IONIC CONDUCTANCE IN SOLID SALTS

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Over a number of years it has become increasingly apparent that the existence and mobility of lattice defects are necessary features of the explanation of a large range of physicochemical phenomena involving ionic solids. Such phenomena include diffusion in solids, the appearance of new absorption bands after irradiation, the growth of a coherent layer of oxide on a metal surface, and the reaction between two ionic salts. The study of ionic conductance in solids is of importance therefore, not only for its own sake, but because the idea of the imperfect lattice is one of such wide application. This Review is concerned with the principal experimental results,* their theoretical interpretation, and the application of the concepts developed to several problems of practical interest. It is limited in scope to purely ionic compounds and no attempt is made to cover the related fields of non-stoicheiometry and semiconductors, except in so far as they impinge on the present problem.

1. Early Work

The first published work of note on the conduction of electricity through crystalline solids was that of the Curies [1] in 1888. Their method of measurement was to place a thin slice cut from a single crystal between two metallic electrodes connected to a high-voltage supply in series with a fibre electrometer. If the electrometer measured a potential δV after isolation from earth for a time δt, the current i flowing through the crystal is given by

$$i = C.\delta V/\delta t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is the total capacity of the crystal, electrometer, and leads. If the applied potential is V_0, then the specific conductance σ is calculated from

$$\sigma = il/V_0 a \quad (2)$$

where l and a are the thickness and cross-sectional area of the crystal respectively.

[1] *Ann. Chim. Phys.*, 1889, **17**, 385; 1889, **18**, 203.

* Details of experimental technique are not considered here. Various important points are discussed, *inter alii*, by von Hevesy (*Z. Physik*, 1922, **10**, 80), Tammann and Veszi (*Z. anorg. Chem.*, 1926, **150**, 355), Menzies and Skinner (*Discuss. Faraday Soc.*, 1949, **5**, 306), Holden (*ibid.*, p. 312), Hochberg and Walther (*Z. Physik*, 1930, **64**, 392), Phipps, Lansing, and Cooke (see ref. 20), Etzel and Maurer (*J. Chem. Phys.*, 1950, **18**, 1003), Toy and Harrison (*Proc. Roy. Soc.*, 1930 *A*, **164**, 151), and du Bridge and Brown (*Rev. Sci. Instr.*, 1933, **4**, 532).

In contrast to the behaviour of metallic conductors where σ is constant, i was observed to be a function of the time, decreasing to a final value sometimes over a period of days. Difficulty therefore arose over the unambiguous definition of the specific conductance of a crystalline solid. Joffé and Röntgen,[2] however, showed that the decrease in current with time was due to the building up of a polarisation voltage, for on disconnection of the upper electrode from the supply voltage and grounding of it, a current flowed through the electrometer in the opposite direction to the primary current. This polarisation voltage P was measured [3, 4] by substituting a voltage of opposite sign for V_0 of magnitude just sufficient to prevent the flow of secondary current, and Ohm's law was found to be accurately obeyed when the resistance R was calculated from the ratio $(V_0 - P)/i$. The true specific conductance is therefore

$$\sigma = il/(V_0 - P)a \quad . \quad . \quad . \quad . \quad (3)$$

Either P must be measured directly or i must be determined the instant that V_0 is applied, while P is still negligibly small. In the latter case the validity of Ohm's law is a necessary and sufficient condition that polarisation has not occurred. This has since been repeatedly verified for a variety of substances over a wide range of temperatures by a number of workers.[5, 6, 7] At high field strengths (of the order of 10 kv/cm.) Ohm's law no longer holds, owing to the onset of dielectric breakdown.[8]

For a metal, the specific conductance is a definite property of the substance, but in ionic solids [9] σ is "structure sensitive", that is, it depends on the history of the particular crystalline sample used. Repeated recrystallisation of several samples of pure ammonium alum under carefully controlled conditions showed that a reproducible specific conductance was finally obtained for several different crystals. This value was about 1/100 of that of the unpurified sample, individual crystals of which had differed amongst themselves by factors of as much as 6 : 1.

In view of the differences in behaviour between metallic and crystalline conductors, it is important to know the nature of the conducting species. Although the migration of ions was qualitatively indicated by the work of Warburg and Tegetmeier [10] and Haber and Tolloczko,[11] the validity of Faraday's law was first established by Tubandt and his co-workers,[12, 13, 14] who found that the alkali and alkaline-earth halides were pure ionic conductors whereas many oxides and sulphides showed electronic conductivity. In a few compounds such as β-silver sulphide and cuprous chloride, the sum of the anion and cation transport numbers is less than unity, so they

[2] *Ann. Physik*, 1913, **41**, 449. [3] Joffé, *ibid.*, 1923, **72**, 461.
[4] *Idem*, "The Physics of Crystals", McGraw-Hill, 1928.
[5] Hochberg and Walther, *Z. Physik*, 1930, **64**, 392.
[6] Lehfeldt, *ibid.*, 1933, **85**, 717. [7] Brennecke, *J. Appl. Physics*, 1940, **2**, 202.
[8] Beran and Quittner, *Z. Physik*, 1930, **64**, 760.
[9] Joffé, *op. cit.*, see ref. (4). [10] *Ann. Phys. Chem.*, 1888, **35**, 455.
[11] *Z. anorg. Chem.*, 1904, **41**, 407.
[12] Tubandt and Eggert, *ibid.*, 1920, **110**, 196.
[13] Tubandt, *ibid.*, 1921, **115**, 105.
[14] Tubandt, Eggert, and Schibbe, *ibid.*, 1921, **117**, 1.

are partly ionic and partly electronic conductors. Tubandt's method of measuring transport numbers is similar in principle to that used for solutions. Three compressed pellets of the salt (for example, silver iodide) were placed in series between a silver anode and a platinum cathode, raised to a suitable temperature, and a known current passed. The platinum cathode and the adjacent silver iodide cylinder gained weight and the anode lost weight, that of the other two cylinders being unaltered. In solutions both ions normally contribute to the conductance, but solid electrolytes are for the most part unipolar conductors. With many substances the metal released at the cathode is not deposited at the electrode–crystal interface, but forms a dendritic growth spreading out from the cathode into the crystal. This is usually prevented by including a pellet of silver iodide, in which this phenomenon does not occur, between the salt and the cathode.[12] The transport numbers of a number of simple salts are shown in Table 1 ; these have been selected mainly from a more complete compilation.[15]

TABLE 1

Salt	Temp.	t_{K+}	t_{A-}	Ref.	Salt	Temp.	t_{K+}	t_{A-}	Ref.
AgCl .	200—350°	1·00	0·00	13	NaF .	600	0·916	0·084	17
AgBr .	200—300	1·00	0·00	16	NaF .	625	0·861	0·139	,,
α-AgI .	150—400	1·00	0·00	,,	NaCl .	425	1·00	0·00	,,
α-Ag_2S	180—450	1·00	0·00	,,	NaCl .	510	0·981	0·019	,,
$BaCl_2$.	400—700	—	1·00	17	NaCl .	600	0·946	0·056	,,
$BaBr_2$.	350—450	—	1·00	,,	NaCl .	625	0·929	0·071	,,
BaF_2 .	500	—	1·00	,,	KCl .	435	0·956	0·044	,,
$PbCl_2$.	200—425	—	1·00	13	KCl .	500	0·941	0·059	,,
PbF_2 .	200	—	1·00	,,	KCl .	550	0·917	0·083	,,
$PbBr_2$.	200—365	—	1·00	,,	KCl .	600	0·880	0·116	18
PbI_2 .	290	0·67	0·33	17	KCl +	600	0·975	0·025	,,
NaF .	500	1·00	0·00	,,	0·4%				
NaF .	550	0·996	0·004	,,	$SrCl_2$				

With one exception, uni-bivalent salts are anion conductors but uni-univalent salts are predominantly cation conductors. With increasing temperature the anion transport number becomes significant in uni-univalent salts, but this effect may be decreased by the addition of a small amount of bivalent cation impurity.

2. Variation of Conductance with Temperature

The variation of conductance with temperature was found by Rasch and Hinrickson [19] to obey the equation

$$\log \sigma = \log A - B/T \quad . \quad . \quad . \quad . \quad (4)$$

[15] Landolt–Börnstein, " Physikalisch-Chemische Tabellen ", Berlin, 1936.

[16] Tubandt and Reinhold, *Z. Elektrochem.*, 1923, **29**, 313 ; 1925, **31**, 84 ; *Z. anorg. Chem.*, 1927, **160**, 222.

[17] Tubandt, Reinhold, and Liebold, *Z. anorg. Chem.*, 1931, **197**, 225.

[18] Wagner and Ronge, *J. Chem. Phys.*, 1950, **18**, 74.

[19] *Z. Elektrochem.*, 1908, **14**, 41.

the validity of which has since been repeatedly verified. Phipps, Lansing, and Cooke [20] observed that the plot of $\log \sigma$ against $1/T$ possessed two distinct parts defined by different values of A and B, so the temperature variation can be expressed throughout the whole range by the single equation [21]

$$\sigma = A_1 \exp(-B_1/T) + A_2 \exp(-B_2/T) \quad . \quad . \quad (5)$$

This equation is well obeyed by the alkali halides (Phipps and his co-workers [20, 22, 23, 24]) the silver and thallium halides (Lehfeldt [6]), and the lead halides (Seith [25]). The constant B is normally written as E/R, where E is the activation energy associated with the conductance process. In general, the low-temperature conductance is more irreproducible than that measured in the high-temperature region, and furthermore, is particularly sensitive to thermal pre-treatment and the presence of impurities. For this reason the two regions are described as the "structure-sensitive conductance" and the "permanent (or characteristic) conductance", respectively.[26] Values of the constants A and E (in kcal./g.-ion) for the alkali

TABLE 2

Salt	A_1	E_1	A_2	E_2	Ref.
LiF	—	—	4×10^7	50·7	6
LiCl	2	13·6	1×10^6	32·6	24
LiBr	4	12·8	5×10^5	28·0	,,
LiI	0·2	8·4	2×10^5	21·2	,,
NaF	—	—	2×10^6	51·9	6
NaCl	0·5	19·5	5×10^5	42·3	Mean—6, 20, 42
NaBr	0·2	18·4	2×10^5	38·4	20
NaI	0·06	13·8	1×10^4	28·3	,,
KF	—	—	3×10^7	54·2	6
KCl	0·04	22·8	1×10^6	46·6	23
KBr	0·01	22·4	9×10^6	45·4	,,
KI	0·2	19·6	4×10^4	37·2	,,
RbCl	—	—	3×10^6	48·9	6
RbI	—	—	2×10^6	46·8	,,

halides are given in Table 2. The ratio A_1/A_2 is about 10^{-6} and the activation energy in the structure-sensitive region is about 0·5—1·0 ev compared with 1—2 ev in the region of permanent conductance.

On the basis of transport experiments (Table 1) Phipps and Leslie [22] suggested that the two sections of the conductance curve were caused by the onset of bipolar conduction at high temperatures, the higher value of the activation energy E_2 being associated with the migration of the anion. Smekal,[21] however, suggested that in an ideal crystal only one exponential required to move an ion from a normal lattice point to the electrode, and

[20] *J. Amer. Chem. Soc.*, 1926, **48**, 112.
[21] Smekal, *Z. Elektrochem.*, 1928, **34**, 472.
[22] Phipps and Leslie, *J. Amer. Chem. Soc.*, 1928, **50**, 2412.
[23] Phipps and Partridge, *ibid.*, 1929, **51**, 1331.
[24] Phipps and Ginnings, *ibid.*, 1930, **52**, 1340.
[25] *Z. Physik*, 1929, **56**, 802.
[26] Smekal, *Z. physikal. Chem.*, 1931, *B*, 443.

term, *viz.*, $A_2 \exp(-E_2/RT)$, would occur, E_2 corresponding to the energy that the first term arose because of the presence of cracks and imperfections causing internal surfaces at which the activation energy necessary to remove an ion was less than that in the perfect lattice. This hypothesis is in accord with the experimental result $E_1 < E_2$, $A_2 \gg A_1$, and with the structure-sensitive nature of the low-temperature conductance. It receives further support from the fact that polycrystalline materials in general show a higher specific conductance than single crystals. Joffé and Zechnowitzer,[27] however, showed that when a single crystal was made microcrystalline by plastic deformation instead of by rapid crystallisation from the melt, the conductance remained unchanged. Furthermore, if E_1, E_2 are respectively the energies required to liberate ions from surface and lattice positions, and if the number of conducting ions is assumed proportional to $\exp(-E/RT)$, impossibly high values of the mobility must exist in order to give the measured conductance.[28] An elegant explanation of the two activation energies is, however, provided by the modern theory of lattice defects put forward by Frenkel [29] and by Wagner and Schottky,[30] the structure-sensitive nature of the low-temperature conduction being due to the production of defects by chemical impurities (foreign ions) and rapid crystallisation.

3. The Mechanism of Ionic Conductance

The phenomena of conductance and diffusion in ionic solids can readily be understood if the crystal contains mobile lattice defects. In an ideal or "perfect" ionic lattice, every lattice point is occupied so that ionic migration can take place only if two ions change places by squeezing past each other, a process which would involve a very high activation energy approaching that of the cohesive energy of the crystal.[31] Diffusion along Smekal cracks has already been dismissed,[32] but there remains the possibility of diffusion *via* lattice defects.

In real crystals in thermodynamic equilibrium, there exist a number of vacant lattice sites from which the ions are missing. Two main types of lattice defect are recognised: in a Frenkel defect an ion leaves a normal lattice site and takes up an interstitial position, whereas in a Schotty defect two ions of opposite charge leave their normal positions in the lattice and take up new positions on the surface of the crystal. If there are n_S Schotty defects per cm.^{3} at equilibrium at a temperature T in a crystal containing N ion-pairs per cm.^{3}, the increase in entropy due to the formation of these defects is

$$\Delta S = 2k \log \frac{N!}{(N - n_S)!\, n_S!} \quad . \quad . \quad . \quad . \quad (6)$$

where the factor 2 arises because there are n_S vacant cation sites and n_S

[27] *Z. physik*, 1926, **35**, 446.
[28] Jost, *Z. physikal. Chem.*, 1929, *B*, **6**, 88; 1930, **7**, 234.
[29] *Z. Physik*, 1926, **35**, 652. [30] *Z. physikal. Chem.*, 1930, *B*, **11**, 163.
[31] Seitz, "Modern Theory of Solids", McGraw-Hill, 1940, p. 495.
[32] See also Jost, *J. Chem. Phys.*, 1933, **1**, 466.

vacant anion sites. Substitution of (6) in the equilibrium condition

$$\left(\frac{\partial \Delta A}{\partial n_S}\right)_T = \frac{\partial(n_S W_S - T.\Delta S)}{\partial n_S} = 0$$

where W_S is the energy required to form a Schottky defect at a temperature T, gives

$$W_S - 2kT \log (N - n_S)/n_S = 0$$

or

$$n_S = N \exp(- W_S/2kT) \quad . \quad . \quad . \quad . \quad (7)$$

when $n_S \ll N$. The analogous formula for the number of Frenkel defects is, by a similar argument,

$$n_F = \sqrt{NN'} \exp(- W_F/2kT) \quad . \quad . \quad . \quad (8)$$

where W_F is the energy required to place an ion in an interstitial position and N' is the number of such positions.

This simple model is subject to the limitation that the vibrational frequencies of the crystal are assumed to be independent of the presence of lattice defects, whereas the vibrational frequency ν' of an ion adjacent to a vacant site, in the direction of the vacancy, will be less than that ν of a normal lattice ion. Account being taken of the change in the contribution from vibrational degrees of freedom to the free energy,[33] (7) becomes

$$n_S = \gamma N \exp(- W_S/2kT) \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\gamma = (\nu/\nu')^s \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

s being the number of ions adjacent to the vacancy.

The application of an electric field cannot create defects—field strengths of the order of a million volts per cm. would be required—but instead it merely directs a random diffusion of the ions already taking place in the absence of the field. Suppose that there are n_S Schottky defects at equilibrium and that in the process of diffusion one of the s ions adjacent to the vacant site jumps into it, a process which involves the surmounting of a potential energy barrier E_S. According to the theory of rate processes, the jump frequency $\tilde{\nu}$ (that is the number of ions crossing the potential barrier in unit time) is given by

$$\tilde{\nu} = s\frac{kT}{h}.\frac{Q^*}{Q} \exp(- E_S/kT) \quad . \quad . \quad . \quad (11)$$

where Q^* is the partition function of the ion in the transition state, Q that of an ion in its normal state, and E_S the difference between the energy of the moving ion in the transition state and the normal state respectively. In the absence of more precise information, the transmission coefficient is set equal to unity. s is a symmetry factor allowing for the fact that there are s equivalent energy barriers around the defect. Since Q^* differs from Q only in having one less vibrational degree of freedom,

$$Q^*/Q = 1 - e^{-h\nu'/kT} \simeq h\nu'/kT \quad . \quad . \quad . \quad (12)$$

where ν' is the frequency of vibration of an ion adjacent to a vacant site in a line normal to the energy barrier. Equation (11) thus reduces to

$$\tilde{\nu} = s\nu' \exp(- E_S/kT) \quad . \quad . \quad . \quad . \quad (13)$$

[33] Mott and Gurney, "Electronic Processes in Ionic Solids", O.U.P., 1948, p. 30.

which is the expression for the jump frequency $\vec{\nu}$ for the random motion of the defects in the absence of a field. When an electrostatic field of intensity F is applied, the saddle point lying in the direction of the field is lowered by an amount $eFa/2$, where a is the distance between two successive equilibrium positions, and that in the reverse direction is increased by $eFa/2$, so that the net jump frequency in the direction of the field is

$$\vec{\nu} = \nu' \exp[-(E_S - \tfrac{1}{2}eFa)/kT] - \nu' \exp[-(E_S + \tfrac{1}{2}eFa)/kT]$$

or, for low field strengths, where $eFa \ll kT$,

$$\vec{\nu} = \nu' \exp(-E_S/kT).eFa/kT \quad . \quad . \quad . \quad (14)$$

The average velocity in the direction of the field is $\bar{v} = \vec{\nu}a$, so that the mobility u is given by

$$u = (\vec{\nu}a/F = \nu' ea^2/kT) \exp(-E_S/kT) \quad . \quad . \quad . \quad (15)$$

The specific conductance σ is therefore,

$$\sigma = (ne^2a^2\nu'/kT) \exp(-E_S/kT) \quad . \quad . \quad . \quad (16)$$

At high temperatures, in the region of permanent conductance, $n = n_S$ [equation (9)], but at low temperatures the number of defects thermally produced is very small so that the structure-sensitive conductance is determined by the number of impurity defects present.[34] In general, $n = y + n_S$, where y is the number of impurity defects, and therefore, from equations (9) and (16)

$$\sigma = \frac{ye^2a^2\nu'}{kT} \exp(-E_S/kT) + \frac{\gamma Ne^2a^2\nu'}{kT} \exp[-(E_S + \tfrac{1}{2}W_S)/kT] \quad . \quad (17)$$

Discrepancies between conductances calculated from equation (17) and experimental values can be accounted for in two ways. First, it is probably incorrect to consider only the moving ion when computing the partition function Q^*, since the transition state may involve a number of ions (for example, the moving ion and the four nearest neighbours in the plane normal to the reaction path between the ion and the vacancy). Since ΔV^* is negligible,[35] the expression for the jump frequency may be written

$$\vec{\nu} = s(kT/h)e^{-\Delta G^*/RT} \quad . \quad . \quad . \quad . \quad (18)$$

where ΔG^* is the free energy of activation, and thus instead of (16),

$$\begin{aligned}\sigma &= (ne^2a^2/h)e^{-\Delta G^*/RT} \\ &= (ne^2a^2/h)e^{\Delta S^*/R}\, e^{-\Delta H^*/RT} \quad . \quad . \quad . \quad (19)\end{aligned}$$

Comparing (19) with the experimental equation for the permanent conductance, $\sigma = A_2 \exp(-E_2/RT)$, we get

$$E_2 = \Delta H^* \quad \text{and} \quad A_2 = (ne^2a^2/h)e^{\Delta S^*/R} \quad . \quad . \quad (20)$$

If the number of ions involved in the transition state is large, ΔS^* may be considerable. No calculations based on equation (19) appear to have been made.

The other possibility [36] is that the activation energies E_S, W_S are func-

[34] Koch and Wagner, *Z. physikal. Chem.*, 1937, *B*, **38**, 295.
[35] Barrer, *Trans. Faraday Soc.*, 1942, **38**, 78, 214.
[36] Jost, *Z. physikal. Chem.*, 1934, *A*, **169**, 129.

tions of the temperature. Owing to the thermal expansion of the crystal, W_S and E_S are likely to decrease with increasing temperature; assuming this variation to be linear,[37] we have

$$\begin{aligned} W_S &= W_0 + (V - V_0)\mathrm{d}W_S/\mathrm{d}V \\ &= W_0 + \alpha V_0 T(\mathrm{d}W_S/\mathrm{d}V) \quad . \quad . \quad . \quad . \quad (21) \end{aligned}$$

where α is the coefficient of thermal expansion of the crystal and W_0 and V_0 are respectively the energy of formation of a Schottky defect and the volume of the crystal at $T = 0°$ K. Similarly

$$E_S = E_0 + \alpha V_0 T(\mathrm{d}E_S/\mathrm{d}V) \quad . \quad . \quad . \quad . \quad (22)$$

Substituting from (21) and (22) in (17), we have

$$\sigma = \frac{yCe^2a^2\nu'}{kT}\exp(-E_0/kT) + \frac{\gamma BCNe^2a^2\nu'}{kT}\exp[-(E_0 + \tfrac{1}{2}W_0)/kT] \quad (23)$$

$$\left.\begin{aligned} &\text{where} \quad B = \exp[-\alpha V_0(\mathrm{d}W_S/\mathrm{d}V)/2k] \\ &\text{and} \quad C = \exp[-\alpha V_0(\mathrm{d}E_S/\mathrm{d}V)/k] \end{aligned}\right\} \quad . \quad . \quad . \quad (24)$$

The theoretical values of the constants are therefore:

$$\left.\begin{aligned} &E_1 = E_0, \qquad A_1 = yCe^2a^2\nu'/kT \\ &\text{and} \quad E_2 = E_0 + \tfrac{1}{2}W_0, \quad A_2 = \gamma BCNe^2a^2\nu'/kT \end{aligned}\right\} \quad . \quad . \quad (25)$$

An exact calculation of the values of γ, B, and C has not yet been performed; it is possible, however, to calculate values of γB and of C from experimental values of the conductance, the validity of equation (23) being assumed. If a mole-fraction x of bivalent cation impurity is added to a uni-univalent salt, the number of impurity defects $y = xN$, is greater than the equilibrium number of defects n_S at any temperature, so the conductance is expressed by the first term in equation (23). Therefore $\sigma_{\text{calc.}}$, obtained from the formula

$$\sigma_{\text{calc.}} = (xNe^2a^2\nu'/kT)\exp(-E_0/kT) \quad . \quad . \quad . \quad (26)$$

will be compared with $\sigma_{\text{expt.}}$, the results of Wagner and Hantlemann [38] on the conductance of potassium chloride with added strontium chloride being used. With the following values of the constants, appropriate to potassium chloride,

$$\begin{aligned} E_0 &= 18{\cdot}2 \text{ kcal. (from the usual plot of } \log\sigma \text{ against } 1/T) \\ N &= 1{\cdot}285 \times 10^{22} \text{ ion-pairs per cm.}^3 \\ e &= 1{\cdot}602 \times 10^{-19} \text{ coulomb} \\ a &= 4{\cdot}44 \times 10^{-8} \text{ cm.}^{39} \\ \nu &= 4{\cdot}51 \times 10^{12} \text{ sec.}^{-1\ 40} \\ Ne^2a^2\nu/k &= 2{\cdot}266 \times 10^5 \text{ ohm}^{-1} \text{ cm.}^{-1} \text{ deg.,} \end{aligned}$$

values of C have been calculated from the ratio $\sigma_{\text{expt.}}/\sigma_{\text{calc.}}$ at each temperature and concentration. These are given in Table 3. The mean value

[37] Ref. 33, pp. 30, 34.

[38] *J. Chem. Phys.*, 1950, **18**, 72.

[39] International Critical Tables, Vol. I, 345.

[40] In the absence of more precise information, the value of ν has been used for ν': *ibid.*, Vol. V, 261.

of C for all concentrations and temperatures is thus 36·4 for potassium chloride.[41]

TABLE 3

$x \times 10^2$	873° K	898° K	923° K	948° K	973° K	998° K
0·1 . . .	35·9	37·3	38·0	38·9	39·5	40·0
0·2 . . .	33·1	34·1	34·3	34·8	35·2	35·7
0·4 . . .	33·8	35·7	36·1	36·2	36·8	40·5

To find γB, experimental values of the conductance of the salt containing a known amount of impurity are used to calculate the mobility from

$$\sigma = xNeu = xF\rho u/M \quad . \quad . \quad . \quad . \quad (27)$$

where F is the Faraday, ρ the density, and M the molecular weight; these values may now be used to compute the number of defects in the pure salt, (27) being used in the form

$$x_S = \sigma t_K M/\rho F u \quad . \quad . \quad . \quad . \quad (28)$$

where t_K is the transference number of the cation. Wagner's values of x_S, the fractional number of cation vacancies in the pure salt, calculated from his own values of the mobility [38] and the conductance measurements of Phipps and Partridge [23] are given in Table 4. The column headed x_S, calc., contains figures calculated from the formula $\exp(-W_0/2RT)$ with $W_0 = 48$ kcal.[38] The ratio x_S, expt./x_S, calc., corresponds to γB.

TABLE 4

T, ° K	$10^5 x_S$, expt.	$10^5 x_S$, calc.	γB
873	0·8	0·99	8·1
898	1·2	1·44	8·3
923	2·1	2·09	10·0
948	3·0	2·92	10·3
973	4·1	4·06	10·1
998	5·7	5·57	10·2

A value of γB less than that of C is unexpected, since for Schottky defects it seems likely that γ will be greater than unity. γ is given by $(\nu/\nu')^s$, whence, with $s = 6$, a value of $\nu' = 0{\cdot}8\nu$ gives $\gamma \simeq 4$, while for $\nu' = 0{\cdot}5\nu$, $\gamma = 64$. The conclusion to be drawn from a value of γB of about 10 is that B is of the order of unity.

Similar calculations have been made for sodium chloride, Etzel and Maurer's experimental data [42] being used. The mean values obtained are $\gamma B = 5{\cdot}1$, $C = 188$. Thus again $B \sim 1$ so that the energy required to form a Schottky defect does not vary greatly with the volume of the crystal. In assessing these results it must be noted that the absolute accuracy of the conductance measurements is probably not greater than $\pm$ 20%.

[41] Compare ref. 33, p. 31.

[42] *J. Chem. Phys.*, 1950, **18**, 1003.

The only other information concerning the values of γ, B, and C is from some experiments by Jost and Nehlep [43] on the variation of σ with pressure. The permanent conductance is given by the second term of equation (17); differentiation at constant temperature yields

$$\left(\frac{\partial \log \sigma}{\partial P}\right)_T = \frac{\partial \log (a^2\nu')}{\partial P} - \frac{1}{kT}\cdot\frac{\partial}{\partial P}(E_S + \tfrac{1}{2}W_S) \quad . \quad . \quad (29)$$

The first term may be neglected in comparison with the second so that (29) reduces to

$$\partial \log \sigma/\partial P = -(\chi/T)\log BC \quad . \quad . \quad . \quad (30)$$

where χ is the coefficient of compressibility. From Jost and Nehlep's results on silver chloride, Mott and Gurney [44] have estimated that $BC \sim 350$; combining this result with the estimate of $\gamma BC \sim 150$, we have $\gamma \sim \frac{1}{2}$. A value of $\gamma < 1$ is consistent with the assumption that Frenkel defects are the conducting species in the silver halides.[45]

Thus the presence of defects accounts adequately for the two sections of the conductance curve and the structure-sensitive nature of the low-temperature region, although a quantitative test of equation (23) must await methods of calculating γ, B, and C. For the salts investigated so far, equation (23) gives calculated values of the permanent conductance of the right order if γBC is about 10^3.

4. Theoretical Calculation of the Activation Energies

According to equation (25), the experimental activation energies E_1 and E_2 are related to the energy required to form a Schottky defect W_0, and the activation energy for migration E_0, by the expressions

$$E_1 = E_0, \quad E_2 = E_0 + \tfrac{1}{2}W_0 \quad . \quad . \quad . \quad (31)$$

The calculation of the energy to form a Schottky defect will be considered first. The work done in removing an atom (or molecule) from the surface layer of an atomic (or molecular) crystal to infinity is the lattice energy W_L, given by the equation

$$W_L = -\frac{1}{2}\sum_{i,k}{}' V_i(r_k) = -\frac{N}{2}\sum_{k}{}' V_i(r_k) \quad . \quad . \quad (32)$$

where $V_i(r_k)$ denotes the potential energy of interaction of the ith with the kth atom at a distance r_k from it, the prime indicates that the term $i = k$ is omitted from the summation, and the factor $\frac{1}{2}$ arises so that the interaction between any pair of atoms shall not be counted twice. The energy W_H to remove a single atom (say the ith) from the centre of the crystal to infinity is

$$W_H = -\sum_{k}{}' V_i(r_k) \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$= -N\sum_{k}{}' V_i(r_k), \text{ per g.-formula-weight}$$

so that $$W_H = 2W_L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

[43] *Z. physikal. Chem.*, 1936, *B*, **34**, 348. [44] Ref. 33, p. 51.
[45] Mitchell and Keith, *Phil. Mag.*, 1951, **42**, 1331.

The energy required to form a Schottky defect is clearly

$$W_S = W_H - W_L = W_L \quad . \quad . \quad . \quad . \quad (35)$$

For ionic crystals, (35) must be rewritten as

$$W_S = W_+ + W_- - W_L \quad . \quad . \quad . \quad . \quad (36)$$

where W_L is now the lattice energy per ion pair and W_+ and W_- are the energy required to remove a single positive and negative ion, respectively, from the interior of the crystal to infinity. In an ionic crystal, a charged ion at a point P will induce dipoles on its neighbouring ions, so there exists at P a potential ϕ due to these dipoles. Thus the total potential at P is the algebraic sum of the electrostatic and polarisation potentials at that point. On removal of an ion out of the crystal the work done is thus W_L (the lattice energy)—W_P (the polarisation energy). After allowance for the polarisation energy, (36) becomes

$$\left.\begin{aligned} W_S &= (W_L - W_P{}^+) + (W_L - W_P{}^-) - W_L \\ &= W_L - W_P{}^+ - W_P{}^- \end{aligned}\right\} \quad . \quad . \quad (37)$$

The importance of the polarisation energy was first emphasised by Jost,[32] who also indicated an approximate method of calculating W_P. Jost assumes that the vacant site may be treated as a spherical cavity of radius R in a medium of uniform dielectric constant ε; in this medium there will exist an electric field $\mathbf{E}$ due to the removal of a charge $+\mathbf{e}$ from the cavity. The field $\mathbf{E}$ and dielectric displacement $\mathbf{D}$ at a distance r from the centre of the cavity are

$$\mathbf{D} = \frac{-\mathbf{e}}{r^2}, \quad \mathbf{E} = \frac{-\mathbf{e}}{\varepsilon r^2}$$

The polarisation potential ϕ is therefore given by

$$\phi = \int_R^\infty (\mathbf{D} - \mathbf{E})\mathrm{d}r = \frac{-\mathbf{e}}{R}\left(1 - \frac{1}{\varepsilon}\right)$$

and the polarisation energy by

$$W_P = \tfrac{1}{2}(-\mathbf{e})\phi = \frac{\mathbf{e}^2}{2R}\left(1 - \frac{1}{\varepsilon}\right) \quad . \quad . \quad . \quad (38)$$

The difficulty lies in choosing a value for R; Jost calculated that with R equal to the interionic distance a, $W_P \simeq 2{\cdot}5$ ev for the alkali halides ($\varepsilon \simeq 5$). Therefore, from (37), $\frac{1}{2}W_S \simeq 1{\cdot}5$ ev. Neglect of the polarisation energy in (37) gives $\frac{1}{2}W_S \simeq 4$ ev, so even this rough calculation has reduced it to a value approaching the right order (about 1 ev for sodium chloride).

Since that time a more precise method for calculating the polarisation energy has been given by Mott and Littleton.[46] They regard Jost's method as being valid at large distances from the hole so that the polarisation is

$$\mathbf{P} = \frac{\mathbf{D} - \mathbf{E}}{4\pi} = \frac{\mathbf{e}}{4\pi r^2}\left(1 - \frac{1}{\varepsilon}\right) \quad . \quad . \quad . \quad (39)$$

This value of $\mathbf{P}$ is used to compute the dipoles μ on the ions, and ϕ is obtained

[46] *Trans. Faraday Soc.*, 1938, **34**, 485.

by summing μ/r^2 over all lattice points. This is the zero-order approximation. In the first-order approximation the field at one of the nearest neighbours (*i.e.*, 100 ions) is found by summing directly that due to the dipoles on the ions outside the ring of nearest neighbours and adding that due to the other five 100 lattice ions. The dipole at this ion is then calculated, and the total potential at the centre of the vacancy obtained by adding that due to the dipoles on the six 100 ions to the zero-order approximation applied to the rest of the lattice. This process can be continued to any desired order ; Mott and Littleton showed that even the first-order approximation gave satisfactory results, and also that Jost's method gave agreement with their results for the alkali halides if R^+ was taken as $0{\cdot}6a$ and R^- as $0{\cdot}9a$.

Mott and Littleton's method has recently been applied by du Pré, Hutner, and Rittner [47] to the calculation of the polarisation energy in 33 substances with the sodium chloride type of lattice.

Published calculations of the activation energy for migration of a defect are few. Some rough calculations were made for silver sulphide by Jost ; [32] Mott and Littleton [46] quote some results for the migration of a cation vacancy in sodium chloride, but give no details of the calculation, and Dienes [48] has recently performed a very thorough calculation of the energy of migration of a coupled pair of vacancies in potassium chloride. In principle, one requires to calculate the changes in electrostatic, repulsive, and polarisation energy as the moving ion and the vacancy change places. In addition, it is necessary to allow for changes in the local distortion of the lattice as this movement takes place.

The results of the main theoretical calculations of W_S and E_S are compared with experimental values in Table 5. The experimental values refer to W_0 and E_0, respectively, but it is not worth while correcting the calculated

TABLE 5

Ref.	Quantity calculated	Result, ev	Exptl. value
46	W_S, NaCl	1·86	1·96
46	W_S, KCl	2·08	2·06
46	W_S, KBr	1·82	1·99
46	E_S, Na^+ in NaCl	0·51	0·86
48	Coupled pair, KCl	0·375	$<0{\cdot}5$

values to $T = 0°$ K since (*a*) $B \sim 1$ and therefore dW_S/dV is negligible, and (*b*) the discrepancy between E_S and E_0 is much larger than the correction $-\alpha V_0 T(dE_S/dV)$. The most important source of error in calculations of E_S is probably our uncertain knowledge concerning the repulsive interaction between the ions in crystalline solids.

[47] *J. Chem. Phys.*, 1949, **17**, 198, 204 ; 1950, **18**, 379.
[48] *Ibid.*, 1948, **16**, 620.

5. Independent Evidence for the Existence of Vacancies

As the theory presented in Section 3 can only be verified semi-quantitatively until such time as independent methods are available for the calculation of γ, B, and C, it is of value to examine other evidence for the existence of vacancies in ionic crystals. The occurrence of Schottky defects, by increasing the volume of the crystal, might be expected to cause a decrease in density. Crystals cooled rapidly from a high temperature without annealing retain a large number of defects in excess of the equilibrium number, because of their low mobility at room temperature. Consequently, such crystals would be expected to show an anomalous decrease in density. Precise density measurements [49] have, however, failed to show any deviations from geometrical perfection greater than the limits of accuracy of one part in 10^4. The calculations in Section 3 have indicated that the fractional number of vacant sites in potassium chloride at 1000° K is about 5×10^{-5}, so the effect may be too small to be detected even in unannealed crystals. Similarly, no anomalies that can be attributed to the existence of vacancies have been observed in lattice constants [49] or coefficients of thermal expansion.[50] However, in silver bromide, the large fractional number of interstitial ions (about 2×10^{-2}) at the melting point led Mott and Gurney [51] to predict an anomalous rise in the molar heat capacity near the melting point, owing to the heat absorbed during the creation of the defects; this has recently been verified by Kanzaki.[52] It is also to be expected that a crystal containing a large number of vacancies would, because of their effect on the vibrational frequencies, show additional absorption bands in the infra-red. This effect does not appear to have been observed. When a high concentration of bivalent foreign ion M^{++} is incorporated in a uni-univalent salt, a number of the cation vacancies produced will be associated as M^{++}–vacancy pairs, since the bivalent ion and the vacancy will not only attract each other electrostatically, but this combination will also tend to reduce local strain in the neighbourhood of the foreign ion. Spectroscopic evidence for the existence of Pb^{++}–cation vacancy pairs in potassium chloride containing lead chloride has been obtained by Burstein, Oberly, Henvis, and Davisson.[53]

Further evidence for the existence of vacant sites may be obtained from dielectric-loss measurements. The dielectric constant of a perfect crystal is made up of two contributions arising from the electronic and the atomic polarisabilities respectively. Since the corresponding resonant frequencies lie in the ultra-violet and infra-red regions, the dielectric constant at audio- and radio-frequencies is substantially independent of frequency and is accompanied by very small dielectric losses. In a crystal containing vacant sites, however, there should exist an anomalous dielectric polarisation due to the motion of vacancies in the alternating field. This effect has been

[49] Birge, *Rep. Progr. Physics*, 1941, **8**, 90; *Amer. J. Phys.*, 1945, **13**, 63.
[50] Ref. 33, p. 31; but see also Strelkow, *Physikal. Z. Sowjetunion*, 1937, **12**, 77.
[51] Ref. 33, p. 48.
[52] *Phys. Review*, 1951, **81**, 884.
[53] *Ibid.*, p. 459.

observed by Breckenbridge [54] in quenched pure crystals and also in crystals containing bivalent impurity ions.

Furthermore, if both ionic conductance and diffusion proceed *via* the same mechanism, namely, the migration of lattice defects, some correlation between the activation energies for conductance and self-diffusion is to be expected. The expression for the jump frequency of an ion has been derived as

$$\tilde{\nu} = s\nu' \exp(-E_S/\boldsymbol{k}T) \quad . \quad . \quad . \quad . \quad (13)$$

The rate of diffusion through unit cross section of one atomic plane to the next is

$$\partial n/\partial t = \tilde{\nu}a^2 . \partial n/\partial x \quad . \quad . \quad . \quad . \quad (40)$$

and by comparing this with the usual one-dimensional diffusion equation, the diffusion coefficient D_i is seen to be equal to $\tilde{\nu}a^2$. The coefficient of self diffusion is

$$D = nD_i/N = na^2\tilde{\nu}/N$$

which on substitution from (9), (13), (21), and (22) becomes

$$D = \gamma BCa^2 s\nu' \exp[-(E_0 + \tfrac{1}{2}W_0)/\boldsymbol{k}T] \quad . \quad . \quad . \quad (41)$$

Comparison of (41) with the empirical equation

$$D = D_0 \exp(-E/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad (42)$$

yields theoretical values of the constants D_0 and E. The theoretical calculation of D_0 is subject to the same limitations as the calculation of A_2 in the conductance equation, namely, our lack of knowledge of γ, B, and C. Comparison of (41) with the second term in (23) gives

$$\sigma/D = Ne^2/s\boldsymbol{k}T \quad . \quad . \quad . \quad . \quad (43)$$

Self-diffusion coefficients have been measured by using radioactive indicator ions; *e.g.* von Hevesy and Seith [55] found for the diffusion of Pb^{++} in lead iodide, the relation

$$D = 10{\cdot}6 \exp(-30{,}000/\boldsymbol{R}T)$$

and for the conductance of lead iodide

$$\sigma = 9{\cdot}78 \times 10^{-4} \exp(-9360/\boldsymbol{R}T) + 1{\cdot}15 \times 10^5 \exp(-30{,}000/\boldsymbol{R}T)$$

The activation energy for the permanent conductance thus agrees well with that for diffusion. According to equation (43), at 700° K

$$\frac{\sigma}{D} = \frac{7 \times 10^{21} \times 2{\cdot}5 \times 10^{-40} \times 10^9}{1{\cdot}38 \times 10^{-16} \times 700} = 1{\cdot}8 \times 10^4$$

in good agreement with the experimental value of $1{\cdot}1 \times 10^4$. Agreement between experimental and theoretical values of σ/D can only be expected if diffusion and ionic conductance proceed by the same mechanism, that is, in lead iodide, the motion of vacant cation sites. The mobility of coupled pairs of vacancies, however, can contribute to diffusion but not to ionic conductance, and the failure of equation (43) under certain conditions can be ascribed to this cause.[56]

[54] *J. Chem. Phys.*, 1948, **16**, 959; 1950, **18**, 913.
[55] *Z. Physik*, 1929, **56**, 790; **57**, 869.
[56] Mapother, Crookes, and Maurer, *J. Chem. Phys.*, 1950, **18**, 1231.

6. Applications of the Concept of Mobile Lattice Defects in Physicochemical Problems

The properties of vacant lattice sites which are most important in the theoretical study of phenomena occurring in ionic crystals are (*a*) their mobility, (*b*) their ability to act as traps for electrons or positive holes, and (*c*) their ability to form aggregates. These properties allow explanations of a diverse range of phenomena, including the appearance of new absorption bands when free electrons and positive holes are produced, *e.g.*, by irradiation, anomalous dielectric polarisation, and the kinetics of solid reactions.

Anomalous Dielectric Polarisation.—The activation energy, U, associated with the relaxation process causing anomalous dielectric loss in the pure alkali halides is found to be significantly less than the experimental value of the activation energy E_0 for the motion of cation vacancies derived from conductance measurements.[54] For example, in sodium chloride $U_1 = 0{\cdot}70$ ev and $E_0 = 0{\cdot}86$ ev. The relaxation process therefore is unlikely to involve the movement of *single* cation vacancies, and Breckenbridge [54] has suggested that it consists of the reorientation of cation–anion vacancy pairs through the migration of cations (Fig. 1*a*). The addition of bivalent cation impurities causes the appearance of three additional dielectric-loss maxima. The peak of highest energy ($U_4 \simeq 0{\cdot}8$ ev in sodium chloride) is independent of heat treatment and thus of the existence of anion vacancies (the number of which will be small except at high temperatures), but the height of the peak is dependent on the concentration of foreign ions, and its energy on the nature of the added impurity. It is thus attributed to the interchange of M^{++} and a cation vacancy associated with it. The peak of next highest energy, U_3, is also independent of heat treatment and hence of the existence of anion vacancies, but is dependent on M^{++}-ion concentration, and its energy is independent of the nature of the foreign ion if the radius of M^{++} exceeds that of the normal lattice ion. It is therefore attributed to the reorientation of an M^{++}–vacancy pair caused by a normal lattice cation exchanging sites with the vacancy. The activation energy obtained when the radius of the foreign ion is equal to that of the normal lattice cation (*i.e.*, about 0·78 ev in sodium chloride) is significantly close to that for self-diffusion in sodium chloride,[56] thus providing confirmation of the suggested mechanism. The peak of lowest energy, U_2, is broader than the others, indicating a distribution of activation energies ; its height depends on the foreign-ion concentration and it appears only in heat-treated crystals. It therefore involves anion vacancies frozen in when the crystal is quenched, and is attributed to the reorientation of a cation–anion vacancy pair associated with a M^{++} ion, by either the M^{++} ion or a normal lattice ion exchanging sites with the cation vacancy. The various relaxation processes contributing to the anomalous dielectric loss in ionic crystals are shown diagrammatically in Fig. 1.

Colour Centres.—The experiments of Pohl and his co-workers at Göt-

tingen [57–63] have shown that, when crystals of the alkali halides are treated in certain ways, they darken, each salt having a characteristic colour. When this coloration is achieved by exposure to an electron beam or to ultra-violet or X-radiation, the darkening is temporary and the crystal returns to its original condition if it is heated. In contrast, in alkali halides coloured by heating in the vapour of their metallic constituent, the colour cannot be completely bleached thermally, though this treatment does result in the production of additional absorption bands. Chemical analysis of the

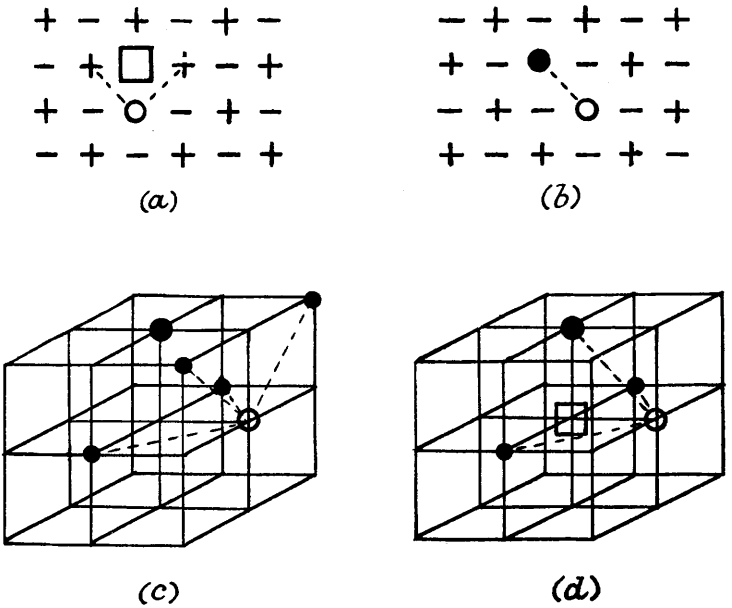


FIG. 1

Relaxation processes involving ion vacancies in an alternating field :
(a) *Interchange of normal lattice cation and cation vacancy* ○ *; activation energy* U_1.
(b) *Exchange of* M^{++} ● *and cation vacancy ; activation energy* U_4.
(c) *Exchange of normal lattice cation* ● *and cation vacancy associated with* M^{++} *; activation energy* U_3.
(d) *Reorientation of cation–anion vacancy pair associated with* M^{++} *; activation energy* U_2.

crystals coloured by the latter method has proved that they contain a stoicheiometric excess of the metallic constituent. Each additional metal atom can be absorbed by the crystal either in an interstitial position (Frenkel defect and trapped electron) or as a normal surface lattice cation. To preserve electroneutrality, the latter mechanism must also result in a vacant anion site and a free electron which will travel through the conduction band

[57] Pohl, *Proc. Phys. Soc.*, 1937, **49** (extra number), 3.
[58] *Idem, Physikal. Z.*, 1938, **39**, 36.
[59] Ottmer, *Z. Physik*, 1928, **46**, 798.
[60] Miescher, *Göttingen Nachr.*, 1933, 329.
[61] Kleinschrod *Ann. Physik*, 1936, **27**, 97.
[62] Smakula, *Z. Physik*, 1930, **63**, 762.
[63] Petroff, *ibid.*, 1950, **127**, 443.

of the crystal until it is trapped at some lattice discontinuity. Mott and Littleton's calculations [46] predict that the energy required to form a Frenkel defect in sodium chloride is 2·9 ev, whereas the energy to form a Schottky defect, or pair of vacant sites, is 1·86 ev. These results show that the excess metal is absorbed into the lattice almost entirely as normal lattice cations and free electrons rather than as interstitial atoms, and that the colour centres (F centres) are formed by the electrons becoming trapped at the equivalent number of anion vacancies.[64, 65] The formation of F centres can thus be represented by the scheme represented in Fig. 2. The supposed

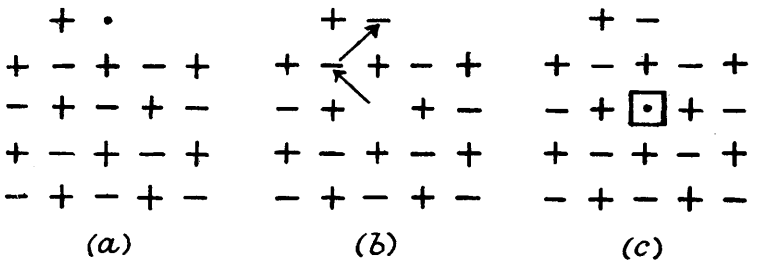


FIG. 2

Formation of an F *centre :* (a) *dissociative adsorption of metal atom, the electron produced entering the conduction band of the salt ;* (b) *anion migration stabilises the new lattice cation and produces an internal anion vacancy ;* (c) *conduction electron trapped at anion vacancy thus producing an* F *centre.*

mobility of the anion vacancies (Fig. 2) is not incompatible with transport-number determinations (Table 1), since in the alkali halides the anion does contribute to the conductance in the temperature region where F centres are produced by heating in the metallic vapour.

The formation of F centres in stoicheiometric halides by, for example, irradiation with ultra-violet light or *X*-rays is caused by the photo-excitation of an electron from the full band and its subsequent trapping at a vacant anion site present in the crystal. The formation of F centres is thus accompanied by the production of an equivalent number of positive holes in the full band. These positive holes are mobile and may become trapped at vacant cation sites forming V centres, which cause another absorption band (at about 2500 Å in potassium chloride).[66] Some confirmation is provided by the close resemblance between this V band and those produced by Mollwo[67] by exposing potassium bromide crystals to bromine vapour so that they absorb a stoicheiometric excess of bromine.

In addition to the F and V bands, a weaker band, designated the M band,[66] is formed at 8200 Å when potassium chloride is irradiated with *X*-rays. When the coloured salt is irradiated in either the F or the M band they are transformed one into the other with a loss in intensity during each

[64] de Boer, *Rec. Trav. chim.*, 1937, **56**, 301.
[65] Gurney and Mott, *Trans. Faraday Soc.*, 1938, **34**, 506.
[66] Molnar : unpublished work quoted by Seitz, *Rev. Mod. Phys.*, 1946, **18**, 384.
[67] *Göttingen Nachr.*, 1935, **1**, 199 ; *Ann. Physik*, 1937, **29**, 394.

transformation. This loss in intensity is associated with the appearance of new bands (the R bands) in the red between 6500 and 7000 Å. These R bands cannot be bleached with visible light. Seitz[68] has suggested that the M centre consists of an F centre combined with a neutral pair of vacant sites and that the R centres are F_2^+ and F_2 centres, *i.e.*, a pair of vacant anion sites with one and two trapped electrons, respectively. The sequence of events is probably as follows: an electron produced by photoelectric excitation from an F centre is trapped at a quartet of vacancies; this results in a weakening of the electrostatic bond between the vacancies and a loss of one or more vacant cation sites. Loss of one cation vacancy results in an M centre, and of two vacancies in an F_2^+ centre. The capture of a second electron, either by the F_2^+ centre or by the M centre, would result in an F_2 centre; F_2^+ and F_2 centres can revert to negative ion vacancies by capturing positive holes, but do not produce photoelectrons when absorbing radiation. This may be because the ground state and first excited level are so close together for large displacements that the excited electron reverts to the ground state by an almost adiabatic transition.

Freshly quenched crystals of additively coloured potassium chloride contain the F, R, and M bands, but on heating, an exceedingly broad band (the R′ band) with a maximum at 7000 Å appears. The R′ band does not appear to be colloidal in nature, but it is not resolved on cooling to liquid-nitrogen temperatures so it must contain a large number of different oscillators. The increased temperature necessary for its development indicates a process involving mobile vacancies. If an anion vacancy diffused to within a few lattice sites of an F centre, the electron could tunnel through the potential barrier from one anion vacancy to the other; repetition of this process represents effectively a diffusion of the F centres, thus enabling them to aggregate.[69] The first stage of aggregation will occur when two F centres diffuse together so that two electrons are associated with two adjacent anion vacancies; this configuration will benefit from the exchange energy resulting from resonance of the electrons between the two vacancies (cf. the formation of a hydrogen molecule) and thus represent a lower ground state than that of a single F centre. Continuation of this process will result in larger aggregates. There is some evidence [70] that the conversion of F into R′ centres goes to completion at 125° C but that at higher temperatures an equilibrium between F and R′ centres exists, dissociation being complete above 500°. Anion vacancies are not mobile in potassium chloride at 125° C, so that aggregation may involve the diffusion of neutral cation–anion vacancy pairs rather than single vacancies.

If additively coloured potassium chloride is irradiated in the F band at − 170° C instead of room temperature,[63] no less than five bands between 6000 and 10,000 Å can be resolved. The detailed assignment of the absorption bands to appropriate models must await further experimental work, but it seems likely that the new bands are associated with the appearance of

[68] *Rev. Mod. Phys.*, 1946, **18**, 384.
[69] Mitchell, *Phil. Mag.*, 1949, **40**, 249.
[70] Scott and Bupp, *Phys. Review*, 1950, **79**, 341.

complex centres consisting of various combinations of F centres and vacant sites. Positions of the various bands found in coloured potassium chloride are given in Table 6.

TABLE 6

Ref.	Band position, in electron-volts							
	K	B	F	A	E, R_1	D, R_2	M, C	G, N
Ottmer [59]			2·19					
Molnar [66]			2·19		1·85	1·68	1·50	
Scott and Bupp [70]			2·19		1·85	1·68	1·50	1·27
Petroff [63] (+ 20° c)			2·19		1·84	1·68	1·50	
Petroff [63] (− 170° c)		2·28	2·19	2·07	1·93	1·70	1·52	1·28
Burstein and Oberly [71]			2·19		1·85	1·68	1·50	1·27
Schneider [72]	2·57				1·94	1·71	1·52	

Photolysis of Ionic Solids.—The main feature of the photochemical decomposition of ionic solids is that, despite uniform illumination of the crystal surface, the reaction product is localised in a limited number of metallic nuclei. Only the photolysis of silver bromide, silver oxalate,[73] barium azide,[74] and potassium azide [75] has so far been the subject of detailed investigation. Irradiation of whole crystals of silver bromide [76] at room temperature with light in the long wave-length tail of the absorption band produces a new absorption band in the visible, originally attributed to the formation of colloidal particles of silver. If irradiation is protracted, the presence of specks of metallic silver is microscopically detected.[77] Photoconductance observed during irradiation [78, 79] indicates the presence of free electrons. The quantum yield of the process is about 0·06,[80] but in the presence of a halogen (or positive hole) acceptor, as in a photographic emulsion, the quantum efficiency approaches unity at room temperature [81] though it is considerably reduced (to about 10^{-5}) at liquid-air temperatures.[82]

To explain the separation of photolytic silver observed after long exposures (the print-out effect), Gurney and Mott [83] assumed that in the first stage of the process corresponding to the formation of the latent image, photoelectrons are trapped at silver sulphide specks. The negatively

[71] Burstein and Oberly, *Phys. Review*, 1949, **76**, 1254.
[72] Schneider, "Photographic Sensitivity", Butterworths, 1951, p. 13.
[73] Tompkins, *Trans. Faraday Soc.*, 1948, **44**, 206.
[74] Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, *A*, **209**, 550.
[75] Jacobs and Tompkins, to be published.
[76] Hilsch and Pohl, *Z. Physik*, 1930, **64**, 606.
[77] Eggert and Noddack, "Handb. d. Photographie", 1932, **5**, 141.
[78] Lehfeldt, *Göttingen Nachr.*, 1935, **1**, 171.
[79] Toy and Harrison, *Proc. Roy. Soc.*, 1930, *A*, **127**, 613, 629.
[80] Yampolskii and Solovev, *J. Phys. Chem. U.S.S.R.*, 1947, **21**, 899.
[81] Eggert and Noddack, *Z. Physik*, 1923, **20**, 299.
[82] Berg and Mendelssohn, *Proc. Phys. Soc.*, 1937, **49**, 38.
[83] *Proc. Roy. Soc.*, 1938, *A*, **164**, 151.

charged speck then traps interstitial Ag^+ ions (responsible for the ionic conductance) and photoelectrons alternately, so forming a metallic nucleus. The metallic nuclei of silver also function as efficient electron traps so that growth of the nucleus to visible size proceeds by a continuation of the process of trapping electrons and interstitial Ag^+. Since this theory was published, Stasiw and Teltow [84] have examined the absorption spectra of silver bromide crystals containing silver sulphide impurity and found a new absorption band extending on the long wave-length side of the normal (pure silver bromide) band. They interpreted it as being due to absorption by $S^=$ ions, but it seems more likely [69] that the sulphide will be absorbed into the lattice as complexes consisting of a singly charged S^- ion associated with an F centre. At the high temperatures necessary to form the solid solution, the F centres will tend to aggregate to form the centres responsible for the new impurity absorption band. It is well known that the sensitivity of photographic emulsions can be increased by the incorporation of sulphide impurity. Isolated S^-–F centre complexes and binary aggregates, possibly formed during the sensitisation process, would provide the electron traps to initiate the photolysis process.

In non-sensitised emulsions it is necessary to postulate the existence of both Schottky and Frenkel defects to retain the above mechanism. If pure silver bromide contains vacant anion sites, on irradiation the photoelectrons will be trapped at the anion vacancies forming F centres. These can then form nuclei by aggregation and by alternate trapping of anion vacancies and electrons. At first Mitchell [69] considered that a nucleus (F centre aggregate) would continue to grow by alternate trapping of photoelectrons and anion vacancies, but in view of the difficulty [85] of reconciling any considerable mobility of the vacant anion sites with a cation-transport number of unity (Table 1) this now seems less certain.[86]

In barium azide the lack of evidence for photoconductance has necessitated the formulation of a different theory [74] involving the reaction between two excitons trapped in adjacent positions at a vacant site.

Thermal Decomposition of Solids.—The first attempt to explain the thermal decomposition of a solid in terms of lattice defect theory was Mott's application of the theory of the photolysis of silver bromide [83] to the decomposition of barium azide.[87] He assumed that BaN_6 is an ionic conductor at room temperature, the mobile species being interstitial Ba^{++}. The presence of metallic nuclei being assumed, the growth mechanism is as follows. An electron is excited thermally from a neighbouring azide ion into the conduction levels of the metallic nucleus, a process requiring an activation energy E_g. The nucleus is now negatively charged and will attract interstitial Ba^{++} ions which diffuse towards it. The first one to reach the nucleus neutralises the negative charge and adds one atom of barium to the nucleus. The positive holes diffuse to the surface where two of them react to give three molecules of gaseous nitrogen. E_g is the activation energy for nuclear

[84] *Ann. Physik*, 1941, **40**, 181; 1947, **1**, 261; 1949, **5**, 151.
[85] Mitchell, *Phil. Mag.*, 1949, **40**, 667.
[86] *Idem*, "Photographic Sensitivity", Butterworths, 1951, p. 242.
[87] Mott, *Proc. Roy. Soc.*, 1939, *A*, **172**, 325.

growth and is, according to Wischin's experimental results,[88] equal to 23·5 kcal.

To explain the formation of nuclei, Mott assumed that in the induction period there is a slow uncatalysed emission of nitrogen from the surface, the stoicheiometric excess of barium going into solid solution as interstitial Ba^{++} and the free electrons into the conduction band. The concentration of free electrons thus increases with the time. When two electrons are trapped at a lattice discontinuity they can be neutralised by a Ba^{++} ion to start a nucleus, which then grows in the manner indicated.

Experimental measurements of the ionic conductance of barium azide [89] have shown, however, that the conductance is too low by a factor of at least 10^6 to account for Wischin's measured rates of nuclear growth.[88] Consequently, an alternative mechanism has been developed [90] involving the reaction of azide radicals at the nucleus–salt interface, thus obviating the need for mobile interstitial cations. An electron excited thermally from a surface azide ion is trapped at some lattice discontinuity, probably a vacant anion site. If an azide ion adjacent to the first one is sufficiently excited, the two positive holes (azide radicals) decompose to give three molecules of nitrogen and leave behind two vacant anion sites. These anions vacancies can trap electrons forming F centres which will tend to aggregate to form a metallic nucleus. The extremely low ionic conductance of BaN_6 unfortunately precludes the possibility of a transport-number determination, but reference to Table 1 shows that in all the barium and lead halides anion defects are mobile. The argument of low mobility does not apply here since mobility is only required during the process of nucleus formation, which is always a much slower process than growth. Once an F centre aggregate is formed it can grow by trapping electrons thermally excited from adjacent azide ions; this is followed by reaction between two azide radicals at the interface, leaving two anion vacancies which become incorporated in the aggregate. The growth mechanism may thus be represented by the following sequence, where h^+ denotes a positive hole, $\square$ a vacant anion site, and F_n an aggregate of n F centres:

(i) $2N_3^- + E \rightarrow 2N_3(h^+) + 2e^-$
(ii) $2e^- + F_n(\text{nucleus}) \rightarrow F_n^=$
(iii) $2N_3 \rightarrow 3N_2 + 2\square$
(iv) $2\square + F_n^= \rightarrow F_{n+2}$

The escape of nitrogen molecules from the interface is facilitated by the fact that decomposition occurs in a dehydrated crystal containing spaces which the water molecules once occupied in the hydrated crystal. As growth proceeds the aggregate of F centres and Ba^{++} ions eventually reaches a certain critical size at which it collapses away from the azide matrix to form a metallic nucleus. This must result in further fissures in the azide lattice thus facilitating the escape of nitrogen.

The Oxidation of Metals.—The term "Anlaufvorgänge", usually trans-

[88] *Proc. Roy. Soc.*, 1939, *A*, **172**, 314.
[89] Jacobs and Tompkins: to be published.
[90] Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, *A*, **210**, 111.

lated as tarnishing reactions, was introduced by Wagner [91] to describe the reaction between a metal M and an electronegative element X, usually in the gaseous or liquid state. In the course of these reactions the metal surface becomes covered with a coherent layer of the product MX, which thus separates the two reactants. For the reaction to proceed, it is necessary that at least one of the reactants should be capable of diffusing through the product layer. In the oxidation of silver by sulphur Wagner showed that on interposing two slabs of silver sulphide between the reactants, only the upper one gained in weight, thus indicating that it was the silver which had diffused through the silver sulphide. This is in accord with a cation transport number of unity in silver sulphide (Table 1), if the silver diffuses as mobile cation vacancies. The diffusing species can therefore be deduced from a knowledge of the mobile species in the product salt.

Cuprous oxide is a deficit semiconductor, *i.e.*, it contains an excess of oxygen ions in lattice sites and a corresponding number of vacant cation sites. To maintain electroneutrality each cation vacancy is associated with a positive hole in the full band. Initial oxidation results in the production of a layer of oxide on the surface of the copper. Dissociative adsorption of oxygen from the gas phase then produces oxygen atoms on the oxide surface; these receive electrons from the full band of the oxide and they become incorporated in the lattice. Each excess O^{2-} ion incorporated is accompanied by two positive holes in the full band and two vacant cation sites. Consequently, a higher concentration of cation vacancies exists at the oxide–gas surface than at the metal–oxide interface, resulting in the diffusion of cation vacancies through the oxide towards the metal. Vacancies at the metal–oxide interface are immediately filled by copper atoms, the surplus electrons neutralising the positive holes in the full band. Since the positive holes possess a much greater mobility than the cation vacancies, they will tend to diffuse inwards at a faster rate than the cation vacancies, but will be held back to some extent by the setting up of a space charge. The diffusion of cation vacancies is therefore the rate-determining step.

According to this mechanism, there will exist a concentration of cation vacancies at the oxide–oxygen surface which is independent of the thickness z of the oxide layer. The concentration gradient is thus proportional to $1/z$ so that

$$\mathrm{d}z/\mathrm{d}t = A/z \quad \text{or} \quad z^2 = 2At \qquad . \quad . \quad . \quad (44)$$

The thickness thus varies as $\sqrt{t}$; this parabolic law has been amply confirmed for the oxidation of many metals where the reaction is diffusion controlled. Deviations from the $\sqrt{t}$ law in the early stages of the reaction[92] are due to either (*a*) nucleation, which, being a slower process than growth, obeys a t^n law with $n > 1$, or (*b*) the surface reaction being the rate-determining step, which is likely for very thin layers. In other reactions, such as the oxidation of zinc above 225° C,[93] failure of the parabolic law is due

[91] *Z. physikal. Chem.*, 1933, *B*, **21**, 25.

[92] Wagner and Grünewald, *ibid.*, 1938, *B*, **40**, 455.

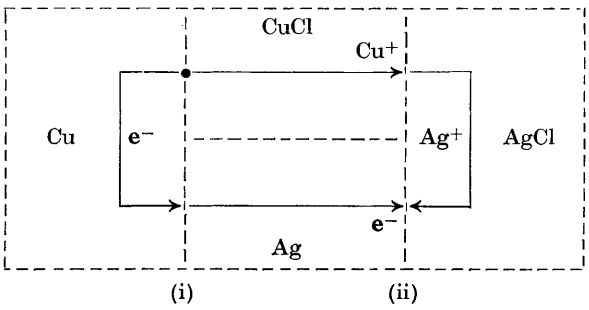
[93] Vernon, Akeroyd, and Stroud, *J. Inst. Met.*, 1939, **65**, 301; Moore and Lee, *Trans. Faraday Soc.*, 1951, **47**, 501.

to recrystallisation of the originally compact film to give a granular oxide layer. The rate-determining step is then the diffusion of oxygen in the cracks of the oxide.

The coefficient A in equation (44) is temperature dependent with an energy of activation of about 40 kcal.[94] Recently, Castellan and Moore [95] have shown that the activation energy for diffusion of radioactive Cu^+ through cuprous oxide films is 38 ± 3 kcal., thus providing strong evidence in favour of the diffusion mechanism. Diffusion of cation vacancies cannot, however, account for the low-temperature oxidation of copper [96] occurring above 240° K, since their mobility will be greatly reduced at such low temperatures. Mott [97] has suggested, however, that if the difference in energy levels, ϕ, between the conduction band of the metal and that of the oxide is sufficiently small, the metal will emit electrons into the conduction band of the oxide and the resulting space charge will drag metal ions through the oxide with an increased mobility.

The formation of protective films on certain metals, notably aluminium, is explained [97] by the fact that ϕ is large and although Al^{3+} ions can dissolve in the oxide layer formed initially (Al_2O_3 is an excess semiconductor) they are held back by the space charge created by the electrons remaining in the metal. For film thicknesses up to about 40 Å, the electrons can tunnel through the film, but when its thickness exceeds the maximum thickness of the potential barrier which the electrons can penetrate, growth ceases.

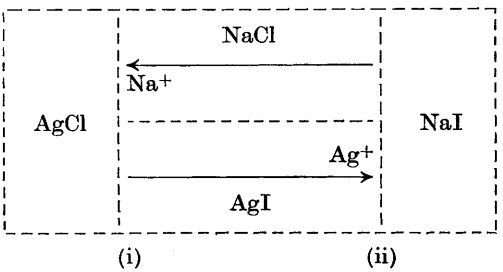
Reactions between Solids.—Reactions of the type $A_{(s)} + B_{(s)} \rightarrow C_{(s)} + D_{(s)}$ have been extensively studied experimentally [98] and it is only comparatively recently that Wagner [99] has demonstrated that the general principles of ionic mobility can be applied to reactions involving solids only. For example in the reaction between AgCl and Cu, the reactant phases soon become separated by the two product phases CuCl and Ag, so that in order for the reaction to proceed one of the reacting cations must diffuse through the product layer. Cu^+ ions are the mobile species in CuCl, so the reaction mechanism can be represented by the scheme



[94] Dunn, *Proc. Roy. Soc.*, 1926, *A*, **111**, 203.
[95] *J. Chem. Phys.*, 1949, **17**, 41.
[96] Allen and Mitchell, *Discuss. Faraday Soc.*, 1950, **8**, 309.
[97] *Trans. Faraday Soc.*, 1940, **36**, 472.
[98] Cohn, *Chem. Reviews*, 1948, **42**, 527.
[99] *Z. anorg. Chem.*, 1938, **236**, 320.

At the phase boundary (i) a Cu atom ionises, the Cu^+ ion diffusing through the CuCl layer and the electron entering the conduction levels of the metallic silver. At the phase boundary (ii) the electron excess combines with mobile (interstitial) Ag^+ ions, adding to the silver lattice. This means a silver deficit in the AgCl adjacent to the CuCl containing excess Cu^+ ions so that the reaction is completed by the extension of the CuCl lattice into the AgCl. The first stage may involve at the phase boundary a more or less disorganised array of Cu^+ and Cl^- ions which gradually assume the CuCl lattice.

When both reactants A and B are salts it is necessary that one ion of each reactant shall be mobile in the product phases. For example, in $AgCl + NaI \rightarrow AgI + NaCl$, Na^+ ions are mobile in NaCl and Ag^+ ions in AgI, so that the reaction is represented by the scheme



By assuming that the electrical resistance of the product layer can be considered as composed of the resistance of the two products C and D in parallel, Wagner [99] has shown that the rate of growth of the product layer is given by

$$\frac{dz}{dt} = \frac{1}{z} \cdot \left\{ \frac{1}{\dfrac{1}{\sigma_C v_C} + \dfrac{1}{\sigma_D v_D}} \cdot \frac{E}{F} \right\} \quad . \quad . \quad . \quad . \quad (45)$$

where σ_C and v_C are respectively the specific conductance and volume per g.-equiv. of C, and similarly for D, and z is the thickness of the product layer, $F = 96{,}500$ coulombs, and E is the e.m.f. of the cell involving the reaction $A + B \rightarrow C + D$. This expression gives calculated thicknesses of the right order for the reaction between Cu and AgCl. Deviations are attributed to the fact that the product layer may not consist of two pure phases but of a mixture of C and D, and consequently allowance must be made for the fact that the conductance in the mixture is not generally the same as in the pure phase.

The number of examples quoted could be considerably extended but they are sufficient to show that the concept of mobile lattice defects is one of great usefulness and wide application in the understanding of equilibrium and kinetic phenomena in the solid state.

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