\cdot 05, \quad 1\cdot 95, \quad 1\cdot 8.$$

A direct comparison with our calculated value would be misleading; the latter was calculated for a crystal at room temperature; now if we write

$$A = A_0 - \beta T$$

the conductivity may be written

$$\sigma = B_0 e^{-A/kT} \qquad . \qquad . \qquad . \qquad (6.1)$$
$$= B_0 e^{\beta/k} e^{-A_0/kT}.$$

Thus the experimental values should be compared with those calculated at $T = 0$.

Now Jost [16] has attempted to calculate the constant term outside the exponential in (6.1); he finds that for all the alkali-halides, to obtain agreement with experiment, $e^{\beta/k}$ must be taken to be of the order 100. Thus

$$\beta \sim 4\cdot 6k$$

and at room temperature $\beta T \sim 0\cdot 1$ e.V. Thus our theoretical value of A will be, at $0°$ K, about $1\cdot 5$ e.V. and $1\cdot 6$ e.V. for the positive and negative ion respectively. The discrepancy between this and the calculated values is probably due to our inaccurate knowledge of the repulsive potentials between ions.

Electrolytic Conductivity According to the Mechanism of Jost.

According to this model, positive ions are supposed to leave their normal positions and go into the centres of cubes—*i.e.*, the position $(\tfrac{1}{2} \cdot \tfrac{1}{2} \cdot \tfrac{1}{2})$.

According to our calculations for NaCl, the four negative ions in contact with the positive are displaced only $\cdot 0003a$, the attractive force due to the positive ion almost exactly balancing the repulsive forces. The work W_2^+ to bring up a positive ion from outside to the point $(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$ is made up as follows:

$$\tfrac{1}{2} \text{ e.V.} \qquad . \qquad . \qquad . \qquad . \qquad -3\cdot 89 \text{ e.V.}$$
$$\text{Repulsive forces} \qquad . \qquad . \qquad . \qquad +2\cdot 18 \text{ e.V.}$$
$$\text{Total } W_2^+ \qquad . \qquad . \qquad . \qquad . \qquad -1\cdot 71 \text{ e.V.}$$

[14] *Handb. Physik*, 1933, **24**/**2**, 883.   [15] *Z. Physik*, 1933, **85**, 717.
[16] *Z. physik. Chem. A*, 1934, **169**, 129.

The work $W_3{}^+ = W_2{}^+ - W_0{}^+$ to bring an ion from its normal position to an interlattice point is thus

$$W_3{}^+ = 2\cdot9 \text{ e.V.}$$

The number of ions in such positions is proportional to $\exp(-\frac{1}{2}W_3{}^+/kT)$. We note that $\frac{1}{2}W_3 > \frac{1}{2}E$ so the number of holes due to the Jost mechanism is negligible compared with the Schottky mechanism.

For an ion in an interlattice point to move, it has to pass through the centre of a face (the point $\frac{1}{2}$, $\frac{1}{2}$, o). The work $W_4{}^+$ to bring an ion from outside to such a point is made up as follows (for NaCl) :

$\frac{1}{2}$ e.V. .	.	.	.	$-$ 3·82 e.V.
Repulsive energy .	.	.		2·58 e.V.
Total $W_4{}^+$.	.	.	.	$-$ 1·24 e.V.

The activation energy $U_2{}^+$ to move the ion from $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to $(\frac{1}{2}, \frac{1}{2}, o)$ is

$$U_2{}^+ = W_4{}^+ - W_2{}^+ = 0\cdot47 \text{ e.V.}$$

The electrolytic conductivity according to the mechanism of Jost is

$$\sigma = \text{const. } \exp(-A_2/kT)$$

where

$$A_2 = \frac{1}{2}W_3{}^+ + U_2{}^+ = 1\cdot92 \text{ e.V.}$$

As will be seen, A_2 is greater than the calculated value of A_1, so the Schottky mechanism will be responsible for by far the greater part of the current.

Summary.

A method, based on Born's lattice theory, is developed for calculating the polarisation round any lattice point in a polar crystal which contains an excess charge. The method is used to obtain the work required to form vacant lattice points of either sign in alkali-halide crystals. It is thus possible to estimate the concentration of vacant lattice points in these crystals in thermal equilibrium.

According to the theories of Wagner, Jost and others, these vacant lattice points are responsible for the electrolytic conductivity. The activation energy for the motion of such a hole is evaluated, and the results compared with the observed conductivity of NaCl.

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