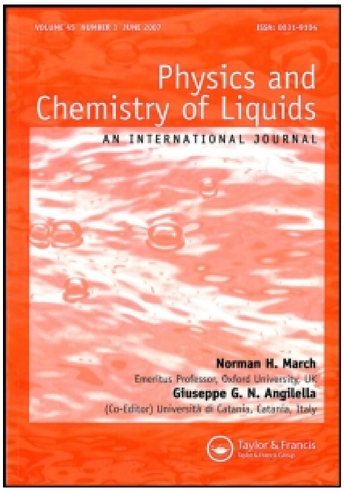

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Review Article

Melting of Ionic Crystals, Defect Energies and Fast Ion Conduction

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The theory of Kurosawa of melting in ionic crystals is first reviewed. The form of the theory, it is pointed out, receives some measure of support from the Barr–Dawson–Lidiard correlation between melting temperature and Schottky defect enthalpy.

Recent work of March *et al.* on fast ion conduction in the fluorite structure, a phenomenon which is often discussed in terms of sub-lattice melting, is then discussed. The superionic transition temperature is shown in this work to be correlated with the Frenkel defect energy. Some brief comments are made on the effect of fast ion conduction on the melting temperature.

1 INTRODUCTION

In this review, we shall first outline the theory of melting of ionic crystals given by Kurosawa.[1] Though some difficulties remain at the foundations of this theory, based on the Debye–Hückel theory of the interaction between charged defects, it will be stressed that the Barr–Dawson–Lidiard correlation[2] between melting temperature and Schottky enthalpy lends some measure of support for this theory. It will be briefly compared and contrasted with the corresponding states argument of Reiss *et al.*[3]

Recent work of March *et al.*[4] on fast ion conduction in the fluorite structure, a phenomenon which is often discussed in terms of sublattice melting,† will then be reviewed. In this work, it is stressed that the theory of superionic conduction is the theory of the interaction between Frenkel defects and the work of March *et al.* uses a modification of the Kurosawa theory to deal with this problem.

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† See, however, Catlow (1980; Comments on Solid State Physics IX, p 157), who argues strongly that this is at best a very rough analogy.

2 MELTING OF IONIC CRYSTALS

The essence of Kurosawa's theory will now be set out briefly. Consider, say in NaCl, Schottky defects, which interact with each other via a Coulomb potential $e^2/\varepsilon r$, ε being the static dielectric constant and r the distance between the defects. This interaction causes a defect to be surrounded by a cloud of oppositely charged defects, just as with an ion in an electrolyte. If W denotes the defect formation free energy, then one can take the interaction into account by means of Debye–Hückel theory. Denoting the concentration of defects by c, we can write, with a the lattice spacing,

$$W + 2k_B T \ln c - 2\pi^{1/2} \frac{e^2}{\varepsilon a}\left(\frac{e^2}{\varepsilon a k_B T}\right)^{1/2} c^{1/2} = 0 \tag{2.1}$$

One can see from this equation that the presence of the Coulomb interaction term increases c above its Arrhenius value $c_0 = \exp(-W/2k_B T)$, and can therefore tend to cause a transition. To see this a little more clearly, one can rewrite Eq. (2.1) by introducing a formation entropy S_s through

$$W = E_s - TS_s \tag{2.2}$$

as

$$\frac{E_s}{2k_B T} - \pi^{1/2}\left(\frac{e^2}{\varepsilon a k_B T}\right)^{3/2} c^{1/2} = \frac{S_s}{2k_B} - \ln c \tag{2.3}$$

Kurosawa examined the consequences of Eq. (2.3) by plotting the LHS and RHS separately against c, with parameters appropriate to NaCl. He thereby demonstrated that there was no solution of Eq. (2.3) for c above a critical temperature which, for NaCl, he estimated at about 1000°K, whereas the melting point of this material is at 1073°K. The melting temperature T_m was therefore identified approximately with the critical temperature referred to above.

It can be seen that the critical concentration of Schottky defects at melting, say c_m, which is to be determined as described above, is related to $E_s/2k_B T_m$ by

$$\frac{E_s}{2k_B T_m} = -\ln c_m + \frac{S_s}{2k_B} + \pi^{1/2}\left(\frac{e^2}{\varepsilon a k_B T_m}\right)^{3/2} c_m^{1/2}. \tag{2.4}$$

It was stressed by Kurosawa that some uncertainty must remain in the above argument, since one is estimating the melting temperature from the properties only of the low temperature phase. Nevertheless, we wish to emphasize two points which bear on the relevance of Kurosawa's approximate treatment of melting. The first is that Barr, Dawson and Lidiard[2] have demonstrated an empirical correlation between melting temperature and Schottky enthalpy.

TABLE I

Melting temperatures correlated with lattice spacing for alkali halides

	LiF	NaF	NaCl	NaBr	NaI	KCl	KBr	KI	RbCl
a (A°)	4.0	4.6	5.6	6.0	6.5	6.3	6.6	7.0	6.5
T_m °K	1120	1270	1080	1020	940	1040	1010	960	990
aT_m (A° °K)	4480	5842	6048	6120	6110	6552	6666	6720	6435
ε	9.3	6.0	5.6	6.0	6.6	4.7	4.8	4.9	5
$\varepsilon a T_m \times 10^{-3}$ (A° °K)	41	35	33	33	40	31	32	34	33

The second is that the corresponding states arguments of Reiss *et al.*[3] demonstrate the relative constancy through the alkali halides, with the exception of the salts of lithium, of the ratio of the thermal energy associated with the melting temperature, namely $k_B T_m$ and e^2/a. Admittedly, the dielectric constant enters the ratio in the last term of Eq. (2.4) but the tabulation of Born and Huang[5] shows that there is not a very large variation in ε through the alkali halides as is also shown in Table I. The approximate constancy of these two dimensionless ratios would indicate, as a first approximation, that melting occurs at approximately the same concentration of Schottky defects for all the alkali halides, with the exception, as we have already remarked, of the salts of lithium.

The most elementary form of Debye–Hückel theory needs refinement. In particular, lattice structure implies a finite distance of closest approach, R say. Then the Kurosawa treatment enables one to write, at the critical temperature which we have identified with T_m:

$$c(T_m) = c_0(T_m)\exp(2\{1 + \alpha R c^{1/2}(T_c)\}), \tag{2.5}$$

with α given by

$$\alpha = \left(\frac{8\pi e^2}{v\,\epsilon\, k_B T_c}\right)^{1/2}, \tag{2.6}$$

where the volume $v \alpha a^3$. If we write this relation (2.5) in terms of an enhancement factor due to Coulomb interactions of the defect concentration, say F_s, above the Arrhenius value $c_0(T_m)$, then it follows that there is a correlation between the enthalpy of formation E_s and the melting temperature which we may write as

$$k_B T_m = \frac{\frac{1}{2}E_s}{\ln F_s + \dfrac{S_s}{2k_B} - \ln c(T_m)} \tag{2.7}$$

The factor ln F_s from the defect interactions is seen from Eq. (2.5) to be $\gtrsim 2$. The Barr-Dawson-Lidiard correlation[2] gives

$$E_s(\mathrm{eV}) = 2.1 \times 10^{-3} T_m \tag{2.8}$$

and implies that the denominator in Eq. (2.7) must be relatively constant, independently of the particular alkali halide.

Because there is some, admittedly indirect, evidence supporting the view that Schottky defect properties enter the melting transition of alkali halides in a fundamental way, March *et al.*[4] have recently generalized the Kurosawa theory to deal with the transition to fast-ion conduction in the fluorite series. We emphasize at this point that the transition to the superionic state has often been discussed in terms of melting of a sublattice, but that picture is not appealed to here.

3 FRENKEL DEFECTS AND FAST ION CONDUCTION IN FLUORITE STRUCTURE

In the work of March *et al.*,[4] attention is focused solely on fast ion conduction in the fluorite lattice. They then show that the superionic transition temperature T_c, which is defined as the temperature corresponding to the maximum of the specific heat anomaly, is empirically correlated with the Frenkel energy E_F, their results being summarized in Table II.

Their work focusses then on this empirical relation, which can be written (cf. Eq (2.8))

$$\frac{k_B T_c}{E_F} \doteqdot \frac{1}{20}. \tag{3.1}$$

That the superionic transition temperature should correlate with a characteristic energy, the Frenkel energy, need occasion no surprise, but as March *et al.* emphasize, the factor of $\frac{1}{20}$ requires some explanation.

TABLE II
Superionic transition temperature T_c correlated with Frenkel formation energy E_F (after March *et al.*[4]) for fluorite series

	T_c (°K)	E_F (eV)	$10\, k_B T_c / E_F$
CaF_2	1423	2.71	0.45
SrF_2	1450	2.28	0.55
BaF_2	1235	1.91	0.56
PbF_2	705	1.0	0.61
$SrCl_2$	993	1.70	0.50
UO_2	2670	5.10	0.45

They therefore modify the Kurosawa theory, and in place of Schottky defects they work out the modification for Frenkel defects. Their approach can be summarized as follows. One writes down the Arrhenius expression for the defect concentration in the limit of non-interacting defects, namely

$$c_0 = \exp\left(-\frac{\{E_F - TS_F\}}{2k_B T}\right) \tag{3.2}$$

Here S_F is the Frenkel formation entropy. They then point out that the modification of Kurosawa's theory allows one to write, at concentrations at which the defects now interact,

$$c = F(c)c_0. \tag{3.3}$$

They use the important scaling property of the Debye–Hückel theory, that the function F depends only on the reduced variable $k_B T/(q^2/\varepsilon a)$. Here q is the defect charge, ε is the static dielectric constant as before, and a is a characteristic distance which it is convenient to take as the F–F distance. We now apply this Eq. (3.3) at the critical concentration c_c of Frenkel defects at which the transition to fast ion conduction occurs. It will be seen then that we can write

$$c_c = F\left(c_c, \frac{k_B T_C}{\{q^2/\varepsilon a\}}\right)c_0(T_c). \tag{3.4}$$

This equation, in conjunction with Eq. (3.2) yields

$$\ln c_c = \ln F(c_c) - \frac{E_F}{2k_B T_C} + \frac{S_B}{2k_B} \tag{3.5}$$

This equation shows us that, within the Debye–Hückel framework, the ratio $E_F/2k_B T_c$ is made up of three contributions coming from:

(i) The critical defect concentration.

(ii) The enhancement factor F in the concentration due to defect interaction.

(iii) The Frenkel formation entropy.

For CaF_2, March *et al.*[4] estimate the contributions (i)–(iii) to $E_F/2k_B T_c$ to be respectively 3.5, 2, and 2.8, the last figure being obtained from the measurements of Jacobs and Ong.[6] This yields

$$\frac{E_F}{2k_B T_c} \doteqdot 8.3 \tag{3.6}$$

which is in fair agreement with the empirical result (3.1) for this particular example of CaF_2.

TABLE III

Ratio of Coulomb interaction between defects to transition temperature in some fluorites

	CaF_2	SrF_2	BaF_2	$SrCl_2$	UO_2
a(A°)	5.46	5.80	6.20	6.98	5.47
T_c (°K)	1423	1450	1235	993	2670
ε	6.63	6.20	6.94	9.2	24
$T_c \varepsilon a/q^2$ ($\times 10^{-3}$)	52	52	53	64	88

As to the constancy through the fluorite series, March *et al.* next note again the important role of the ratio $k_B T_c/(q^2/\varepsilon a)$ in the Debye–Hückel theory. They use empirical data to establish that this ratio is precisely the same for three members of the fluorite series, CaF_2, BaF_2 and $SrCl_2$, as summarized in Table III. It follows that the Helmholtz free energy $F(T_c)$ divided by $k_B T_c$ should be constant for these three materials from the modified Kurosawa theory. The variation in the ratio $E_F/2k_B T_c$ from Table II then implies that the formation entropy should be somewhat smaller for BaF_2 and SrF_2 than for CaF_2. There seems no difficulty in reconciling Debye–Hückel theory and the relative constancy of $k_B T_c/E_F$ for these materials.

But it is stressed by March *et al.*[4] that the ratio $k_B T_c/(q^2/\varepsilon a)$ is considerably different for PbF_2 and for UO_2. This implies, from Debye–Hückel theory, a larger concentration of Frenkel defects at the transition temperature in PbF_2 for example. It is the large dielectric constant of PbF_2 that is the cause, and this prediction is in general accord with the experimental findings of Hayes *et al.*[7]

Nevertheless, though there is considerable variation of $k_B T_c/(q^2/\varepsilon a)$ given in Table III, it can be seen from Table II that the empirical correlation (3.1) is still maintained throughout the fluorite series. Obviously, it would be of considerable interest to have data on the formation entropies of Frenkel defects for the other fluorites than CaF_2.

3.1 Elementary models of defect energies related to Coulomb energies

We want to stress again that there are two dimensionless quantities which play an important role in fast ion conduction, namely $k_B T_c/E_F$ and $k_B T_c/(q^2/\varepsilon a)$. From Table II we have seen that the relative constancy of the first ratio is maintained throughout the fluorite series, whereas the second ratio is constant for CaF_2, BaF_2 and SrF_2 from Table III.

It is of interest therefore, for these three members of the fluorite series, to enquire whether there is a simple way to relate E_F to the Coulomb energy $q^2/\varepsilon a$. The answer appears to lie in the Jost continuum model. In particular, in his book, Flynn[8] gives an argument for the defect formation energy which relates it to the inverse of the "cavity dimension" in a continuum model. Since this must surely be closely related to the lattice spacing, we expect that it is for CaF_2, BaF_2 and SrF_2 that such a simple model will be most appropriate. However, with present refined ways of calculating defect energies, one should obviously not overemphasise such a simple model.

3.2 Melting of superionic conductor

March *et al.* also emphasize that the melting of a superionic conductor is expected to be influenced by the fact that below T_c the Frenkel defects are dominant. One can then consider, to discuss the melting of a fast ion conductor, mixed Frenkel and Schottky disorder. One can show, by these arguments, that the concentration of Schottky defects at melting is enhanced by the presence of Frenkel defects.[4] However, there does not seem enough evidence to presently warrant quantitative study.

It is worth pointing out here that an elementary, necessary condition for superionic conduction is that the Frenkel energy E_F shall be less than the Schottky energy E_S. However, it is obviously also necessary for T_c, the transition temperature for fast ionic conduction, to lie below the melting temperature.

From the Barr–Dawson–Lidiard correlation between E_s and T_m and the correlation between E_F and T_c displayed in Eq. (3.1), we conjecture that a necessary and sufficient condition for superionic conduction may be

$$E_s \gtrsim 1.3E_F$$

but it may well be necessary, in refining this, to consider mixed Frenkel and Schottky disorder, as discussed above.

4 DISCUSSION AND SUMMARY

It has been pointed out that Kurosawa's theory of the melting of ionic crystals receives some support from the Barr–Dawson–Lidiard correlation. One can have little doubt that the Schottky defect enthalpy plays an important role in the melting process. Furthermore, and in favour of the Debye–Hückel treatment of the Coulomb interaction between defects, the dimensionless ratio of $k_B T_m$ to $e^2/\varepsilon q$ is relatively constant through the alkali halides. However, it has to be said that the presence of the dielectric constant has relatively little effect on this constancy, and that the corresponding states argument of Reiss *et al.* then leads to a similar prediction.

There are questions which remain about the way in which the melting transition arises in the Kurosawa theory. One might well ask whether the properties he used to exhibit melting will find a place in a more fundamental theory. It is the writer's view, though he knows of no proof, that the most fundamental property of the long-range Coulomb interaction will turn out to be a scaling property (cf. Eq. 3.4), in which the critical defect concentration at the transition will turn out to be a function only of the ratio $k_B T_m/(q^2/\varepsilon a)$. Provided only that this is maintained, the main conclusion of this review should continue to hold, even when Debye–Hückel theory is transcended. Though, as we remarked above, there can be little doubt as to the fundamental role of the Schottky defect enthalpy in melting, it may well be that a melting mechanism such as a dislocation model can incorporate this feature and this question of the detailed mechanism remains an open matter in our view.

Nevertheless, the generalization of Kurosawa's treatment using Debye–Hückel theory to account for the interaction between Frenkel defects has been shown by March *et al.*[4] to throw light on the transition in the fluorites to a superionic state. Furthermore, for CaF_2, BrF_2 and SrF_2, it is shown that both dimensionless ratios $k_B T_c/E_F$ and $k_B T_c/(q^2/\varepsilon a)$ are sensibly constant. This can be understood by appeal to a continuum model of defect energies in these materials, though it is cautioned that such a model cannot have general applicability.

Though the objections that can be raised against Kurosawa's treatment of melting apply with equal force to the work of March *et al.*,[4] it is significant that Catlow[9] has developed a phenomenological theory of the transition to a superionic state in which he can successfully treat the defect concentration on both sides of the transition, the phenomenology being guided by the general framework of Debye–Hückel theory.

What is emerging clearly from these studies is that we can expect to see both the melting of ionic materials, and the transition to fast ion conduction, embraced by the theory of charged defects and their interaction in such materials. Obviously, a treatment of the interactions between defects which is valid at much larger concentrations than Debye–Hückel theory (e.g. in PbF_2) is going to be required in a fully quantitative treatment of these transitions.

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