Correlations between Parameters of Melting and Conductivity of Solid Ionic Compounds

N. F. UVAROV, E. F. HAIRETDINOV, AND V. V. BOLDYREV

Institute of the Solid State Chemistry, Siberian Division of the Academy of Sciences, Novosibirsk 91, Derzhavina 18, USSR

Analysis of the literature data allows one to correlate the melting parameters and the activation enthalpy H_0 of the charge carrier formation in an ionic crystal. The melting enthalpy H_m and H_0 values are connected by the basic relation $H_0 = 9.2\,H_m$. The well-known Barr–Lidiard relation is shown to be a particular case of this basic relation. It is demonstrated that the conductivity jump at the melting temperature of an ionic crystal may be predicted from the melting entropy. Correlations of the form mentioned above may be useful in predicting the conductivity values of ionic crystals as well as in looking for new types of superionic conductors.

Introduction

The investigation of ionic transport in solids is of great interest being mainly connected with the discovery of superionic conductors for which the ionic conductivity of the solid state is comparable to that of the molten state. In a search for new compounds with high ionic conductivities the following crystallographic considerations are useful:

(i) There must exist more than one energetically equivalent site in the crystal lattice for a normal unexcited ion. It should meet the condition $E_0 = 0$, i.e., the formation energy of the free carriers is close to zero.

(ii) The relation of the radius of the mobile ion and that of the conductivity channels must be optimized.

For proper use of these factors it is necessary to study the crystal structure of the compound and to determine accurately the coordinates of the atoms. This usually presents a difficult problem.

Another approach is known which bases the prediction of the high ionic conductivity on analyses of data for the enthalpy H_m and entropy S_m of melting, and for the enthalpy and entropy of phase transitions in the solid state (H_t and S_t). According to O'Keefe (*1, 2*) three classes of solid ionic conductors exist which are distinguished by their behavior at the melting point.

(i) the normal salts ($CaCl_2$, $BaCl_2$, $BaBr_2$, $PbCl_2$, etc.) which exhibit no phase transition in the solid state; for these $S_m \simeq 6$ e.u., and the value of ionic conductivity near the melting point does not exceed 10^{-3} ohm^{-1} cm^{-1};

(ii) salts with phase transitions to the superionic state (AgJ, CuBr, LuF_3, $CaBr_3$, etc.) which have values of S_t and S_m equal to 2–4 e.u.; the value of the ionic conductivity of such crystals at the melting tem-

perature is close to that of the melt: $\sigma_{Tm} \simeq$ 10 ohm^{-1} cm^{-1};

(iii) salts with a diffuse phase transition (CaF$_2$, SrCl$_2$, AgBr, etc.) which have $S_t \simeq$ 0, $S_m \simeq$ 4–6 e.u., and $\sigma_{Tm} \simeq$ 10 ohm^{-1} cm^{-1}.

A similar approach has been used by analyzing the phase transitions of the alkali sulfates (3). In Cs$_2$SO$_4$, the $\beta \rightarrow \alpha$ phase transition is close to a second order transition: $H_t \simeq 0$, $S_t \simeq 0$, and $S_m = 7.5$ e.u. In the series of sulfates of Cs$^+$, Rb$^+$, K$^+$, Na$^+$, Ag$^+$, Li$^+$, S_m and H_m decrease, H_t and S_t increase, and the conductivity of the α phase increases considerably. Li$_2$SO$_4$ exhibits a phase transition to the superionic phase with $H_t = 6.53$ kcal/mole, $S_t = 7.6$ e.u., while H_m and S_m are anomalously low and equal to 1.833 kcal/mole and 1.6 e.u., respectively. These facts suggest that phase transitions to the superionic state are accompanied by significant decreases in H_m and S_m. As the phase transition of this type leads to disorder in one of sublattices, the values of H_m or S_m are bound to depend on the extent of disorder of this sublattice at the melting point. In ordinary ionic crystals the disorder arises from individual defects, with their concentration exponentially dependent on the formation energy E_0. Therefore compounds with low values of S_m and H_m should be associated with low values of E_0, high concentrations of defects at the melting temperature T_m, and high ionic conductivity whatever the phase transitions might be in the solid state.

In this paper an attempt is made to find quantitive correlations between the thermodynamic characteristics of melting H_m, S_m, and the conductive properties of ionic crystals.

A number of structurally related monovalent metal (Li, Na, K, Rb, Cs, Ag, Tl) halides was chosen for their investigation. The ionic conductivities of these salts has been thoroughly studied over the last years. In Table I are presented the experimental

and theoretical values of the formation enthalpy H_0, the migration enthalpy H_μ and the enthalpy of melting H_m for ionic compounds having the rocksalt structure as well as for the crystals CaF$_2$, BaF$_2$, SrCl$_2$, SrF$_2$, based on the data of (4–29). In Fig. 1 is shown the dependence of the enthalpy of defect formation H_0 on the enthalpy of melting H_m for the series under study. The correlation is linear and may be presented as

$$H_0 = 9.2H_m. \tag{1}$$

The analysis of the data plotted in Fig. 2 suggests that there also is a correlation between the migration enthalpy and the enthalpy of fusion given by

$$H_\mu = 2.76H_m. \tag{2}$$

We now assume the following dependence of the intrinsic conductivity on the temperature

$$\sigma T = (\sigma T)_0 \exp\left(-\frac{H_0/2 + H_\mu}{RT}\right).$$

Supposing the crystal to conduct by only one type of ion, and using Eqs. (1) and (2) we have

$$\log \sigma T = \log (\sigma T)_0 - \frac{1.61 \times 10^3}{T} H_m \tag{3}$$
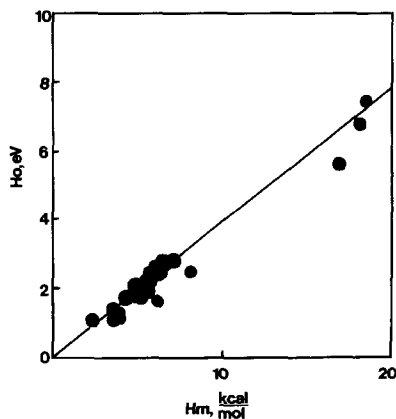

FIG. 1. Defect formation energy E_0 vs melting enthalpy H_m for a series of ionic crystals.

TABLE I

SUMMARY OF KNOWN THEORETICAL AND EXPERIMENTAL VALUES FOR THE ACTIVATION ENTHALPIES OF DEFECT FORMATION H_0, OF DEFECT MIGRATION H_μ, AND CRYSTAL MELTING ENTHALPIES H_m FOR SOME IONIC CRYSTALS

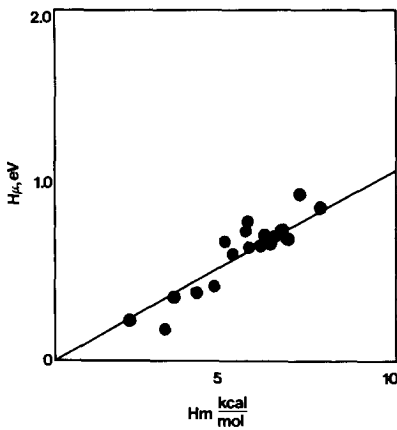| 1 Crystal	2 H_0 (eV) exper.	3 H_0 (eV) theor.	4 H_μ (eV) exper.	5 H_μ (eV) theor.	6 H_m (kcal/mole)
LiF	2.74(5); 2.34(4); 2.40(4)	2.66(4)	0.65–0.75(19); 0.70(5)		6.47(25)
LiCl	2.12(6)	2.16(4)	0.40(6); 0.62(24)		4.76(25)
LiBr	1.80(6)	2.01(4)	0.39(6); 0.54(24)		4.22(25)
LiI	1.06(7)		0.38–0.43(23); 0.43(7); 0.38(24)		3.50(25)
NaF	2.42(8)	2.98(4)	0.95(8)		7.78(25)
NaCl	2.2–2.75(9); 2.44(10)	2.54(4)	0.65–0.80(19); 0.69(20)	0.70(19)	6.69(25)
NaBr	1.68–1.72(9)	2.40(4)	0.80(19)	0.67(19)	6.24(25)
NaI	1.46–2.27(9); 2.00–2.14(10)	2.14(4)	0.47–0.78(19)	0.61(19)	5.64(25)
KF	2.64–2.72(4)	2.52(4)	1.02(15)		6.75(25)
KCl	2.30–2.59(9); 2.54(10)	2.56(4)	0.67–0.76(19); 0.73(20)	0.73(19)	6.34(25)
KBr	2.33–2.53(9)	2.54(4)	0.65–0.73(19); 0.65(22)	0.73(19)	6.10(25)
KI	1.60–2.21(9)	2.34(4)	0.63–0.76(19); 0.63(21)	0.72(19)	5.74(25)
RbCl	2.04–2.44(9)	2.44(4)	0.54–0.93(19)	0.76(19)	5.67(25)
RbBr	1.98(9)	2.46(4)	0.80(19)	0.74(19)	5.57(25)
RbI	2.1(9)	2.30(4)	0.60(19)	0.74(19)	5.27(25)
CsCl	1.77–1.86(11); 2.1–2.3(12)	1.79(19)	0.34(19); 0.2–0.3(12)	0.37(19)	4.84(25)
CsBr	2.02(12)	1.86(19)	0.27(19)	0.38(19)	5.64(25)
CsI	1.9(12)	1.82(19)	0.3(19)	0.37(19)	5.64(25)
AgCl	1.462(13); 1.452(14); 1.25(15)		0.16; 0.055(15); 0.151(15); 0.10(16);		3.16(26)
AgBr	1.06(15); 1.13(16)		0.15(15); 0.28(16)		2.28(1)
TlCl	1.36(17)		0.2(15); 0.10(17)		3.7(27)
TlBr	1.1(17)		0.25(17)		3.6(26)
CaF₂	2.80(15)		1.69(15)		7.1(1)
BaF₂	1.91(16); 1.78(15)		0.78(15); 0.57(16)		5.0(29)
SrCl₂	1.82; 1.60(15)				3.87(28)
SrF₂	1.74; 2.28(15)		0.94; 1.0(15)		7.1(29)
MgO	7.5(18)	7.72(18)			18.1(27)
CaO	6.7(18)	6.43(18)			18(27)
SrO	5.9(18)	5.45(18)			16.5(27)
BaO	3.4(18)	3.48(18)			13.6(27)
MnO	4.92(18)	5.61(18)			9(27)
FeO	6.09(18)	6.49(18)			7.5(27)
CoO	6.39(18)	7.16(18)			13(27)
NiO	6.86(18)	7.37(18)			13.3(27)

FIG. 2. Defect migration enthalpy H_μ vs melting enthalpy H_m for the halogenides of the metals of the I and II groups of the periodic table.

where σ is the conductivity in ohm^{-1} cm^{-1}; T is the temperature in K; H_m is the enthalpy of melting in kcal/mol. Assuming the prefactor $(\sigma T)_0$ to be identical for all salts under investigation and to be equal to 10^{10}, one can obtain the following linear dependence of log σ_{T_i} on H_m, where σ_{T_i} is the conductivity at the fixed temperature T_i:

$$\log \sigma_{T_i} = 10 - \log T_i - \frac{1.61 \times 10^3}{T_i} H_m. \tag{4}$$

We have analyzed the experimental data of different authors on the ionic conductivity of monocrystals of a number of salts. As reliable data on the conductivity of LiCl and of LiBr seem to be unavailable, we have investigated the conductivity of these salts as well. Measurements have been taken on pure and doped crystals, as grown from the melt, using ac at a frequency of 10 kHz with platinum electrodes in a vacuum of 10^{-2} Torr. The doped crystals of LiCl and LiBr contained 10^{-7}–10^{-2} mole% CaCl$_2$ and CaBr$_2$, respectively.

In Fig. 3 the dependence of log σ on $1/T$ plotted for the salts under study use the data of (5, 7, 10, 11, 17, 20–22, 24, 30–36). Here the ionic conductivity of the crystals

in the intrinsic region, the conductivity jump at the melting temperature, and the conductivity of these salts in the liquid state are demonstrated. At $T_i = 496°C$ (or $1/T_i = 1.3 \times 10^{-3}$ K^{-1}) the following dependence of log σ on H_m is obtained from the data presented in Fig. 3:

$$\log \sigma_{496} = 4.1 - 1.6 H_m \tag{5}$$

which markedly differs from the dependence predicted by Eq. (4) for the same temperature, namely,

$$\log \sigma_{496} = 7.11 - 2.1 H_m. \tag{6}$$

The main cause for this discrepancy likely arises from the assumption that $(\sigma T)_0$ is identical for all crystals. A review of the experimental results allowed us to suggest that the prefactor depends on the entropy of fusion in accordance with the following equation:

$$\log (\sigma T)_0 = 6.9 + 0.4 S_m, \tag{7}$$

where S_m is measured in entropy units.

Combining Eqs. (7) and (3), and taking into account $S_m = (H_m/T_m) \times 10^3$, we obtain

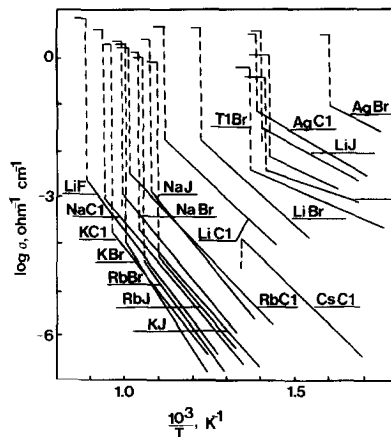$$\log \sigma_{T_i} = 4.1 - \frac{H_m}{T_i} 10^3 (1.61 - (T_i/T_m) 0.4). \tag{8}$$

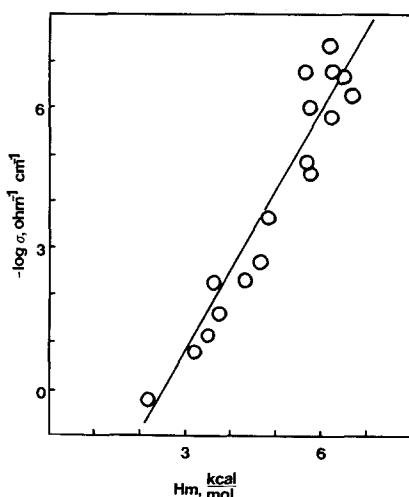FIG. 3. Arrhenius plots of conductivity of some ionic crystals.

FIG. 4. The values of ionic conductivity at $T = 496°C$ for halogenides of the type MeX as a function of the melting enthalpy.

At $T_i \simeq T_m$ the predicted dependence is close to the observed one (6):

$$\log \sigma_{496} = 4.0 - 1.57 H_m.$$

At the temperature of melting the sudden jump of the conductivity due to the process of fusion takes place, with

$$\Delta \log \sigma = \log \sigma_L - \log \sigma_{T_m}$$

where σ_L is the conductivity of the molten salt. It is known that at the temperature $T_i = T_m$,

$$\log \sigma_L = \log \sigma_{0L} - \frac{E_L}{2.3 R T_m},$$

where $\log \sigma_{0L}$ and E_L are certain constants. The value of $\log \sigma_L$ is equal to $\simeq 0.3 \pm 0.3$ for all compounds under study. Then from Eq. (8), for $T_i = T_m$, we have

$$\Delta \log \sigma = -3.8 \pm 0.3 + 1.21 S_m \quad (9)$$

where S_m is measured in entropy units.

The dependence of $\Delta \log \sigma$ on S_m for a series of these salts is shown in Fig. 4. The experimental points for the monovalent metal halides fit well to the line calculated according to Eq. (9).

Discussion

The melting of ionic crystals can be assumed to involve the intensive defect formation, resulting in absorption of the main part of the heat of melting, in which the concentration of defect increases from 10^{-3}–10^{-2} to 10–20 ionic percent. As a result of collective interactions of vacancies and ions the migration enthalpy of the moving species H_μ and the vibrational frequencies of the ions decrease. In such a case the thermal vibrations cause great fluctuations in the displacement of ions from their equilibrium positions, so that it is impossible to maintain long-range order in the substance.

The energy of the quasicrystalline lattice of the liquid differs only slightly from that of the crystal. Therefore, the value of the enthalpy of melting H_m is approximately an order of magnitude below the enthalpy of formation of the crystal or the liquid at the melting temperature. This indicates an approximate equality of the characteristic energy of ions in crystals and in the corresponding liquids. The main distinction between ionic melts and solids seems to be the existence of a large free volume which could be regarded as the volume of vacancies in the ionic liquid. In superionic compounds with a gradually diminishing defect concentration one can observe an abrupt drop of conductivity which is caused by the decrease of the migration enthalpy H_μ due to interionic interactions (37, 38). The decrease in defect concentration down to a definite threshold value causes the conductivity suddenly to decrease and one of the sublattices to crystallize. In a similar manner it is possible to treat the process of melt crystallization.

The minimal concentration of defects needed to stabilize the liquid phase we take to be the constant n_d/N for all structurally related substances. This concentration is analogous to the threshold charge carrier

concentration in superionic compounds. The formation enthalpy of n_d noninteracting defects is equal to $n_d H_0$ and equal to the minimal energy needed for stabilizing the liquid phase, H_m:

$$H_m = n_d H_0 \qquad (10)$$

With the correlations (1) and Eq. (10) one can estimate the defect concentration in melt as $n_d/N = 11$ mole%. The corresponding change of the configurational entropy at the melting point is equal to

$$S_C = k \ln \frac{(N + 0.11N)!}{N! \cdot (0.11N)!},$$

where N is the overall number of ions disordered in $N + 0.11N$ sites of the quasilattice, and k is Boltzmann's constant. For compounds with the rocksalt structure $N = 2N_A$, where N_A is Avogadro's number, and $S_C = 1.6$ e.u.

For salts of the NaCl type with the Schottky disorder (39),

$$\log \sigma T = \log \frac{e^2 N' 4 a^2 \nu_0}{k} + \frac{S_\mu}{2.3k}$$

$$+ \frac{S_0}{4.6k} - \frac{H_0/2 + H_\mu}{2.3kT} \qquad (11)$$

where e is the electron charge, N' is the number of ions in 1 cm³ of substance, a is the distance between similar ions, ν_0 is the vibrational frequency of ions, S_μ is the migration entropy, and S_0 is the vacancy formation entropy caused by the change of the vibrational entropy of ions around defects:

$$S_0 = zk\Sigma \ln \frac{\nu_{0i}}{\nu_{di}}$$

where ν_{0i} and ν_{di} are vibrational frequencies of perfect and imperfect crystal, respectively, and z is the coordination number of a vacancy.

The values of $\log (e^2 N' 4 a^2 \nu_0/k)$ and S_μ/k are equal correspondingly to 5.6 ± 0.2 and 1.2 ± 0.1 for all salts under examination, so that

$$\log (\sigma T)_0 = 6.8 \pm 0.3 + S_0/4.6k. \quad (12)$$

Equation (12), when compared with Eq. (7), allows us to assume that

$$\frac{S_0}{4.6k} \simeq 0.4 S_m \quad \text{or} \quad S_0 \simeq 3.7 S_m \quad (13)$$

where S_0 and S_m are measured in entropy units.

The calculated value of S_0, for NaCl, namely 22 e.u., is close to that estimated in (20), i.e., 20 e.u. For $n_d/N = 0.11$ the overall vibrational entropy of defects in the melt is equal to 2.4 e.u. For the given value of $S_m = 6$ e.u. the change of the vibrational entropy at the melting equals 2.4 e.u., and the entropy of melting reaches the value

$$S_m = S_C + S_\nu + S_{op}$$
$$= 1.6 + 2.4 + S_{op} = 4.0 + S_{op}.$$

The contribution of other processes to the entropy of melting S_{op} for alkali halides seems to be no more than 1.5–1.8 e.u. The abovementioned 10% concentration of defects and the 1.6-e.u. change of the configurational entropy at melting agree well with the data of Ref. (40) where S_m was estimated by use of the quasilattice theory of liquids where individual vacancies are formed. This may explain the considerable increase of molar volume at the melting point of the alkali halides. The change of the vibrational entropy is also reasonable.

Besides alkali halides, crystals such as AgBr, AgCl, TlCl, CaF_2, BaF_2, $SrCl_2$, $BaCl_2$, SrF_2 with the Frenkel disorder and some alkali-earth oxides with the Schottky disorder also meet the correlation (1). There exist similar dependences for metals (41) and for semiconductors (42).

In general, the temperature dependence of the ionic conductivity may be written as

$$\sigma T = (\sigma T)_0 \exp \left(- \frac{H_0/z + H_\mu}{kT} \right) \quad (14)$$

where z is the number of species taking part in the process of defect formation. From
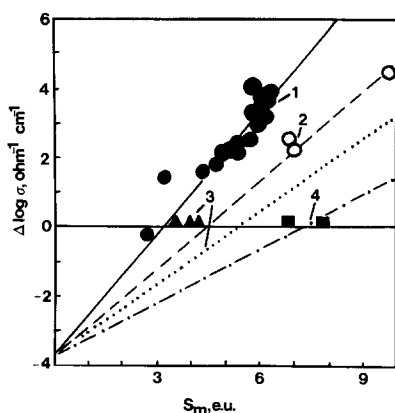
FIG. 5. The calculated (lines) the experimentally observed (points) plots of $\Delta \log \sigma$ vs S_m for some ionic crystals: 1. NaCl type 2. CaBr$_2$ type 3. CaF$_2$ type 4. CeF$_3$ type.

correlations (1) and (2) and Eqs. (7) and (14), we can calculate for different z the values of some parameters in the linear dependence of $\Delta \log \sigma$ on S_m, written in the form

$$\Delta \log \sigma = \alpha(S_m - S_m^0). \qquad (15)$$

Equation (15) for compounds of NaCl type ($z = 2$) coincides with Eq. (9), where

$z = 2; \qquad S_m^0 = 3.14$ e.u.;

$$\alpha = 1.21. \quad (15a)$$

For halides such as CaBr$_2$, BaBr$_2$, MgCl$_2$ with Schottky disorder,

$z = 3; \qquad S_m^0 = 4.33$ e.u.;

$$\alpha = 0.87. \quad (15b)$$

For compounds of the fluorite type with Frenkel disorder,

$z = 4; \qquad S_m^0 = 5.3$ e.u.;

$$\alpha = 0.71. \quad (15c)$$

For compounds of CeF$_3$ type with Frenkel disorder,

$z = 6; \qquad S_m^0 = 7.0$ e.u.;

$$\alpha = 0.54. \quad (15d)$$

Experimental points for some of these cases are entered in Fig. 5. The dependence of $\Delta \log \sigma$ on S_m calculated in accord with

Eq. (15) fit well with the experimental observations. This is most evident in the case of NaCl-type ionic crystals, apparently due to existence of a large body of reliable experimental data.

Thus starting from the thermodynamic parameters of melting H_m and S_m, one can evaluate some characteristics of defect formation and ionic conductivity, such as

(1) the formation energy of defects in ionic crystals: At present only the Barr–Lidiard dependence (43) of the form

$$H_0 = 2.14 \times 10^{-3} T_m \qquad (16)$$

has been postulated, where H_0 is the enthalpy of defect formation (in eV), and T_m is the melting temperature in K.

Equation (16) is a particular case of correlation (1), restricted by the condition that for all ionic crystals the relation Const. = $S_m = 5.35$ e.u. is assumed to hold. The H_0 values calculated using the Barr–Lidiard equation, the ones estimated in accord with the correlation (1), the theoretical values given by various authors (4, 19, 41) and experimentally observed value are presented in Table II. In most cases the correlation (1) provides more accurate values of H_0.

(2) the value of the ionic conductivity when examining a series of structurally related compounds: In this case the prefactors in the relation $\log \sigma T$ vs $1/T$ must correspond to the correlation (7), and a linear dependence of $\log \sigma_{T_i}$ on H_m will be observed. The decrease of the heat of melting in a series should correlate with an increase of ionic conductivity at the temperature T_i. Such a phenomenon is observed in a number of sulfates of monovalent metals (3, 44), in sodium compounds of the type of Na$_2A$O$_4$, where $A = $ S, Mo, W (46), in alkali nitrates (45), and, as stated above, in alkali halides.

(3) the magnitude of the change of conductivity at melting: With the aid of the correlations of the type (15) one may estimate

TABLE 2

H_0 VALUES DETERMINED IN ACCORD WITH THE
BARR–LIDIARD RELATION (H_B), EQ. (1) [H_0 (1)],
THEORETICALLY CALCULATED VALUES (H_{th}), AND
EXPERIMENTALLY OBSERVED VALUES (H_{exp})

Crystal	H_B(eV)	H_0(1)(eV)	H_{th}(eV)	H_{exp}(eV)
LiF	2.40	2.60	2.66(4)	2.74(5)
LiCl	1.89	1.90	2.16(4)	2.12(6)
LiBr	1.76	1.69	2.01(4)	1.80(6)
LiJ	1.59	1.40	—	1.06(7)
NaF	2.71	3.11	2.98(4)	2.42(8)
NaCl	2.30	2.68	2.54(4)	2.44(10)
NaJ	2.00	2.26	2.14(4)	2.00(10)
KF	2.42	2.70	2.52(4)	2.72(4)
KCl	2.23	2.54	2.56(4)	2.54(10)
KBr	2.15	2.44	2.45(4)	2.53(9)
KJ	2.04	2.30	2.34(4)	2.21(9)
RbCl	2.13	2.27	2.44(4)	2.44(9)
RbBr	2.07	2.23	2.46(4)	1.98(9)
RbJ	1.97	2.11	2.30(4)	2.10(9)
CsCl	1.96	1.94	1.79(19)	1.77—1.86(11)
CsBr	1.95	2.26	1.86(19)	2.0(12)
CsJ	1.92	2.26	1.82(19)	1.9(12)
AgCl	1.56	1.26	1.48(41)	1.462(13)
AgBr	1.56	0.87	—	1.06(15)
TlCl	1.48	1.48	—	1.36(17)
TlBr	1.57	1.44	—	1.1(17)
CaF$_2$	3.62	2.84	—	2.80(15)
BaF$_2$	3.51	2.00	—	1.91(16)
SrCl$_2$	2.45	1.55	—	1.60(15)
SrF$_2$	3.75	2.84	—	2.28(15)

the values of $\Delta \log \sigma$ from known S_m values in a series of structurally related compounds. The dependence of $\Delta \log \sigma$ on S_m for sulfates of monovalent metals is shown
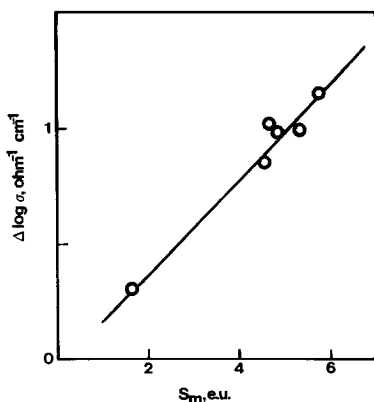

FIG. 6. $\Delta \log \sigma$ vs S_m plot for some sulfates of the type Me$_2$SO$_4$.

in Fig. 6. A linear dependence with small slope is observed. The small slope may indicate a great value of z, i.e., demonstrate the complex mechanism of defect formation in Me$_2$SO$_4$ at melting.

(4) superionic properties of solids: The most unusual feature of these substances is that $\Delta \log \sigma \lesssim 0$ on melting. In accordance with calculated dependence of $\Delta \log \sigma$ as a function of S_m a region in which $\Delta \log \sigma \lesssim 0$ corresponds to the case $S_m \lesssim S_m^0$. For compounds of NaCl type the superionic conductivity may be observed for cases where S_m is smaller than 3.1 ± 0.2 e.u. Such crystals as CuJ (2.26 e.u.), CuBr (2.26 e.u.),

TABLE 3

PREDICTIONS OF HIGH VALUES OF CRYSTALLINE
IONIC CONDUCTIVITIES AND THEIR COMPARISON
WITH KNOWN RESULTS

No.	Crystal	S_m(e.u.)	Experimentally observed high ionic conductivity
1	Na$_2$S	1.3	+
2	Li$_2$SO$_4$	1.6	+
3	Cu$_2$S	1.92	+
4	CuJ	2.26	+
5	CuBr	2.26	+
6	RbNO$_3$	2.28	+
7	KOH	2.60	+
8	AgJ	2.71	+
9	RbOH	2.82	?
10	NaOH	2.9	?
11	CsOH	2.93	?
12	BaF$_2$	3.0	+
13	MnF$_2$	3.0	?
14	Ag$_2$S	3.01	+
15	KHF$_2$	3.09	+
16	AgBr	3.25	+
17	SrCl$_2$	3.4	+
18	CuCl	3.48	+
19	Na$_2$MoO$_4$	3.8	+
20	TlJ	3.8	−
21	KCN	3.84	?
22	K$_2$S	3.9	?
23	PbF$_2$	3.92	+
24	K$_2$MoO$_4$	4.0	?
25	SrF$_2$	4.0	+
26	CaF$_2$	4.0	+

AgJ (2.71 e.u.) and AgBr (3.25 e.u.) meet this requirement, and all of these except for the last one are superionic conductors. Moreover, the ionic conductivity of AgJ at the temperature point in the solid phase is higher than that of the liquid, i.e., $\Delta \log \sigma <$ 0, as predicted by Eq. (15). In a number of compounds of the CaF_2 type, superionic properties should appear in substances for which $S_m \lesssim 5.3 \pm 0.2$ e.u. Crystals of BaF_2 (3.0 e.u.), $SrCl_2$ (3.4 e.u.), SrF_2 (4.0 e.u.), CaF_2 (4.2 e.u.), PbF_2 (3.92 e.u.), K_2S (3.9 e.u.), and Na_2S (1.3 e.u.) meet this requirement and all but K_2S are in fact superionic conductors at high temperatures (*1, 2*). As to K_2S there are no available data in literature concerning the conductivity of this substance. For compounds of the CeF_3 type the abovementioned requirement is given by $S_m \lesssim 7.0 \pm 0.2$ e.u. LaF_3 (6.8 e.u.), YF_3 (4.68 e.u.), LuF_3 (4.96 e.u.), AcF_3 (7.2 e.u.), and PuF_3 (5.6 e.u.) answer this demand, and most of these are superionic conductors (*1, 2*). A number of ionic compounds having minimal values of entropy of melting and for which the ionic conductivity would be expected to be high are presented in Table III. Of 26 substances analyzed, 17 exhibit high ionic conductivity, 4 hydroxides—NaOH, KOH, RbOH, CsOH—have solid state phase transitions to the disordered state; the conductivities of MnF_2, K_2S, K_2MoO_4, and KCN have not been studied.

Finally the conclusion may be drawn that there is an interconnection between the conductive properties of ionic crystals and the thermodynamics of melting. The correlations proposed above may be useful in understanding the nature of solid state ionics, and possibly may help in the search for new solid electrolytes.

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