

## Some Factors Responsible for High Ionic Conductivity in Simple Solid Compounds

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The ionic conductivities, activation energies for mobility, and crystal structures of solid electrolytes are reviewed. The high conductivity of a group of compounds containing simple anions is examined in some detail.

For a solid to possess high ionic conductivity there must be: (a) an excess of acceptable lattice sites for the mobile ion, (b) only a small energy difference between the ordered and disordered distribution of the mobile ions over these sites, and (c) a low heat of activation for movement of the mobile ion. These conditions are most readily realized when the cations are monovalent and stable in both 4-coordinated (tetrahedral) and 3-coordinated configurations. Since only  $\text{Ag}^+$  and  $\text{Cu}^+$  satisfy these requirements, their nearly unique conduction properties become understandable. Moreover, these requirements appear to be satisfied only with highly polarizable anions; a characteristic of the anions present in the good conductors.

### 1. Introduction

The ionic conductivities of most solids are very low at temperatures well below their melting points, being usually less than  $10^{-10}$   $\text{ohm}^{-1} \text{cm}^{-1}$  at room temperature. For some time, however, a few exceptions to this rule have been known, notably  $\text{AgI}$  which has an ionic conductivity of about  $1 \text{ ohm}^{-1} \text{cm}^{-1}$  at  $150^\circ\text{C}$ . More recently a number of other solids have been found to possess appreciable ionic conductivities at moderate temperatures. Such compounds may conveniently be classified according as to whether they contain simple or complex anions. The latter group, which includes compounds such as  $\text{Ag}_2\text{SO}_4$ ,  $\beta$ -alumina and the oxysalts of lithium, will not be considered here. Well-established conducting compounds with simple anions are listed in Table I together with some of their properties.

Although there has been considerable comment (28-31) on the conductivities and structures of the compounds listed in this table, a satisfactory explanation of their unusual properties is still lacking. Some factors which help to explain these characteristics are considered here. The com-

pounds to be discussed will be referred to as good, moderate or poor conductors depending upon the conductivity they would be expected to show at  $150^\circ\text{C}$ . The good conductors have ionic conductivities in excess of  $10^{-2} \text{ ohm}^{-1} \text{cm}^{-1}$ ; this class includes all the compounds listed in Table I, with the possible exception of  $\alpha\text{-Cu}_2\text{HgI}_4$ . Moderate conductors have ionic conductivities between  $10^{-2}$  and  $10^{-5} \text{ ohm}^{-1} \text{cm}^{-1}$ . The members of this group include  $\beta\text{-AgI}$ ,  $\text{AgCl}$ , and  $\text{AgBr}$ . When the ionic conductivity is below  $10^{-5} \text{ ohm}^{-1} \text{cm}^{-1}$ , we shall term the compound a poor conductor; the majority of compounds fall into this class.

Most of the good conductors exist in both a high-temperature and a low-temperature form. The former modification frequently possesses a conductivity  $10^2$ - $10^3$  times that of the low-temperature form. The mobile ion in all these compounds is always  $\text{Ag}^+$  or  $\text{Cu}^+$ .

### 2. The Concentrations of Mobile Species and Their Mobilities

In general, the conductivity ( $\sigma$ ) of an ionic conductor is related to the concentration of

TABLE I  
CHARACTERISTICS OF THE GOOD CONDUCTORS

Compound	Temperatures at which stable (°C)	Ionic conductivity $\sigma$ (ohm <sup>-1</sup> cm <sup>-1</sup> ) at T (°C)	Mobile ion	$E_A$ in $\sigma = \sigma_0 e^{-E_A/RT}$ (kJ mole <sup>-1</sup> )	Structure
$\alpha$ -AgI	>146 (1)	1.6 (2) to 1.9 (6) at 200	Ag <sup>I</sup> (3)	5 (2), 6 (6)	b.c.c.I; 2 Ag distributed over 42 2-, 3-, and 4-coordinated sites (1, 4)
$\alpha$ -Ag <sub>2</sub> S	>179 (5)	4.1 at 200 (8)	Ag <sup>I</sup> (7)	7 (8)	b.c.c.S; 4 Ag distributed over 42 sites as in $\alpha$ -AgI (5)
$\alpha$ -Ag <sub>2</sub> Se	>133 (5)	3.1 at 200 (8)	Ag <sup>I</sup> (7)	7 (8)	b.c.c. Se; Ag as in $\alpha$ -Ag <sub>2</sub> S, but slight preference for larger holes (5)
$\alpha$ -Ag <sub>3</sub> SI	>245 (9)	1.0 at 250 (9)	Ag <sup>I</sup> (9)	4 (9)	b.c.c. S, I (random); 3 Ag as in $\alpha$ -AgI (10)
$\beta$ -Ag <sub>3</sub> SI	<235 (9)	0.09 at 200 (14) <sup>a</sup> 10 <sup>-2</sup> at 20 (14)	Ag <sup>I</sup> (9)	14 (14)	b.c.c. S, I, with S at centre, I at corners of cube; 3 Ag distributed over 12 positions (10)
Ag <sub>3</sub> SBr	<300 (9)	2 × 10 <sup>-3</sup> at 20 (9)	Ag <sup>I</sup> (9)	23 (9)	as $\beta$ -Ag <sub>3</sub> SI, with Br in place of I (10)
$\alpha$ -Ag <sub>2</sub> Te	>150 (5)	1.0 at 200 (7)	Ag <sup>I</sup> (7)	10 (7) <sup>a</sup>	f.c.c. Te; 4 Ag in Zn-blende tetrahedral sites, remaining 4 distributed over 20 3-, 4-, and 6-coordinated positions (5)
$\alpha$ -Ag <sub>2</sub> HgI <sub>4</sub>	>50 (11)	1.5 × 10 <sup>-3</sup> at 60 (25) 0.9 × 10 <sup>-3</sup> at 60 (26)	Ag <sup>I</sup> , Hg <sup>II</sup> } (11) t <sub>Hg</sub> ≈ 0.06 }	43 (25) 59 (26)	f.c.c. I; 2 Ag and 1 Hg distributed over 4 tetrahedral Zn-blende sites (11)
Ag <sub>4</sub> RbI <sub>5</sub>	>-155 (12)	0.1 (13) to 0.2 (12) at 20	Ag <sup>I</sup> (13, 15)	7 (16)	complicated cubic I; alkali metal occupies 6-coordinated sites, 16 Ag distributed over 72 (15) or 56 (17) 4-coordinated positions
K NH <sub>4</sub> (Cs)	>-136 (12)	0.06 at 20 (13) <sup>a</sup>		9 (13)	—
Ag <sub>13</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>12</sub> I <sub>13</sub> <sup>b</sup>	—	—	—	—	—
$\alpha$ -CuBr	>469 (20) <sup>a</sup>	0.04 at 20 (18)	Ag <sup>I</sup> (18)	16 (18)	complicated hexagonal I; 39 Ag distributed over 123 tetrahedral sites (19)
$\alpha$ -CuI	>407 (20) <sup>a</sup>	0.3 at 470 (20) <sup>a</sup> 0.1 at 450 (20) <sup>a</sup>	Cu <sup>I</sup> (20)	small (20)	as $\alpha$ -AgI, but some temperature dependence (21)
$\alpha$ -Cu <sub>2</sub> S	>91 (5)	0.2 at 400 (22)	Cu <sup>I</sup> (20)	small (20)	disordered modification of Zn-blende structure (21)
(Cu-deficient)	>110 (5)	0.2 at 130 (23)	Cu <sup>I</sup> (23)	25 (23)	similar to $\alpha$ -Ag <sub>2</sub> Te (5)
$\alpha$ -Cu <sub>1.56</sub> Se	>67 (25)	0.47 at 200 (24)	Cu <sup>I</sup> (24)	16 (24)	similar to $\alpha$ -Ag <sub>2</sub> Te (5)
$\alpha$ -Cu <sub>2</sub> HgI <sub>4</sub>	>67 (25)	10 <sup>-5</sup> at 67 (25)	Cu <sup>I</sup> (11)	60 (25)	as $\alpha$ -Ag <sub>2</sub> HgI <sub>4</sub> (27)

<sup>a</sup> Value estimated from data in reference.

<sup>b</sup> A series of compounds of this type exists, in which the quaternary ammonium ion can contain a variety of organic groups. The conductivities at room temperature have values of up to 0.06 ohm<sup>-1</sup> cm<sup>-1</sup>. The example chosen is the most extensively investigated one.

charge carriers ( $n$ ) and their mobility ( $v$ ) by the equation

$$\sigma = nzev \tag{1}$$

where  $ze$  is the charge on the mobile species. This expression applies when only one type of mobile species makes a significant contribution to the observed conductivity.

2.1. The value of  $n$

In the poor and moderate conductors, the charge carriers are thermally induced interstitial ions or vacancies in the crystal structure. The equilibrium concentration of either type of defect is given to a good approximation by

$$n = Bn_0 \exp(-\Delta H_f/2 RT), \tag{2}$$

where  $\Delta H_f$  is the heat of formation of a defect pair at the temperature  $T$ ,  $n_0$  the concentration of normal lattice sites, and  $B$  an entropy factor which depends upon the crystal structure and the type of defect involved (32). The data presented in Table II show that at 150°C the concentration of mobile species compared with  $n_0$  is very small in the poor conductors and is appreciably larger, though still small, in the moderate conductors.

No direct method has been reported for determining the concentration of mobile species in the good conductors. In these compounds, X-ray analysis indicates that the mobile cations are randomly distributed over an excess of lattice

sites. This type of distribution, known as an "average structure", together with the low temperature-dependence of the conductivity strongly suggests that the conduction mechanism involves the movement of ions between the sites seen to be occupied, and that the concentration of mobile species equals the total concentration of the appropriate cation. Although, as will be shown later, the latter conclusion may not be strictly correct, it is unlikely to be seriously wrong. The concentrations of mobile species deduced on this basis are also shown in Table II and can be seen to be several orders of magnitude larger than the concentrations of defects in the moderate and poor conductors.

2.2. The Mobility  $v$

For all classes of conductor, the mobility of the mobile species varies with temperature. With the poor and moderate conductors, this variation may be expressed by

$$v = (A/T) \exp(-\Delta H_m/RT), \tag{3}$$

where

$$A = Ca^2 e v/k. \tag{4}$$

In these equations,  $\Delta H_m$  is the heat of activation for movement of the mobile species through the lattice,  $v$  the frequency of vibration of this species in its potential well,  $a$  the distance between adjacent potential wells in the conduction path, and  $C$  includes an entropy factor and a term depending upon the crystal structure of the compound.  $C$  has a value for the alkali halides of about  $10^2$ .

TABLE II

CONCENTRATIONS OF MOBILE SPECIES IN SOME IONIC CONDUCTORS

Compound	Intrinsic concentration of mobile species at 150°C (cm <sup>-3</sup> )
KCl (33)	10 <sup>9</sup>
NaCl (34)	10 <sup>10</sup>
LiF (35)	10 <sup>9</sup>
LiI (35)	10 <sup>17</sup>
AgCl (36)	10 <sup>17</sup>
AgBr (37)	10 <sup>18</sup>
$\beta$ -AgI (38)	10 <sup>20</sup>
$\alpha$ -AgI	} 10 <sup>22a</sup>
$\alpha$ -Ag <sub>2</sub> HgI <sub>4</sub>	
$\alpha$ -Ag <sub>2</sub> Te	
Ag <sub>4</sub> RbI <sub>5</sub>	

<sup>a</sup> Calculated assuming every Ag<sup>+</sup> ion mobile.

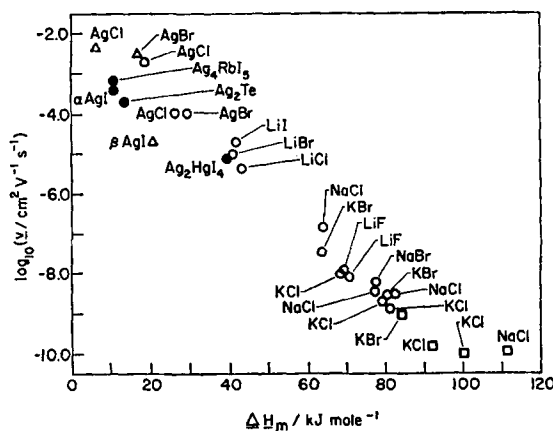


FIG. 1. Variation of mobility at 150°C with  $\Delta H_m$ . The mobile species are; ○, cation vacancy; □, anion vacancy; Δ, interstitial cation; ●, Ag<sup>+</sup>.

TABLE III  
MOBILITIES OF CURRENT-CARRIERS IN SOME COMPOUNDS<sup>a</sup>

Compound	$\Delta H_m$ (kJ mole <sup>-1</sup> )	$A$ (K cm <sup>2</sup> V <sup>-2</sup> sec <sup>-1</sup> )	$v$ at 150°C (cm <sup>2</sup> V <sup>-1</sup> sec <sup>-1</sup> )	Defect <sup>c</sup>	Ref.
LiF	71	$1.9 \times 10^3$	$1 \times 10^{-8}$	$V'$	61
	69	$1.0 \times 10^3$	$1 \times 10^{-8}$	$V'$	35
LiCl	43	$1.4 \times 10^2$	$4 \times 10^{-6}$	$V'$	35
LiBr	41	$1.9 \times 10^2$	$1 \times 10^{-5}$	$V'$	35
LiI	42	$1.0 \times 10^3$	$2 \times 10^{-5}$	$V'$	35
NaF	50	$2.3 \times 10^1$	$4 \times 10^{-8}$	$V'$	62
NaCl	77	$4.8 \times 10^3$	$3 \times 10^{-9}$	$V'$	63
	82	$2.0 \times 10^4$	$3 \times 10^{-9}$	$V'$	34
	64	$4.3 \times 10^3$	$1 \times 10^{-7}$	$V'$	64
	111	$2.3 \times 10^6$	$1 \times 10^{-8}$	$V^*$	64
NaBr	77	$9.1 \times 10^3$	$7 \times 10^{-9}$	$V'$	65
KCl	81	$5.6 \times 10^3$	$1 \times 10^{-9}$	$V'$	63
	79	$5.0 \times 10^3$	$2 \times 10^{-9}$	$V'$	33
	100	$1.0 \times 10^5$	$1 \times 10^{-10}$	$V^*$	66
KBr	64	$1.1 \times 10^3$	$4 \times 10^{-8}$	$V'$	67
	80	$9.2 \times 10^3$	$3 \times 10^{-9}$	$V'$	68
AgCl	84	$8.6 \times 10^3$	$1 \times 10^{-9}$	$V^*$	67
	18	$1.5 \times 10^2$	$2 \times 10^{-3}$	$V'$	36
	26	$6.6 \times 10^1$	$1 \times 10^{-4}$	$V'$	69
AgBr	5	8.4	$4 \times 10^{-3}$	$Ag_i$	69
	29	$1.7 \times 10^1$	$1 \times 10^{-4}$	$V'$	39
$\beta$ -AgI <sup>b</sup>	16	$1.4 \times 10^1$	$3 \times 10^{-3}$	$Ag_i$	39
	20	2.5	$2 \times 10^{-5}$	$Ag_i$	38, 40
$\alpha$ -AgI	10	2.9	$4 \times 10^{-4}$	$Ag^+$	2
$\alpha$ -Ag <sub>2</sub> HgI <sub>4</sub>	39	$2.2 \times 10^2$	$8 \times 10^{-6}$	$Ag^+$	11
$\alpha$ -Ag <sub>2</sub> Te	13	3.4	$2 \times 10^{-4}$	$Ag^+$	7
$\alpha$ -Ag <sub>4</sub> RbI <sub>5</sub>	10	4.4	$6 \times 10^{-4}$	$Ag^+$	16

<sup>a</sup> Parameters in the equation  $v = A/T \exp(-\Delta H_m/RT)$ .

<sup>b</sup> Some doubt must be attached to the values given for  $\beta$ -AgI;  $\Delta H_m$  was obtained from  $E_A$  for the overall conductivity (40) and  $E_f$ , the energy of formation of defects determined by specific heat measurements (38). However, the conductivity temperature relationship is unusual; Lieser suggests (40) that  $E_A$ ,  $E_f$  and  $\Delta H_m$  all depend upon temperature. The parameters given in the table are calculated from values of these quantities corresponding to 147°C.

<sup>c</sup>  $V'$ , Cation vacancy;  $V^*$ , anion vacancy;  $Ag_i$ , interstitial Ag ion.

It is to be expected that a similar relationship to Eq. (3) will also apply to the good conductors; an empirical relationship of this form has indeed been found to apply (28). Values of  $C$  estimated from the experimental values of  $A$  are low and close to unity.

Although the value of  $A$  varies from one compound to another, generally decreasing as  $\Delta H_m$  decreases, the effect of this variation on the observed mobilities is small. This can be seen from Table III and Fig. 1, where the logarithm of the mobility expected at 150°C decreases with increasing  $\Delta H_m$ , in spite of a concomitant increase in  $A$ . In most cases, the poor conductors

have low values of mobility, associated with high values of  $\Delta H_m$ , whereas the moderate and good conductors have high mobilities as a result of lower  $\Delta H_m$  values.

### 3. The Good Conductors

In the previous section, it has been suggested that the conduction path in the good conductors involves all the lattice sites. The high conductivities of these compounds were attributed to high concentrations of mobile ions and low heats of activation for motion. The origins of these properties are discussed in this section.

The distinction between mobile and non-mobile ions is made on the basis of their contributions to the total ionic conductivity. This contribution depends upon the concentration and the mobility of the ion, the latter in turn depending upon the number and nature of the pathways available for its movement. In order to describe these factors more quantitatively, we consider a simple model crystal and derive a general expression for the rate of movement of the cations when an electric field is applied. In general, the following four types of ionic movement may occur: (i) normal ions into adjacent empty interstitial sites (rate  $R_{Li}$ ), (ii) interstitial ions into adjacent empty normal sites ( $R_{iL}$ ), (iii) normal ions into adjacent empty normal sites ( $R_{LL}$ ), and (iv) interstitial ions into adjacent empty interstitial sites ( $R_{ii}$ ).

For a crystal with one set of equivalent normal lattice sites of concentration  $N_L$ , and one set of equivalent interstitial sites of concentration  $N_i$ , application of the absolute rate theory leads<sup>1</sup> to the following expressions for the jump rates:

$$R_{Li} = v[n_L(N_i - n_i)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_L^*/RT), \quad (5)$$

$$R_{iL} = v[n_i(N_L - n_L)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_i^*/RT), \quad (6)$$

$$R_{LL} = v[n_L(N_L - n_L)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_L^*/RT), \quad (7)$$

$$R_{ii} = v[n_i(N_i - n_i)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_i^*/RT). \quad (8)$$

The total rate of movement  $R$  is given by the sum of these four contributions. Adding Eqs. (5–8), replacing  $\Delta G_L^* - \Delta G_i^*$  by  $\Delta G_t$  the standard free energy of transfer of an ion from a normal to an interstitial site, and replacing  $\Delta G_i^*$  by  $\Delta G_m$ , the standard free energy of activation for mobility out of an interstitial site, then rearranging, we obtain

$$R = \{[n_i + n_L \exp(-\Delta G_t/RT)] N_i/(N_i + N_L)\} \times (v zeaE/kT) \exp(-\Delta G_m/RT).$$

The specific conductivity is therefore (32) given as

$$\sigma = \{[n_i + n_L \exp(-\Delta G_t/RT)] N_i/(N_i + N_L)\} \times v(zea)^2/kT \exp(-\Delta G_m/RT). \quad (9)$$

<sup>1</sup> See Appendix for derivation of expressions and meaning of symbols.

The term enclosed in the curly brackets can be taken as the concentration of mobile ions and the remainder of the expression, when divided by  $ze$ , as their mobility.

### 3.1. The Concentration of Mobile Ions

Two limiting cases of Eq. (9) can be demonstrated.

(a) When  $\Delta G_t$  becomes large it can be shown that, despite the fact that  $n_L$  becomes large, the second term in the square brackets becomes very small compared with  $n_i$ , and the expression reduces to:

$$\sigma = [n_i N_i/(N_i + N_L)] v(zea)^2/kT \exp(-\Delta G_m/RT) \quad (10)$$

which is the expression for the rate of movement of interstitial ions between interstitial sites, when  $n_i \ll N_i$ . Expressions commonly written (32, 41) for the conductivity of the poor and moderate conductors are very similar to Eq. (10), usually differing only in the factor  $N_i/(N_i + N_L)$ . The concentration and mobility terms in Eq. (10) correspond to the expressions given in Eqs. (2 and 3) earlier in this paper.

(b) On the other hand, when  $\Delta G_t = 0$ , i.e., when we have an average structure, Eq. (9) reduces to:

$$\sigma = [(n_i + n_L) N_i/(N_i + N_L)] v(zea)^2/kT \exp(-\Delta G_m/RT) \quad (11)$$

which is the expression we should write if all the ions were equally free to move between any of the sites. Distinction between normal and interstitial sites is now not meaningful, and we have a total concentration of sites ( $N_i + N_L$ ), of which  $N_L$  is the concentration occupied. The factor  $N_i/(N_i + N_L)$  allows for the fact that all the ions can be considered as mobile only if each ion is surrounded by empty sites.

We can conclude, therefore, that for a large concentration of mobile ions, the following conditions should be satisfied: (i)  $\Delta G_t$  should be small, i.e., the difference in the energies of the cation-anion interactions in the different sites should be small, and (ii) a large excess of sites should be available.

All 1:1 compounds have an excess of sites, and hence  $N_i/(N_i + N_L)$  will not be zero. We should expect the value of  $\Delta G_t$  to be small if the co-

ordination number in the new position is the same as in the original position. If these coordination numbers differ, the value of  $\Delta G_i$  is likely to be small only if the vacant site has a coordination number which is observed in the normal compounds of the cation concerned. In 1:1 compounds, if the anions are arranged in a close-packed or nearly close-packed manner, vacant lattice sites of the same coordination number as the occupied sites are possible only if the cation occupies sites of 4- or lower coordination. For example, with the anions arranged in a body-centred cubic array, there are 12 equivalent tetrahedral holes per cation, and in a close-packed array there are 2 tetrahedral holes per cation. If the cations are 6- or 8-coordinated, however, vacant lattice sites of equal coordination number would not be expected in a defect-free crystal, although holes of lower coordination number do exist. For example, tetrahedral and 3-coordinated holes are present in compounds with the sodium chloride structure, while square planar holes exist in compounds with the caesium chloride structure. Cations which are normally 6- or 8-coordinated, however, rarely form compounds in which they display lower coordination numbers. For these cations, therefore, we should expect the value of  $\Delta G_i$  to be high, and the concentration of mobile species to be low. Conversely, the concentration of mobile species can be high for cations which display coordination numbers of 4 or less. Since similar considerations also apply to compounds in which the cation-to-anion ratio is greater than unity, the predominance of coordination numbers of 4 and less for the mobile species in the good conductors is understandable.

When the cation-to-anion ratio is less than unity, vacant lattice sites of the same coordination number as the occupied sites will normally exist even if the cations are 6- or 8-coordinated. In such compounds, the cations must have a valency greater than unity. As explained below, it is possible that under these circumstances cation-cation interactions will result in a large value for  $\Delta G_i$ .

*3.1.1. Effect of Cation-Cation Interactions.* Cation-cation interactions, which have been ignored so far, would lead to nonideal behaviour. Equation (20) (Appendix) should then be written as

$$n_i(N_L - n_L)/n_L(N_i - n_i) = \exp(-\Delta G_i/RT) \exp(-\Delta G^E/RT)$$

where  $\Delta G^E$  is an excess free energy due to cation-cation interactions and will depend on the concentration  $n_i$ . Under these circumstances, a large concentration of mobile ions will be observed only if both  $\Delta G_i$  and  $\Delta G^E$  are small. The internal energy term involved in  $\Delta G^E$  may be derived by use of a modified form of the Bragg-Williams theory (42, 43).

This theory deals with the effect of interactions on the average distribution of the two types of atom in a binary alloy. More sophisticated treatments (44, 45) also take account of the detailed arrangements of the atoms around each other (local ordering), but predict similar results for the average distribution of the atoms.

In a binary alloy, an ordered arrangement can occur when the two types of atom each occupy one regular set of sites. Disorder occurs when atoms of different type exchange places. Bragg and Williams define a degree of order  $S$  which equals unity at complete order and zero at complete disorder. They then demonstrate that the total energy  $E$  of the alloy varies with the degree of disorder according to:

$$E - E_{\text{order}} = -QV_0(S^2 - 1), \quad (12)$$

where  $Q$  is a constant which depends on the structure of the crystal (60) and  $V_0$  is the energy to exchange two atoms when the remainder of the structure is completely ordered. Kirkwood's more rigorous theory (45) predicts a similar dependence of  $E$  on  $V_0$  and  $S$ , when local ordering is ignored.

In applying the Bragg-Williams theory to solid electrolyte systems, we have regarded the two sets of sites as the normal and interstitial sites, and the two sets of atoms as the cations and the vacancies. Thus at complete order, the cations occupy all the normal sites and all the interstitial sites are empty, whereas increasing disorder corresponds to "exchange" of ions and vacancies. Converting to the terminology used in the present paper gives

$$Q = N_i N_L / 2(N_L + N_i) \quad (13)$$

and

$$S = 1 - n_i(N_i + N_L) / N_L N_i. \quad (14)$$

Since at complete order  $n_i = 0$ , whereas at complete disorder

$$n_L/N_L = n_i/N_i = (n_i + n_L)/(N_i + N_L).$$

$S$  still has the limits of 1 and 0.

Combining Eqs. (12–14) gives:

$$(E - E_{\text{order}}) = V_0 n_i [1 - n_i(N_i + N_L)/2N_L N_i]$$

and

$$(\partial E/\partial n_i)_{V,T} = \Delta U^E = V_0 S. \quad (15)$$

The quantity  $(\partial E/\partial n_i)_{V,T}$  which has been designated as  $\Delta U^E$ , is the internal energy contribution to  $\Delta G^E$  arising from cation–cation interactions. According to Eq. (15), if  $V_0$  is positive,  $\Delta U^E$  will also be positive for values of  $n_i$  covering the range from order to complete disorder. For a given value of  $n_i$ ,  $\Delta U^E$  will increase as  $V_0$  increases.

If, in the ordered arrangement, the cations occupy positions of minimum potential energy in the potential field generated by the other cations, exchange of a cation and a vacancy will normally involve an increase in energy, i.e.,  $V_0$  will be positive. Since the interactions between the cations will be essentially coulombic,  $V_0$  would be expected to depend on the square of the charge on the cations. In general, then,  $\Delta U^E$  and hence  $\Delta G^E$  would be expected to be positive and much greater with multivalent cations than monovalent ones.

We can, therefore, conclude that the conditions favouring a low value of  $\Delta G_i$  and  $\Delta G^E$ , and hence a large concentration of mobile ions at moderate temperatures are: (1) the cations should be stable with coordination numbers of 4 or less with the anions concerned, and (2) the cations should be monovalent.

### 3.2. The High Mobility of the Charge-Carrying Ions

For a cation to move from one position to a neighbouring one, it must pass through one or more intermediate states in which its effective coordination number and distances from adjacent anions will be different from those in the initial state. We are supposing that the energy difference between this intermediate state and the initial state is important in determining the magnitude of  $\Delta H_m$ . This energy difference will depend upon several factors, including both ionic and covalent interactions. Below, we consider the effects of the coordination numbers of the cation and the interatomic distances in the two states.

The coordination numbers displayed by a cation in the centres of a face and an edge of a number of regular polyhedra are shown in Table IV; if the anions are close-packed, how-

TABLE IV

COORDINATION NUMBERS OF CATIONS WITH VARIOUS ARRANGEMENTS OF ANIONS

Anion arrangement around cation site	Coordination number of cation			Ratio R (see text)
	in centre of polyhedron	in centre of face	in edge	
Cubic	8	4	2	0.817
Octahedral	6	3	2	0.817
Tetrahedral	4	3	2	0.942

ever, movement through the edges is clearly not possible. The ratio (R) of the cation–anion distance in the face to that in the centre of the polyhedron, calculated from the geometry of the figures, is also given.

It is clear that the energy of the intermediate position is likely to be very high unless the cation is capable of forming 4-coplanar, 3-coplanar or 2-collinear bonds. As pointed out previously, however, ions displaying 6- or 8-coordination are rarely stable in states of lower coordination number. Consequently a low value of  $\Delta H_m$  and hence a high mobility at moderate temperatures is likely only if the cations are stable in 4-, 3-, and perhaps 2-coordinated states.

Even for an intermediate state of favourable coordination number, the energy of the intermediate position will be a minimum for a particular interionic distance. While no satisfactory theoretical basis is apparent for predicting this distance, stable interionic distances for different coordination arrangements can be obtained from experimental data. Thus, if  $X$  is the coordinating atom, the ratio of the  $\text{Cu}^1\text{-}X$  distance for trigonally coordinated  $\text{Cu}^1$  (46, 47) to that for tetrahedral coordination (47–49) lies between 0.93 and 0.975, the most reliable value probably being for  $\text{Cu}^1\text{-S}$  distances, where the ratio is 0.965. These values are near that of 0.942 given in Table IV.

For trigonal and octahedral arrangements, information is more scarce; values of the mean trigonal  $\text{Ag-Cl}$  distance (50) and that for octahedral coordination in solid  $\text{AgCl}$  (51) give a ratio of 0.916, which is considerably greater than the “geometrical” value of 0.817 (Table IV). These considerations indicate that even if the appropriate coordination numbers are ac-

TABLE V

SOME SOLID COMPOUNDS OF  $\text{Ag}^{\text{I}}$  AND  $\text{Cu}^{\text{I}}$  IN WHICH THE CATION IS 2- OR 3-COORDINATED

Co-ordination number	Examples	Reference	Notes
2	$\text{Ag}_2\text{O}$ , $\text{AgCN}$ , $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$ , $\text{CsAgAuCl}_6$ , $\text{Cu}_2\text{O}$	52, 53	2 collinear bonds
	$(\text{C}_{18}\text{H}_{24}\text{NPO})^+(\text{CuCl}_2)^-$	54	$(\text{CuCl}_2)^-$ discrete linear anion
	$\text{AgSCN}$ , $\text{AgSbS}_3$ , $\text{AgAsS}_3$	52	2 non-linear bonds
3	$(\text{Me}_2\text{NC}_6\text{H}_4\text{PET}_2)_2\text{AgI}$	53	Some doubt about co-ordination state of $\text{Ag}^{\text{I}}$
	$(\text{NH}_4)_6(\text{AuCl}_4)_3\text{Ag}_2\text{Cl}_5$	50	—
	$(\text{C}_6\text{H}_{11}\text{C}_6\text{H}_5)_2\text{AgClO}_4$	55	3 bonds not coplanar
	$\text{AgNCS}[\text{SC}(\text{NH}_2)\text{-NHNH}_2]_2$	56	3 trigonal bonds, and 1 "long" $\text{Ag}\text{---}\text{S}$ interaction
	$\text{KCu}(\text{CN})_2$	57	3 planar bonds, 2 strong and 1 weak
	$\text{Cu}[\text{SC}(\text{NH}_2)_2]_2\text{Cl}$	58	3 trigonal almost planar bonds, and 1 "long" $\text{Cu}\text{---}\text{Cl}$ interaction
	$\text{Cu}(\text{SPMe}_3)_3\text{ClO}_4$	46	Discrete trigonal planar $[\text{Cu}(\text{SPMe}_3)_3]^{\text{I}}$ species
$[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}_2\text{Cl}_2$	47	Dimer—one $\text{Cu}^{\text{I}}$ has trigonal planar co-ordination	

ceptable, movement of a cation between 6-coordinated positions in a crystal may be hindered due to unfavourable interionic distances in the intermediate sites, whereas this is probably not so for ions moving between 4-coordinated positions.

### 3.3. The Characteristics of $\text{Ag}^{\text{I}}$ and $\text{Cu}^{\text{I}}$

The analysis presented in the last two sections leads to the conclusion that a large concentration of highly mobile cations is likely to exist at moderate temperatures, only in those compounds where the mobile cations are monovalent and are stable in 4-, 3-, and perhaps 2-coordinate arrangements with the anions. In line with this, the mobile species in all the good conductors is either  $\text{Ag}^{\text{I}}$  or  $\text{Cu}^{\text{I}}$ , and these ions always occupy 4-coordinated sites. In several compounds, there is evidence for the occupation of 3- and 2-coordinated positions; in one or two compounds, 6-coordinated positions are also occupied.

We believe the preponderance of  $\text{Ag}^{\text{I}}$  and  $\text{Cu}^{\text{I}}$  arises because these ions are very unusual among the monovalent metals in displaying 4-coordination in several of their solid compounds; most monovalent cations have coordination numbers of 6 or 8 in their simple salts. Silver and copper are, moreover, the only monovalent cations to form a substantial number of solid compounds in which they have coordination numbers of 3

and 2 (52, 53); some of these compounds are listed in Table V.

The arguments we have presented indicate that the stability of these coordination states with  $\text{Ag}^{\text{I}}$  and  $\text{Cu}^{\text{I}}$ , which is essentially a covalent characteristic, is of paramount importance in determining the high ionic conductivities of the good conductors. As far as we are aware, the almost unique conduction properties of these compounds have not been explained previously, although it has been noted (29) that the interatomic distances involved are more characteristic of covalent than ionic bonding. The covalent characteristics of silver and copper arise from the highly polarizing [or "soft-acid" (70)] properties of their ions, due in turn to incomplete shielding of their nuclear charge by the  $d^{10}$  electrons.

It is evident that not all the simple compounds of  $\text{Ag}^{\text{I}}$  and  $\text{Cu}^{\text{I}}$  satisfy the conditions for high conductivity. For example the bromide, chloride and fluoride of silver are essentially ionic compounds in which the cations are 6-coordinated by the anions (59), and these compounds are not good conductors. To obtain partially covalent bonding, however, it is necessary to have not only strongly polarizing cations but also highly polarizable (or "soft-base") anions. It is noteworthy that only the more highly polarizable anions ( $\text{I}^-$ ,  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ,  $\text{Te}^{2-}$ ) form conducting compounds with silver, the list being extended to include  $\text{Cl}^-$  and  $\text{Br}^-$  in the case of copper.



### Appendix: Derivation of a General Expression for the Rate of Movement of Cations Through a Crystal

Consider a crystal in which there is one set of equivalent normal cation sites, of concentration  $N_L$ , and one set of equivalent interstitial sites, of concentration  $N_i$ . Let the total concentration of cations ( $N_L$ ) be distributed over these sites so that  $n_L$  and  $n_i$  are the equilibrium concentrations residing in normal and interstitial sites, respectively. Let the distance between all pairs of adjacent sites be the same, and equal to  $a$ .

There are four possible types of ionic movement: (i) from normal sites into adjacent empty normal sites, (ii) from normal sites into adjacent empty interstitial sites, (iii) from interstitial sites into adjacent empty interstitial sites, and (iv) from interstitial sites into adjacent empty normal sites.

#### With No Applied Electric Field

The rate of movement of cations from normal sites into adjacent interstitial sites may be expressed in terms of the absolute rate theory. The jump frequency for an individual ion into a vacant interstitial site,  $v_{Li}$ , being given by

$$v_{Li} = v \exp(-\Delta G_L^*/RT) \quad (16)$$

where  $\Delta G_L^*$  is the difference in standard free energy between ions at the saddle point and in normal lattice positions and  $v$  is an effective frequency associated with vibration of the ion in the direction of the saddle point. Since only those cations adjacent to vacant interstitial sites will be mobile, their concentration will be

$$n_L^* = n_L(N_i - n_i)/(N_i + N_L). \quad (17)$$

The total rate at which normal ions pass into interstitial sites ( $R'_{Li}$ ) is, therefore,

$$R'_{Li} = n_L^* v_{Li} = v[n_L(N_i - n_i)/(N_i + N_L)] \exp(-\Delta G_L^*/RT). \quad (18)$$

Similarly the rate at which interstitial ions move into normal sites is given by

$$R'_{iL} = v[n_i(N_L - n_L)/(N_i + N_L)] \exp(-\Delta G_i^*/RT), \quad (19)$$

where  $\Delta G_i^*$  is the free energy for movement out of an interstitial position. The vibration frequency has been assumed to be the same for

ions in both normal and interstitial sites; any difference between these quantities being accommodated in the entropies of activation (71).

At equilibrium, the rates  $R'_{Li}$  and  $R'_{iL}$  are equal, so that

$$n_i(N_L - n_L)/n_L(N_i - n_i) = \exp(-\Delta G_i/RT), \quad (20)$$

where  $\Delta G_i = \Delta G_L^* - \Delta G_i^*$ .

#### With an Applied Field

When an electric field is applied, the free energy barrier in the direction of the field is reduced, and against the field it is increased, by an amount  $zeaE$  for ions of charge  $ze$ . This results in a net drift of ions in the direction of the field. If the jump rate in the absence of a field is  $R'$  then (32), in the presence of the field, when  $zeaE \ll kT$ , the jump rate is given by

$$R = R' zeaE/kT. \quad (21)$$

Expressions for the field-free rates of normal-interstitial and interstitial-normal movement have been derived above; for normal-normal and interstitial-interstitial movement, the reasoning and final equations are analogous. When a field is applied, therefore, we would obtain four similar expressions for the net jump rates in the direction of the field. The four equations are thus:

$$R_{Li} = v[n_L(N_i - n_i)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_L^*/RT) \quad (22)$$

$$R_{iL} = v[n_i(N_L - n_L)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_i^*/RT) \quad (23)$$

$$R_{LL} = v[n_L(N_L - n_L)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_L^*/RT) \quad (24)$$

$$R_{ii} = v[n_i(N_i - n_i)/(N_i + N_L)] \times (zeaE/kT) \exp(-\Delta G_i^*/RT). \quad (25)$$

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