

## The Compensation Law for Conductivity of Ionic Crystals

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The conductivity prefactor  $A$  is specified as a function of the conductivity activation energy  $E_A$  for a large series of alkali halide type crystals and of superionic conductors (SIC). A linear dependence of the form  $\log A = 2.1E_A + 5.3$  is observed for classical ionic conductors (CIC) with values of  $E_A > 0.9$  eV, as well as for SIC with  $E_A > 0.4$  eV. Such behavior, known as the compensation law (CL) cannot be understood within the framework of the conventional assumption of temperature-dependent  $E_A$  values. It is demonstrated that the CL is characteristic for defect formation as well as for defect migration processes, with corresponding isokinetic temperatures  $T_0 = 2.8 \times 10^3$  K and  $T_\mu = 2.1 \times 10^3$  K, respectively. For lower values of  $E_A$  ( $E_A < 0.9$  eV for CIC and  $E_A < 0.4$  eV for SIC) a considerable decrease in the prefactor is observed. This is interpreted in terms of melting or positional disordering of mobile ions in the cation sublattice of the crystal. This means that entropy change for mobility  $S_\mu$  is quite small, or even vanishes for these crystals. It is demonstrated that the conventional practice of using as the jump attempt frequency  $\nu_0$  the Debye frequency  $\nu_D$  for the mobile ion seems to be invalid. We propose to use instead the expression suggested by Rice and Roth:  $\nu_0 = (1/\pi) \cdot \sqrt{2H_\mu/a^2m}$ .

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The nonempirical solution to the problem of a directed search for new solid electrolytes cannot be attained without understanding (at least at the "Rule-of-Thumb" level) the peculiarities of different classes of ionically conducting crystals. The ion migration process in classical ionic solids may be described in terms of the simple hopping model. In the case of superionic conductors (SIC) the ion conduction mechanism is not yet known. Formally in both cases the temperature dependence of conductivity  $\sigma(T)$  is known from experience to be reasonably well described by the Arrhenius equation

$$\sigma T = A \cdot \exp(-E_A/kT), \quad (1)$$

where  $T$  is the temperature in K,  $k$  is Boltzmann's constant,  $E_A$  is the activation energy, and  $A$  is the conductivity prefactor.

For ionic solids of the NaCl type typical values of activation energy and those of prefactors lie in the range 1.0–2.5 eV and  $10^7$ – $10^{11}$  S · K/cm, respectively. The conductivity values at  $T = 300^\circ\text{C}$  change from  $10^{-10}$  to  $10^{-3}$  S/cm. For SIC,  $E_A$  and  $A$  values remain in the range 0.05–0.4 eV and  $10^3$ – $10^6$  S · K/cm, respectively, the values of  $\sigma$  at  $T = 300^\circ\text{C}$  being equal to  $10^{-2}$ – $10^0$  S/cm (1, 2). It is not clear how to classify the crystals characterized by defect concentrations as high as those in SIC (1–10 mole%) and by activation energies as high as 0.4–1.0 eV. Until lately no thorough studies of the conductivity prefactor in SIC were published, though a considerable body of data permit such an investigation to be carried out.

It has been observed that linear depen-

TABLE I  
EXPERIMENTAL DATA ON IONIC CONDUCTIVITY OF ORDINARY IONIC CRYSTALS

Salt	$E_A$ (eV)	$\log A$ $\left(\frac{\text{S} \cdot \text{K}}{\text{cm}}\right)$	Ref.	Salt	$E_A$ (eV)	$\log A$ $\left(\frac{\text{S} \cdot \text{K}}{\text{cm}}\right)$	Ref.
LiF	2.07	9.78	11	CsBr	1.44	8.1	14
LiCl	1.47	9.28	12	CsI	1.43	8.0	14
LiBr	1.29	9.00	12	CsNO <sub>3</sub>	1.05	7.7	14
LiI	0.96	7.2	13	TlCl	0.87	6.95	14
LiN <sub>3</sub>	1.87	10.1	14	TlBr	0.785	5.97	22
NaF	2.2	9.7	15	$\alpha$ -TlI	0.68	5.34	22
NaCl	2.18	10.3	16	AgCl	0.99	7.6	14
NaBr	1.68	8.3	14	AgBr	0.87	7.8	14
NaI	1.66	9.26	17	$\alpha$ -AgI	0.97	6.8	14
NaNO <sub>2</sub>	1.15	7.8	14	AgN <sub>3</sub>	0.82	7.0	14
NaN <sub>3</sub>	1.82	9.8	14	$\beta$ -CaF <sub>2</sub>	2.13	11	14
KF	2.34	10.0	14	$\beta$ -SrF <sub>2</sub>	2.14	9.75	14
KCl	2.36	10.75	14	$\beta$ -SrCl <sub>2</sub>	1.25	7.3	14
KBr	2.21	9.85	14	$\beta$ -BaF <sub>2</sub>	1.64	8.83	14
KI	1.93	9.40	18	CdCl <sub>2</sub>	1.03	8.0	14
RbCl	1.59	8.6	19	PbCl <sub>2</sub>	0.89	6.1	14
RbBr	2.02	9.50	20	PbBr <sub>2</sub>	0.71	4.7	14
RbI	2.16	9.54	21	PbI <sub>2</sub>	1.3	5.3	14
CsF	1.55	8.2	14	CuSO <sub>4</sub>	2.21	10.1	14
$\alpha$ -CsCl	1.67	8.0	14	$\gamma$ -SnF <sub>2</sub>	0.74	6.3	23
$\beta$ -CsCl	1.33	7.9	14	$\beta$ -PbF <sub>2</sub>	0.45	4.8	24

dences between  $\log A$  and  $E_A$  are encountered in some groups of crystals (3–5). A similar dependence between  $D_0$  and  $E_D$  is known for metals (6), where  $E_D$  is the activation energy for the self-diffusion and  $D_0$  is its preexponential factor. Such a relationship is likely to be characteristic of diffusion-controlled reactions and is known as the compensation law (CL) (4–7). While some explanations of the CL (7, 9) have been provided, no real theory of the law has so far been proposed.

In this paper an attempt is made to obtain quantitative correlations between the values of  $\log A$  and  $E_A$  in the alkali halides (AH), in some other inorganic crystals as well as in SIC, and to apply these correlations to the analysis of the conductivity mechanism in the above-mentioned ionic solids.

### Alkali Halide-Type Crystals

The ionic conductivity of AH type crystals has been intensively investigated. However, the considerable discrepancy in values of  $E_A$  and  $A$  cited by different authors raise many questions concerning the earlier CL studies in AH type crystals. According to Dosdale and Brook (10) a CL in conductivity is observed for the same crystals when measurements are carried out in different parts of the region intermediate between the intrinsic and extrinsic regions of conductivity. According to the authors, the correct  $A$  and  $E_A$  values are the highest ones obtained in a series of independent measurements made for the same compound. Such values for AH and for other ionic crystals are presented in Table I, taken from previous investigations of dif-

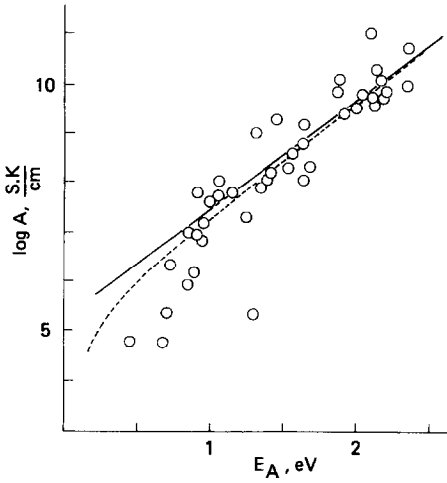


FIG. 1. The compensation law for conductivity of ionic crystals. Full and dashed lines are computed on the basis of Eqs. (2) and (11), respectively. Apparent deviations from the straight-line correlation are seen for  $E_A < 0.9$  eV.

ferent authors. The experimental values with activation energies exceeding  $0.9 \pm 0.1$  eV satisfied reasonably well a linear dependence of the type

$$\log A = (5.3 \pm 0.3) + (2.1 \pm 0.2) \cdot E_A, \quad (2)$$

where  $E_A$  is measured in eV and  $A$  in  $S \cdot K/cm$ . The variation (2) is shown in Fig. 1. It is to be noted that the conductivity prefactor for some silver, lead, tin, and thallium salts with the conductivity activation energies not exceeding  $0.9 \pm 0.1$  eV seems to be abnormally low.

We now analyze the prefactor  $A$  in detail. The volume concentration of defects ( $n$ ) and the mobility of these defects ( $\mu$ ) being two factors in the expression for ionic conductivity  $\sigma = q \cdot n \cdot \mu$  (where  $q$  is the defect charge) are known to depend exponentially on the reciprocal temperature:

$$n = N \exp(-H_0/kTz) \quad (3)$$

$$\mu = M \exp(-H_\mu/kT), \quad (4)$$

where  $H_0$  and  $H_\mu$  are the enthalpy of defect formation and the free enthalpy of defect

migration, respectively, and  $z$  is the number of species taking part in the quasichemical reaction of defect formation. The compensation law may arise either from that for defect formation or from that for the defect migration process, i.e., as a consequence of the dependence of  $N$  or  $M$  on  $H_0$  or  $H_\mu$ , respectively. Assuming  $H_\mu$  and  $H_0$  values to be temperature independent one can write for  $N$  and  $M$  (25):

$$N = N_0 \exp(S_0/zk) \quad (5)$$

$$M = (\gamma qa^2 \nu_0)/kT \cdot \exp(S_\mu/k), \quad (6)$$

where  $N_0$  is the total number of ions in  $1 \text{ cm}^3$  of a crystal,  $\gamma$  is the steric factor,  $a$  is the hopping distance,  $\nu_0$  is an attempt frequency to overcome the potential barrier,  $S_0$  and  $S_\mu$  are the entropies for defect formation and migration, respectively. If we suppose the defect formation as well as the defect migration enthalpies to decrease linearly with temperature (8) as:  $H_0 = H'_0(1 - \alpha_1 T)$ ,  $H_\mu = H'_\mu(1 - \alpha_2 T)$ , where  $H'_0$  and  $H'_\mu$  are the corresponding values at  $T = 0$  K, the  $N$  and  $M$  values increase by the factors  $\exp(H_0 \alpha_1 / zk)$  and  $\exp(H_\mu \alpha_2 / k)$ , respectively. Assuming  $\alpha_1 \cong \alpha_2 = \alpha$  for the case of AH type crystals, when  $z = 2$ ,  $\gamma = 4$  and  $E_A = H_0/2 + H_\mu$  the prefactor  $A$  should be equal to

$$\log A = \log(N_0 4q^2 a^2 \nu_0/k) + (S_0/2 + S_\mu + \alpha E_A)/2.3k. \quad (7)$$

From comparison of Eq. (7) with the empirical relation given by Eq. (2) the values of  $\log(N_0 4q^2 a^2 \nu_0/k) + (S_0/2 + S_\mu)/2.3k$  and of  $\alpha/2.3k$  would be equal to  $5.3 \pm 0.3$  and to  $2.1 \pm 0.2$  1/eV, respectively. The first term in Eq. (7) changes weakly in a series of AH type crystals and for the typical values of  $\nu_0 = 3 \times 10^{12} \text{ s}^{-1}$ ,  $a = 3 \times 10^{-8} \text{ cm}$ ,  $N_0 = 10^{22} \text{ cm}^{-3}$  is equal to 5.2. In such a case both  $S_0$  and  $S_\mu$  would be nearly equal to zero and the CL is caused entirely by the temperature dependence of the activation energies. Theoretical estimates show, how-

TABLE II  
ENTHALPIES AND ENTROPIES OF THE DEFECT  
FORMATION  $H_0$ ,  $S_0$  AND OF THE DEFECT MIGRATION  
 $H_\mu$ ,  $S_\mu$ ,  $S_\mu^*$  ( $S_\mu^*$  WERE ESTIMATED AT  $\nu_0 = \nu_D$ ,  $S_\mu$   
ARE REESTIMATED BY US ASSUMING THAT  $\nu_0 = \nu_h$ )  
IN ORDINARY IONIC CRYSTALS

Salt	$H_0$ (eV)	$S_0/k$	Defect type	$H_\mu$ (eV)	$S_\mu^*/k$	$S_\mu/k$	Ref.
LiI	1.06	4.5	V <sub>Li</sub>	0.43	—	—	13
NaF	2.5	9.4	V <sub>Na</sub>	0.95	—	—	15
NaCl	2.44	9.8	V <sub>Na</sub>	0.69	1.64	2.9	29
			V <sub>Cl</sub>	0.77	1.38	3.0	29
NaBr	1.78	4.68	V <sub>Na</sub>	0.79	4.26	5.6	30
			V <sub>Br</sub>	1.25	7.25	8.5	36
NaI	2.00	7.64	V <sub>Na</sub>	0.58	3.23	4.0	17
			V <sub>I</sub>	0.77	2.91	2.9	17
KCl	2.59	9.61	V <sub>K</sub>	0.73	2.70	4.0	31
			V <sub>Cl</sub>	0.99	4.14	5.0	31
KBr	2.53	10.3	V <sub>K</sub>	0.65	1.89	3.1	32
			V <sub>Br</sub>	1.22	7.30	8.6	32
KI	2.21	8.87	V <sub>K</sub>	0.63	1.58	2.4	31
			V <sub>I</sub>	1.29	9.33	9.8	31
RbCl	2.44	—	V <sub>Rb</sub>	0.54	1.73	3.3	33
AgCl	1.46	5.44	V <sub>Ag</sub>	0.28	-0.48	1.4	34
AgBr	1.13	6.55	V <sub>Ag</sub>	0.32	1.16	2.7	35
TlCl	1.25	6.3	V <sub>Tl</sub>	0.38	2.04	2.6	36
			V <sub>Cl</sub>	0.10	-2.21	-0.3	36
$\beta$ -CaF <sub>2</sub>	2.72	4.9	V <sub>F</sub>	0.43	1.6	3.2	37
			F <sub>i</sub>	0.78	4.5	5.8	37
$\beta$ -BaF <sub>2</sub>	1.85	3.5	V <sub>F</sub>	0.55	3.4	3.8	37
			F <sub>i</sub>	0.73	4.5	4.8	37
$\beta$ -SrF <sub>2</sub>	2.39	4.1	V <sub>F</sub>	0.55	3.4	4.4	37
			F <sub>i</sub>	0.75	2.8	3.7	37
$\beta$ -PbF <sub>2</sub>	1.07	4.1	V <sub>F</sub>	0.23	1.1	1.9	37
			F <sub>i</sub>	0.5	4.2	3.6	37
$\beta$ -SrCl <sub>2</sub>	1.97	3.3	V <sub>Cl</sub>	0.4	1.0	2.4	37

ever, that both defect formation and defect migration processes cause a considerable entropy change (26, 27). Therefore it is reasonable to suppose that values of  $H_0$  and  $H_\mu$  are only weakly dependent on (or entirely independent of) temperature and that the CL must be explained by the existing linear dependences of the type

$$S_0 = H_0/T_0 \quad (8)$$

$$S_\mu = H_\mu/T_\mu, \quad (9)$$

where  $T_0$  and  $T_\mu$  are some so-called isokinetic temperatures.

For the estimation of  $S_\mu$  from experimental data the Debye frequency  $\nu_D$  is generally used. After Rice and Roth (28) we consider

that it is more reliable to take as  $\nu_0$  the quantity

$$\nu_h = (1/\pi) \cdot \sqrt{2H_\mu/a^2m} \quad (10)$$

which is valid for an ion moving in harmonic potential,  $m$  being the ion mass. In Table II the values of  $H_0$ ,  $H_\mu$ ,  $S_0$ ,  $S_\mu^*$ , and  $S_\mu$  are presented where  $S_\mu^*$  is obtained for  $\nu_D = \nu_0$  and  $S_\mu$  is estimated for  $\nu_h = \nu_0$ . As is seen from Fig. 2 the  $S_0$  values change linearly with  $H_0$ . As for mobility,  $S_\mu$  becomes linearly correlated with  $H_\mu$  when  $\nu_h$  is used in place of  $\nu_D$  (see Figs. 3a and b). The mean values of isokinetic temperatures  $T_0$  and  $T_\mu$  are equal to  $2.8 \times 10^3$  and  $2.1 \times 10^3$  K, respectively. The mean value of  $T_0$  for fluorite-type crystals seems to be higher than for AH type crystals. Assuming  $H_\mu = 0.3H_0$  (38) for AH type crystals from Eqs. (8), (9), and (10) one can obtain the relation

$$\log A = \log \left( \frac{N_0 q^2 a \sqrt{0.75}}{\pi k \sqrt{m}} \sqrt{E_A} \right) + E_A(0.27/kT_0 + 0.16/kT_\mu). \quad (11)$$

As seen from Fig. 1 the calculated dependence (11) with  $N_0 = 10^{22} \text{ cm}^{-3}$ ,  $a = 3 \times$

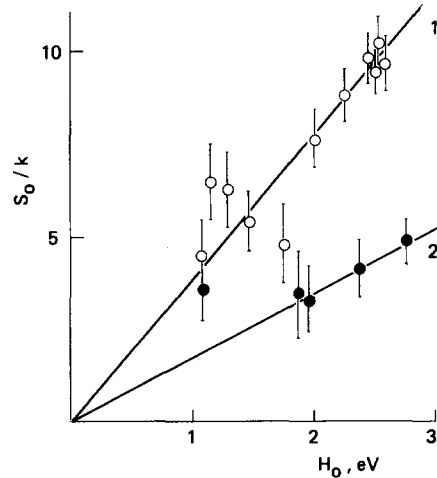


FIG. 2. The compensation law for the defect formation reaction in NaCl-type crystals (1) and in fluorite-type crystals (2). These data obey Eq. (8) with  $T_0 = 2.8 \times 10^3$  K (AH crystals),  $6.1 \times 10^3$  K (CaF<sub>2</sub>-type crystals).

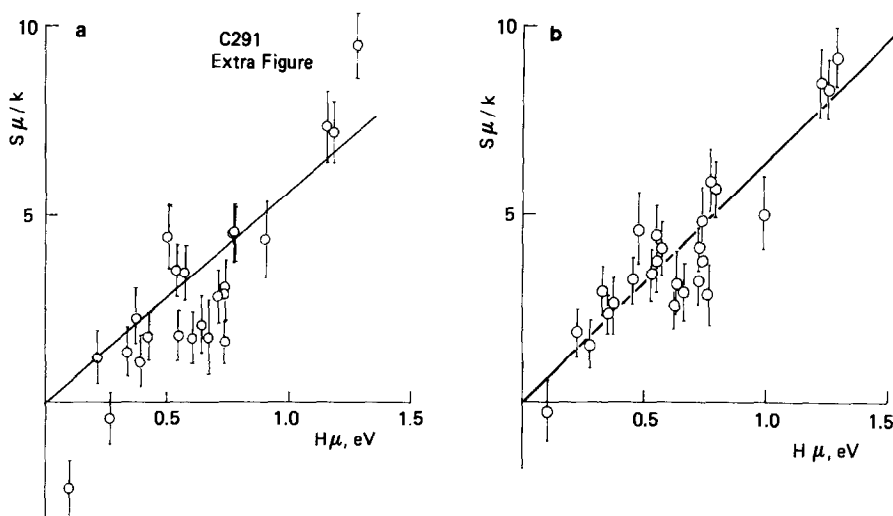


FIG. 3. The correlation between the entropy of migration  $S_\mu$  and the activation enthalpy for mobility  $H_\mu$  in ionic crystals. (a)  $S_\mu$  calculated on the assumption  $\nu_0 = \nu_D$ ; physically unacceptable negative  $S_\mu$  cause deviations from linear dependence. (b)  $S_\mu$  calculated using  $\nu_0 = \nu_h = (1/\pi a)(2H_\mu/m)^{1/2}$ . The slope of the improved straight-line fit yields  $T_\mu = 2.1 \times 10^3$  K.

$10^{-8}$  cm,  $m = 4 \times 10^{-23}$  g,  $T_0 = 2.8 \times 10^3$  K,  $T_\mu = 2.1 \times 10^3$  K is in accord with the experimentally observed one for AH type crystals having activation energies  $E_A > 0.9 \pm 0.1$  eV. The dependence (11) is in qualitative agreement with the experimentally observed abnormal decrease of  $A$  values for compounds having small activation energies. However, there are considerable quantitative discrepancies between the calculated and experimentally observed relations in the low-value region of  $E_A$ . For a careful analysis of the CL in this region of  $E_A$  a survey of conductivity data for SIC must be made.

### Superionic Conductors

A compilation of experimental data on the ionic conductivities of SIC is presented in Table III. The principal difference of SIC from classical ionic conductors is assumed to be the high defect concentration  $n = N_0$  in crystal lattice of SIC. For this case  $H_0 = 0$ ,  $S_0 = 0$ ,  $E_A = H_\mu$ , and so Eq. (11) may be rewritten in the form

$$\log A = \log(N_0 q^2 a \sqrt{2E_A/\pi k \sqrt{m}}) + E_A/2.3kT. \quad (12)$$

Experimental values of  $\log A$  and  $E_A$  are presented in Figs. 4, 5, and 6 and compared with the dependence specified by Eq. (12) for silver, copper, thallium, indium, and cadmium salts (see Fig. 4), for alkali metals

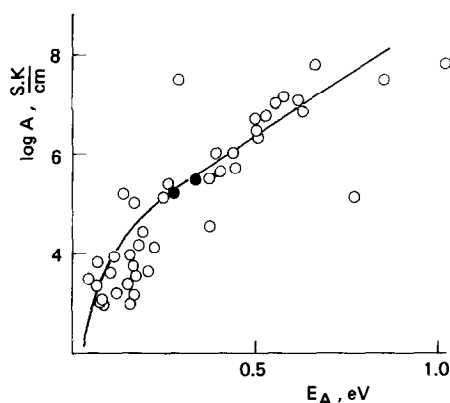


FIG. 4. Prefactor vs activation energy for conductivity of silver, copper, thallium superionic conductors. The full circles correspond to hypothetical values for AgCl and AgBr crystals calculated assuming  $n = N_0 = 10^{22}$  cm $^{-3}$ . The curve is plotted in accord with Eq. (12).

TABLE III  
EXPERIMENTAL VALUES OF  $E_A$  AND  $\log A$  IN SUPERIONIC CONDUCTORS

Substance	$E_A$ (eV)	$\log A$ ( $\frac{S \cdot K}{cm}$ )	Ref.	Substance	$E_A$ (eV)	$\log A$ ( $\frac{S \cdot K}{cm}$ )	Ref.
$\alpha$ -Ag <sub>3</sub> SI	0.042	3.5	39	Na <sub>5</sub> YSi <sub>4</sub> O <sub>12</sub> ( $\parallel$ c)	0.221	4.3	47
$\alpha$ -AgI	0.052	3.32	39	LiNa- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.23	4.4	48
$\alpha$ -Ag <sub>2</sub> Se	0.059	3.8	40	Na <sub>0.7</sub> Ga <sub>4.72</sub> Ti <sub>0.29</sub> O <sub>8</sub>	0.25	2.3	49
$\alpha$ -Ag <sub>2</sub> S	0.066	3.02	40	Li <sub>3</sub> N ( $\perp$ c)	0.25	4.2	50
Ag <sub>4</sub> KI <sub>5</sub>	0.07	3.0	41	Na <sub>0.75</sub> K <sub>0.25</sub> - $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.27	2.9	51
Ag <sub>4</sub> RbI <sub>5</sub>	0.07	3.0	41	K- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.28	3.6	42
Ag <sub>2</sub> Te	0.10	3.7	41	Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub>	0.30	4.4	52
$\alpha$ -Cu <sub>1.6</sub> Rb <sub>1</sub> Cl <sub>5.6</sub>	0.104	4.0	41	Na- $\beta'$ -Al <sub>2</sub> O <sub>3</sub>	0.33	6.6	42
Cu <sub>4</sub> RbCl <sub>4</sub> (I <sub>1-x</sub> ,Cl <sub>x</sub> )	0.117	3.2	41	Na <sub>0.1</sub> K <sub>0.9</sub> - $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.36	4.1	51
Ag <sub>19</sub> I <sub>15</sub> P <sub>2</sub> O <sub>7</sub>	0.143	5.2	41	$\alpha$ -Li <sub>2</sub> SO <sub>4</sub>	0.36	4.7	14
Ag <sub>6</sub> I <sub>4</sub> WO <sub>4</sub>	0.156	4.0	41	Li <sub>4</sub> Ge <sub>0.85</sub> Mo <sub>0.15</sub> O <sub>4</sub>	0.37	4.6	53
Ag- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.16	3.0	42	Li <sub>4</sub> Ge <sub>0.9</sub> Mo <sub>0.1</sub> O <sub>4</sub>	0.38	4.7	53
(CH <sub>3</sub> ) <sub>4</sub> NAg <sub>6</sub> I <sub>7</sub>	0.16	5.0	41	Rb- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.39	4.3	42
Ag <sub>7</sub> I <sub>4</sub> PO <sub>4</sub>	0.165	3.7	41	Na <sub>0.55</sub> K <sub>0.45</sub> - $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.40	4.6	51
$\beta$ -Ag <sub>3</sub> SI	0.17	3.5	41	Li <sub>4</sub> Ge <sub>0.95</sub> Mo <sub>0.05</sub> O <sub>4</sub>	0.42	4.5	53
Cu <sub>2</sub> Se	0.17	4.1	14	$\alpha$ -Li <sub>3</sub> NI <sub>2</sub>	0.44	4.1	54
Ag <sub>7</sub> I <sub>4</sub> AsO <sub>4</sub>	0.174	3.2	41	Na <sub>0.15</sub> K <sub>0.85</sub> - $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.44	4.4	51
Ag <sub>7</sub> I <sub>4</sub> VO <sub>4</sub>	0.174	3.4	41	K <sub>0.76</sub> Zn <sub>0.33</sub> Sn <sub>0.65</sub> O <sub>2</sub>	0.45	5.1	55
Ag- $\beta''$ -Al <sub>2</sub> O <sub>3</sub>	0.19	4.4	42	Li <sub>6</sub> NBr <sub>3</sub>	0.45	3.3	54
Ag <sub>13</sub> ((CH <sub>3</sub> ) <sub>4</sub> N) <sub>2</sub> I <sub>15</sub>	0.19	4.4	41	NaK- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.45	4.6	51
Cu <sub>2</sub> RbCl <sub>3</sub>	0.203	3.6	43	Na <sub>2</sub> ZrYb(PO <sub>4</sub> ) <sub>3</sub>	0.46	5.0	56
(C <sub>5</sub> H <sub>5</sub> NH)Ag <sub>18</sub> I <sub>23</sub>	0.21	4.1	41	Na <sub>6</sub> CaP <sub>2</sub> O <sub>9</sub>	0.46	5.4	57
$\alpha$ -Cu <sub>2</sub> S	0.25	5.1	41	$\alpha$ -Li <sub>13</sub> N <sub>4</sub> Br	0.47	4.0	54
Ag <sub>13</sub> ((C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N) <sub>2</sub> I <sub>15</sub>	0.26	5.3	41	Na <sub>1.8</sub> Zr <sub>1.2</sub> Yb <sub>0.8</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.48	5.2	56
$\alpha$ -Cu <sub>1.6</sub> Rb <sub>1</sub> I <sub>7</sub>	0.29	7.5	41	K <sub>1.12</sub> Ta <sub>1.12</sub> W <sub>0.88</sub> O <sub>6</sub>	0.48	5.3	45
$\alpha$ -CuPb <sub>3</sub> Br <sub>7</sub>	0.34	1.4	44	Li <sub>1.8</sub> N <sub>0.4</sub> Cl <sub>0.6</sub>	0.49	4.9	54
Ag <sub>2</sub> HgI <sub>4</sub>	0.37	5.3	39	Na <sub>1.5</sub> Zr <sub>1.5</sub> Yb <sub>0.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.50	5.0	56
TiTaWO <sub>6</sub>	0.38	4.5	45	$\beta$ -Li <sub>3</sub> NI <sub>2</sub>	0.50	5.0	54
Tl <sub>1.9</sub> Ta <sub>1.9</sub> W <sub>0.1</sub> O <sub>6</sub>	0.39	6.0	45	Na <sub>2.5</sub> Zr <sub>0.5</sub> Yb <sub>1.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.50	5.3	56
Tl <sub>1.95</sub> Ta <sub>1.95</sub> W <sub>0.05</sub> O <sub>6</sub>	0.40	5.7	45	Na <sub>1.7</sub> Al <sub>1.7</sub> Si <sub>0.3</sub> O <sub>4</sub>	0.50	6.8	57
Ag <sub>2</sub> CdI <sub>4</sub>	0.43	6.0	39	Na <sub>0.2</sub> K <sub>0.8</sub> - $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.52	4.9	51
Ag <sub>2</sub> ZnI <sub>4</sub>	0.44	5.6	39	K <sub>0.8</sub> Li <sub>0.2</sub> - $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.52	5.1	48
Tl <sub>1.25</sub> Ta <sub>1.25</sub> W <sub>0.75</sub> O <sub>6</sub>	0.50	6.3	45	Li <sub>4</sub> Ge <sub>0.35</sub> Mo <sub>0.45</sub> O <sub>4</sub>	0.52	5.2	53
Tl <sub>1.3</sub> Ta <sub>1.3</sub> W <sub>0.7</sub> O <sub>6</sub>	0.50	6.4	45	K <sub>0.7</sub> Mg <sub>0.35</sub> Sn <sub>0.65</sub> O <sub>2</sub>	0.52	5.7	55
Tl <sub>1.6</sub> Ta <sub>1.6</sub> W <sub>0.4</sub> O <sub>6</sub>	0.50	6.8	45	K <sub>0.7</sub> Ca <sub>0.35</sub> Sn <sub>0.65</sub> O <sub>2</sub>	0.54	5.1	55
Tl <sub>1.5</sub> Ta <sub>1.5</sub> W <sub>0.5</sub> O <sub>6</sub>	0.52	6.8	45	Na <sub>1.6</sub> Al <sub>1.6</sub> Si <sub>0.4</sub> O <sub>4</sub>	0.55	7.5	57
Tl <sub>1.75</sub> Ta <sub>1.75</sub> W <sub>0.25</sub> O <sub>6</sub>	0.55	7.0	45	$\beta$ -Na <sub>3</sub> Sc <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.55	7.9	46
Tl <sub>1.8</sub> Ta <sub>1.8</sub> W <sub>0.2</sub> O <sub>6</sub>	0.57	7.1	45	Li <sub>14</sub> Zn(GeO <sub>4</sub> ) <sub>4</sub>	0.56	5.9	50
Cd- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.61	7.0	42	Li <sub>3.6</sub> Si <sub>0.6</sub> P <sub>0.4</sub> O <sub>4</sub>	0.57	6.0	50
Cu <sub>2</sub> HgI <sub>4</sub>	0.62	6.9	39	K <sub>1.3</sub> Ta <sub>1.3</sub> W <sub>0.7</sub> O <sub>6</sub>	0.57	6.0	45
In <sub>2</sub> ZnI <sub>4</sub>	0.75	6.8	39	Na <sub>2.6</sub> Zr <sub>0.4</sub> Yb <sub>1.6</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.58	6.0	56
Tl <sub>2</sub> ZnI <sub>4</sub>	0.87	5.1	39	NaAlSiO <sub>4</sub>	0.58	6.1	57
In <sub>2</sub> CdI <sub>6</sub>	0.95	7.4	39	Na <sub>1.3</sub> Al <sub>1.3</sub> Si <sub>0.7</sub> O <sub>4</sub>	0.58	6.7	57
Tl <sub>2</sub> ZnBr <sub>4</sub>	1.03	7.7	39	Na <sub>1.4</sub> Al <sub>1.4</sub> Si <sub>0.6</sub> O <sub>4</sub>	0.59	7.3	57
Na- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	0.15	3.6	42	K <sub>1.4</sub> Ta <sub>1.4</sub> W <sub>0.6</sub> O <sub>6</sub>	0.60	6.1	45
K- $\beta''$ -Al <sub>2</sub> O <sub>3</sub>	0.15	4.2	42	Li <sub>7</sub> TaO <sub>6</sub>	0.60	6.3	58
Na <sub>3</sub> Sc <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.19	2.4	46	Na <sub>2.8</sub> Zr <sub>0.2</sub> Yb <sub>1.8</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.61	6.2	57
Na <sub>5</sub> YSi <sub>4</sub> O <sub>12</sub> ( $\perp$ c)	0.203	3.6	47	Na <sub>1.2</sub> Al <sub>1.2</sub> Si <sub>0.80</sub> O <sub>4</sub>	0.61	7.6	58

TABLE III—Continued

Substance	$E_A$ (eV)	$\log A$ $\left(\frac{S \cdot K}{cm}\right)$	Ref.	Substance	$E_A$ (eV)	$\log A$ $\left(\frac{S \cdot K}{cm}\right)$	Ref.
Li <sub>7</sub> NbO <sub>6</sub>	0.64	5.7	55	$\alpha$ -TlBiF <sub>4</sub>	0.38	4.0	1
K <sub>0.72</sub> In <sub>0.72</sub> Zr <sub>0.28</sub> O <sub>2</sub>	0.65	6.6	55	Pb <sub>0.88</sub> Th <sub>0.12</sub> F <sub>2.24</sub>	0.38	4.3	62
K <sub>0.72</sub> In <sub>0.72</sub> Hf <sub>0.28</sub> O <sub>2</sub>	0.67	7.5	50	Pb <sub>0.73</sub> Bi <sub>0.27</sub> F <sub>2.27</sub>	0.38	4.5	61
Li <sub>5</sub> AlO <sub>4</sub>	0.68	8.1	57	Pb <sub>0.88</sub> Zr <sub>0.12</sub> F <sub>2.24</sub>	0.38	4.8	62
Na <sub>2</sub> SiAlO <sub>4.5</sub>	0.68	8.4	45	Pb <sub>0.81</sub> Th <sub>0.19</sub> F <sub>2.38</sub>	0.38	4.9	62
K <sub>1.5</sub> Ta <sub>1.5</sub> W <sub>0.5</sub> O <sub>6</sub>	0.69	6.3	55	KBiF <sub>4</sub>	0.38	5.0	63
K <sub>0.72</sub> In <sub>0.72</sub> Sn <sub>0.28</sub> O <sub>2</sub>	0.69	7.0	55	Pb <sub>0.82</sub> Sb <sub>0.18</sub> F <sub>2.18</sub>	0.39	5.1	61
$\beta$ -Li <sub>13</sub> N <sub>4</sub> Br	0.73	5.9	54	Pb <sub>0.86</sub> Zr <sub>0.14</sub> F <sub>2.28</sub>	0.40	4.9	62
Na <sub>2.9</sub> Zr <sub>0.1</sub> Yb <sub>1.9</sub> (PO <sub>4</sub> )	0.77	7.7	56	Pb <sub>0.92</sub> Zr <sub>0.08</sub> F <sub>2.16</sub>	0.41	5.2	61
LiAlSiO <sub>4</sub>	0.78	4.4	50	Pb <sub>0.63</sub> Sb <sub>0.37</sub> F <sub>2.37</sub>	0.42	5.9	61
Li <sub>3</sub> N (   c)	0.79	8.2	50	$\beta$ -PbSnF <sub>4</sub>	0.42	6.8	60
Li <sub>6</sub> In <sub>2</sub> O <sub>6</sub>	0.80	6.4	58	Pb <sub>0.8</sub> Bi <sub>0.2</sub> F <sub>2.2</sub>	0.43	5.0	61
Li <sub>9.1</sub> N <sub>2.7</sub> I	0.80	6.8	54	Pb <sub>0.9</sub> Sb <sub>0.1</sub> F <sub>2.1</sub>	0.43	5.3	61
Na <sub>1.12</sub> Ta <sub>1.12</sub> W <sub>0.88</sub> O <sub>6</sub>	0.80	6.6	45	Pb <sub>0.4</sub> Bi <sub>0.6</sub> F <sub>2.2</sub>	0.44	5.2	63
Li <sub>11</sub> N <sub>3</sub> Cl <sub>2</sub>	0.83	6.1	54	Pb <sub>0.95</sub> Zr <sub>0.05</sub> F <sub>2.1</sub>	0.44	5.3	62
Na <sub>1.8</sub> Ta <sub>1.8</sub> W <sub>0.2</sub> O <sub>6</sub>	0.85	7.6	45	Pb <sub>0.82</sub> Bi <sub>0.18</sub> F <sub>2.18</sub>	0.45	5.0	61
Na <sub>1.4</sub> Ta <sub>1.4</sub> W <sub>0.60</sub> O <sub>6</sub>	0.86	7.7	45	Pb <sub>0.77</sub> Th <sub>0.23</sub> F <sub>2.46</sub>	0.45	5.1	62
Na <sub>1.62</sub> Ta <sub>1.62</sub> W <sub>0.38</sub> O <sub>6</sub>	0.90	8.2	45	Pb <sub>0.95</sub> Th <sub>0.05</sub> F <sub>2.1</sub>	0.45	5.2	62
Li <sub>8</sub> SnO <sub>6</sub>	0.91	8.5	58	LaF <sub>3</sub>	0.46	5.3	64
Li <sub>6</sub> Ge <sub>2</sub> O <sub>7</sub>	0.91	6.4	58	Na <sub>0.4</sub> Bi <sub>0.6</sub> F <sub>2.2</sub>	0.46	5.8	63
Na <sub>0.9</sub> In <sub>0.9</sub> Sn <sub>0.1</sub> O <sub>2</sub>	0.93	4.9	55	Pb <sub>0.82</sub> Zr <sub>0.18</sub> F <sub>2.36</sub>	0.48	5.4	62
Li <sub>4</sub> GeO <sub>4</sub>	0.94	6.1	53	Pb <sub>0.59</sub> Sb <sub>0.41</sub> F <sub>2.41</sub>	0.48	6.4	61
NaInO <sub>2</sub>	1.09	5.6	55	Pb <sub>0.97</sub> Sb <sub>0.03</sub> F <sub>2.03</sub>	0.49	5.4	61
—	—	—	—	Pb <sub>0.9</sub> Bi <sub>0.1</sub> F <sub>2.1</sub>	0.51	5.4	61
$\alpha$ -PbSnF <sub>4</sub>	0.17	3.5	60	Na <sub>0.38</sub> Bi <sub>0.62</sub> F <sub>2.24</sub>	0.51	6.3	63
Pb <sub>0.73</sub> Sb <sub>0.27</sub> F <sub>2.27</sub>	0.30	4.4	61	Na <sub>0.36</sub> Bi <sub>0.64</sub> F <sub>2.28</sub>	0.53	6.4	63
Pb <sub>0.9</sub> Th <sub>0.1</sub> F <sub>2.2</sub>	0.35	4.5	62	Pb <sub>0.75</sub> Th <sub>0.25</sub> F <sub>2.5</sub>	0.55	5.8	62
Pb <sub>0.85</sub> Th <sub>0.15</sub> F <sub>2.30</sub>	0.35	4.6	62	Na <sub>0.33</sub> Th <sub>0.67</sub> F <sub>2.34</sub>	0.56	6.5	63
Pb <sub>0.8</sub> Sb <sub>0.2</sub> F <sub>2.2</sub>	0.35	4.9	61	Pb <sub>0.97</sub> Bi <sub>0.03</sub> F <sub>2.03</sub>	0.57	5.9	61
Pb <sub>0.68</sub> Sb <sub>0.32</sub> F <sub>2.27</sub>	0.36	5.2	61	Pb <sub>3</sub> ZrF <sub>10</sub>	0.62	5.9	63
RbBiF <sub>4</sub>	0.37	4.5	63	NaBiF <sub>4</sub>	0.65	5.9	63
Pb <sub>0.9</sub> Zr <sub>0.1</sub> F <sub>2.2</sub>	0.37	4.8	62	Na <sub>0.3</sub> Bi <sub>0.7</sub> F <sub>2.4</sub>	0.65	7.3	63

ion SIC (Fig. 5), and for fluorine ion solid electrolytes (Fig. 6). It is interesting that values of  $\log A$  for AH and for AgCl, AgBr calculated from experimental data of the conductivity of doped crystals assuming  $n = N_0$  are in rather good accord with Eq. (12). Experimental data for most of the SIC with  $E_A > 0.4 \pm 0.1$  eV are in fair agreement with the calculated relation. In the range of activation energies  $0.3 < E_A < 0.5$  eV the prefactor  $A$  falls sharply with decreasing  $E_A$  and at  $E_A = 0.3$  eV it assumes a value characteristic for ionic melts.

From the above as well as from previous studies the following mechanism for ion migration in SIC may be suggested.

(i) In solid electrolytes with  $E_A > 0.4 \pm 0.1$  eV the ion transport mechanism is likely to be similar to that which is characteristic of classical ionic crystals and involves the simple jump process. The values of  $S_\mu$  and  $\nu_0$  are close to that of AH, for which relations (9) and (10) apply.

(ii) The apparent decrease in the prefactor  $A$  in SIC for which  $0.3 < E_A < 0.5$  eV may be explained in terms of two main

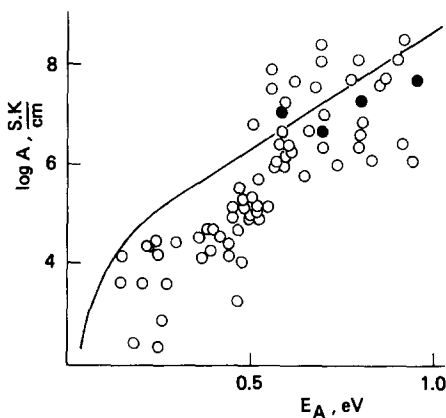


FIG. 5. The calculated in accord with Eq. (12) (the curve) and experimentally observed (the points) compensation law for alkali-metal conducting SIC. Full circles are hypothetical values calculated assuming  $n = N_0 = 10^{22} \text{ cm}^{-3}$  for NaF, NaCl, NaBr, and NaI crystals.

causes. First, the migration entropy decreases to zero as a result of positional disordering of mobile sublattice ions, whenever ions can stay in interstitials for a relatively long time. Second, the jump attempt frequency decreases due to the strong anharmonicity of ion vibrations.

(iii) SIC with  $E_A < 0.3 \text{ eV}$  are not different from ionic melts in conductivity parameters. For a description of the mechanism

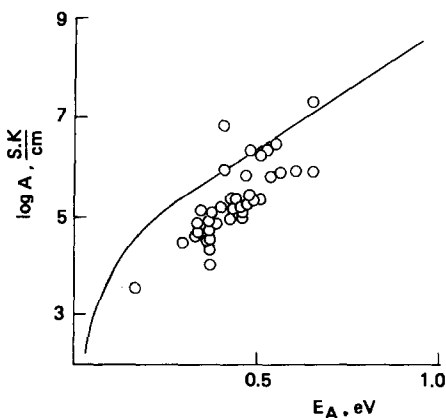


FIG. 6. The compensation law for fluorine-conducting SIC. The curve is plotted in accord with Eq. (12).

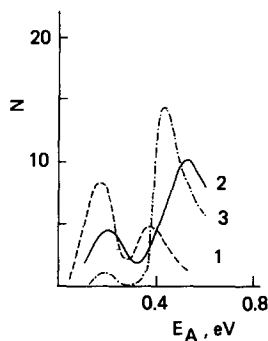


FIG. 7. The distribution curves of the number of SIC with a given value of  $E_A$  vs  $E_A$  for  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Tl}^+$ ,  $\text{In}^+$ ,  $\text{Cd}^{2+}$  ion conducting (1), alkali ion conducting (2),  $\text{F}^-$  ion conducting (3) ionic solids. The analyzed data are those presented in Table III.

of migration in these materials a stochastic model may be used (65).

Thus the CL allows one to follow the consequent stages of melting of the mobile ion sublattice. In a large number of compounds only a partially fused sublattice occurs. As a sharp change of energy parameters takes place at melting, a similar change must be observed in  $E_A$  values. In Fig. 7 the number of compounds in a certain interval of activation energy vs  $E_A$  are plotted for SIC of different types. These variations were obtained by means of histogram analysis for the  $E_A$  interval from 0 to 0.8 eV in steps of 0.05 eV for all compounds in Table III. The  $E_A$  curve yields a rather acute minimum at  $0.3 < E_A < 0.4 \text{ eV}$  i.e., there seems to be an analog of the "forbidden gap" for  $E_A$  values of SIC.

## Conclusion

The CL in conductivity of AH type crystals and of SIC is investigated. The CL in AH type crystals may be explained by assuming similar ones exist in the defect formation process (Eq. (8)) as well as in defect mobility (Eq. (9)), with the isokinetic temperatures  $2.8 \times 10^3$  and  $2.1 \times 10^3 \text{ K}$ , respectively. It is also shown that the values of  $\nu_h$



determined by Eq. (10) are likely to be preferable to the Debye frequency. The dependence between  $\log A$  and  $E_A$  exhibits an anomalous decrease in  $\log A$  values for low  $E_A$  which seems to be caused by the melting of the mobile ion sublattice. The above relations can be employed for the prediction of transport properties of ionic solids (66, 67), and could be of advantage for further understanding of the ion transport mechanisms in solids.

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