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Simple phenomenological approach to premelting and sublattice melting in Frenkel disordered ionic crystals

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The occurrence of anomalously high ionic-defect concentrations in solids at temperatures approaching the transition to a molten or superionic (i.e., molten cation or anion sublattice) phase is a well-known phenomenon. We show that this premelting phenomenon can be quantitatively described by a cube-root law not only for the Frenkel disordered AgCl, AgBr, and AgI, but also for the anti-Frenkel disordered PbF_2. In all cases, the computed defect-defect interaction leads to a phase instability of first order or of higher order at a temperature which is very close to the actual transition point. Moreover, the specific heat data can be consistently explained by the same effect. The validity of the cube-root law is discussed in particular regarding the unexpectedly good prediction of the transition temperatures. Implications for the melting behavior of ionic conductors and for doping effects are briefly touched upon. A criterion for the transition order is given.

I. INTRODUCTION

Point defects in solids are basic constituents of the solid state. Not only do they enable ionic conduction and mass transport, they also carry information about the thermodynamic state of the solid, notably with respect to temperature and the ambient chemistry. They are also decisive for the propagation of chemical signals. In this sense they are the relevant particles to consider in the context of storage or transformation of chemical energy and chemical information. Although the formation of a single defect increases the energy of the immediate environment, all ionic crystals exhibit at finite temperatures a finite concentration of point defects which is due to a compensating gain in a configurational entropy. The conventional way to express the free enthalpy for defective solid G is

$$G = G_{\text{perfect}} + \int_0^c \Delta G^* dc - TS_{\text{conf}},$$

where G_{perfect} is the free enthalpy of the perfect crystal (i.e., without point defects, but including other contributions such as phonon contributions), and c and $\Delta\ G^*$ denote the defect concentration and the defect formation free energy without the configuration entropy S_{conf}. The minimum of the free energy as a function of defect concentration appears usually at very low c values. This is caused by the extremely steep influence of the configurational part at $c \longrightarrow 0$ $[(\partial S_{\text{conf}}/\partial c) \to \infty]$ which soon flattens compared to the steep increase of the formation free energy. If the defect distribution is at random, ΔG^* is a constant with respect to c and the equilibrium concentration $\hat{c}$, obtained via free enthalpy minimization, is given by the usual expression

$$\frac{\hat{c}}{c^*} = \exp\left(-\frac{\Delta G^*}{kT}\right) \equiv \exp\left(-\frac{\Delta H^* - T\Delta S^*}{kT}\right), \quad (1)$$

where ΔG^* is the sum of a formation enthalpy ΔH^* and a term proportional to the change in the vibrational entropy ΔS^*. In the case of a Frenkel-disordered ionic crystal we have to consider two oppositely charged defects, the vacancy and the interstitial ion. Owing to electroneutrality the two equilibrium concentrations are equal in a pure material. If they are again denoted by $\hat{c}$, ΔG^* means half of the formation value of a Frenkel pair. The reference concentration c^* is proportional to the geometrical mean of the number of nonoccupied sites available for the interstitial and vacant defects, or more specifically

$$c^{*2} = g_i g_v (\alpha_i - \hat{c})(\alpha_v - \hat{c}). \quad (2)$$

In Eq. (2) the α's denote the number of occupiable crystallographic sites; the g's denote the degeneracy of those sites. Thus, the product $g\alpha$ is equal to the maximum number of sites per lattice molecules available to the first defect. By this distinction g- and α-value double interstitials are excluded and statistics become straightforward. For AgBr and AgCl (rocksalt structure) the g values are taken as 1, and α is taken as 1 for the vacancy and 2 for the interstitial defect. So, in the above dilute case, $c^*=\sqrt{2}$. For PbF_2 (fluorite structure) the most probable values are $\alpha_v = g_v = g_i = 1$ and $\alpha_i = 1/2$. In the AgI case we set all α's and g's to 1. Equation (1) describes an Arrhenius behavior for the defect concentration with the slope

$$-k\frac{\Delta(\ln \hat{c})}{\Delta(1/T)} = \Delta H^*$$

as long as ΔH^*, i.e., half of the first Frenkel formation enthalpy, is independent of temperature and concentration.

In many examples an anomalous increase of $\hat{c}$, as compared to Eq. (1), has been observed in a more or less extended temperature range below the phase transition.

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In the case of β-AgI this phase transition is the first-order superionic transition to the α phase which exhibits a "molten" Ag^+ sublattice; for AgCl and AgBr it is the melting point, and for PbF_2 it is a continuous (or diffusive) superionic phase transition, resulting in a highly disordered F^- sublattice. The ionic conductivity measurements on those materials [AgCl (Refs. 1–3), AgBr (Refs. 4–6), AgI (Refs. 7, 8) and PbF_2 (Refs. 9–12) are considered here as the most obvious and well-studied examples] allow one to detect sensitively the deviation from Eq. (1) (typically, $\hat{c} \geq\simeq 10^{-5}$) because of the defined concentration dependence of the conductivity.

Several attempts have been undertaken in the literature to explain this phenomenon. Schmalzried[13] following an idea of Jost investigated the effect of volume changes due to the Frenkel reaction on both the free energy of formation and the energy of migration. In the light of later precision experiments (cf. also the review by Friauf[14]) the effect seems to be too low to explain the major part of the anomaly. Batra and Slifkin[15,16] as well as Friauf showed that the prime reason consists in anomalous concentration changes rather than mobility changes. The attempts to explain the results in terms of Debye-Hückel interactions or in term of *ad hoc* models, which introduce a partial defect-defect interaction free enthalpy ($\mu_{\rm int}$) being proportional to the concentration, have not led to a satisfactory agreement.

On the other hand, Kurosawa[17] showed in an early paper that Debye-Hückel effects ($\mu_{\rm int} \sim \hat{c}^{1/2}$) may lead to an instability reflecting a phase transition. Later Strässler and Kittel,[18] Rice, Strässler and Tombs (RST),[19] and Huberman[20] proposed models in which $\mu_{\rm int}$ is proportional to the defect concentration (quadratic decrease of the total free energy) with the explicit aim to explain superionic phase transitions. In the RST approach the proportional behavior is attributed to strain effects stemming from volume changes during the defect formation; in this context the reader is also referred to Refs. 20(a) and 20(b). The approaches are very much in the tradition of early melting theories (Frenkel,[21] Lennard-Jones and Devonshire,[22] O'Reilly,[23] and others). Again, though qualitatively helpful, these models are — from a quantitative point of view — not satisfactory. In terms of phase transitions Welch and Dienes[24] discussed the linear models in detail, even allowing for a linear temperature dependence of the interaction free energy. According to their analysis eventually the low disordered phase transforms into a phase exhibiting a very high defect concentration, which is better viewed as a "weakly disordered interstitial crystal." This means — in a more or less symmetrical way — that the crystal with $\hat{c} \sim \delta \ll 1$ has transformed into a crystal with $\hat{c} \sim (1-\delta)$, resulting in a rather smooth change of the ionic conductivity. However, for most of the phase transitions to be considered here, the conductivity changes abruptly from a weakly disordered crystal with $\hat{c} \sim \delta \ll 1$ to a disordered state where $\hat{c} \sim 0.5$, i.e., where cations or anions are disordered over regular and interstitial sites. For this reason Welch and Dienes introduced an *ad hoc* exponential damping term in their model. Since the symmetry of the phase changes in the examples to be discussed (with the exception of PbF_2), a complete agreement between phase transition temperatures which have been calculated in this way and those which have been experimentally determined cannot be expected. This is especially valid if the crystal melts. This point has been particularly stressed by Tallon.[25] His statement, however, that both states are thermodynamically independent is exaggerated since both states contain the same composition and the same ions; thus basically the same nature of interactions occurs. As will be touched upon later, factors leading to the conductivity anomalies in the low-temperature phase are also the factors causing a destabilization of a highly disordered high-temperature phase and thus a decreased transition point compared to the ideal "Arrhenius crystal." This is also strikingly confirmed by the existence of semiempirical relationships between properties of the solid phase (e.g., disorder energy, time constant of solid state reactions) and melting temperatures.[26]

In all the models discussed and in the model to be described Eq. (1) may be rewritten as

$$\frac{\hat{c}}{c^*} = \exp\left(-\frac{\Delta G^0 + \mu_{\rm int}(\hat{c})}{kT}\right),$$

where ΔG^0 denotes now the standard formation value of a defect pair, i.e., $2\Delta G^*$ for $\hat{c} \to 0$, i.e., so to speak the first formation value. The interaction has been put into $\mu_{\rm int}$ which can also be expressed in the electrochemical language, as $kT \ln f(\hat{c})$, f being the activity coefficient.

II. CUBE-ROOT MODEL: GENERAL REMARKS

In the following we will show that the premelting conductivity anomaly can be quantitatively described by cube-root law for the excess chemical potential,

$$\mu_{\rm int} = -Jc^{1/3} = kT \ln f,$$

for AgCl, AgBr, AgI, and PbF_2. In addition, it will be shown that the same data set leads to a transition to a really disordered state ($\hat{c}$ of the order 1/2) at the temperature which is close to the actual transition temperature (first-order superionic transition into α-AgI exhibiting cation sublattice disorder; continuous superionic transition for PbF_2 into the high-temperature phase exhibiting partial anion sublattice disorder; first-order transition from the solid phase into the molten state, i.e., total lattice disorder for AgCl and AgBr). Moreover, the same model is shown to be nicely consistent with data on the specific heat.

Figure 1 shows how well the excess data given by Aboague and Friauf[1,14] for AgCl and AgBr can be fitted by a $c^{1/3}$ law. In addition to this experimental argument, it is worth mentioning that a cube-root law is known in liquid electrolytes to describe the activity coefficients in concentrated solutions[27] above the validity limit of the Debye-Hückel approach. The natural explanation is that the defective solid can be effectively described — in a mean field sense — by superimposing to the regular ion lattice a defect lattice, which is characterized by a mean defect-defect distance given by $c^{-1/3}$. Cube-root models are also known to be fulfilled in different examples with respect to band gap narrowing rather than to Debye-Hückel- or Thomas-Fermi-type models.[28] The interaction of excess electrons discussed in that context is phenomenologically quite analogous to the interaction of excess cations and cation vacancies in the silver halides. Kurosawa[17] also mentioned a $c^{1/3}$ dependence of the defect interactions in the context of assessing the latent heat of melting. Unlike the $c^{1/2}$ dependence of the Debye-Hückel and the c dependence in the Huberman model, the $c^{1/3}$ dependence fulfills the requirement of a sufficiently steep dependence on c to cause a transition into disordered state.

III. THERMODYNAMICS, EQUILIBRIUM DEFECT CONCENTRATION, AND PHASE TRANSITION

Introducing the term $-Jc^{1/3}$ into the logarithm of the activity coefficient and thus into the chemical potential leads to an interaction term in the total free enthalpy,

$$\Delta G_{\text{int}} = \int_0^c \mu_{\text{int}}(c')dc' \propto -\frac{3}{4}Jc^{4/3} \equiv -J'c^{4/3},$$

and to a mean chemical potential $\overline{\mu}_{\text{int}} = \Delta G_{\text{int}}/c$ or $\frac{4}{3}\mu_{\text{int}}(c)$.

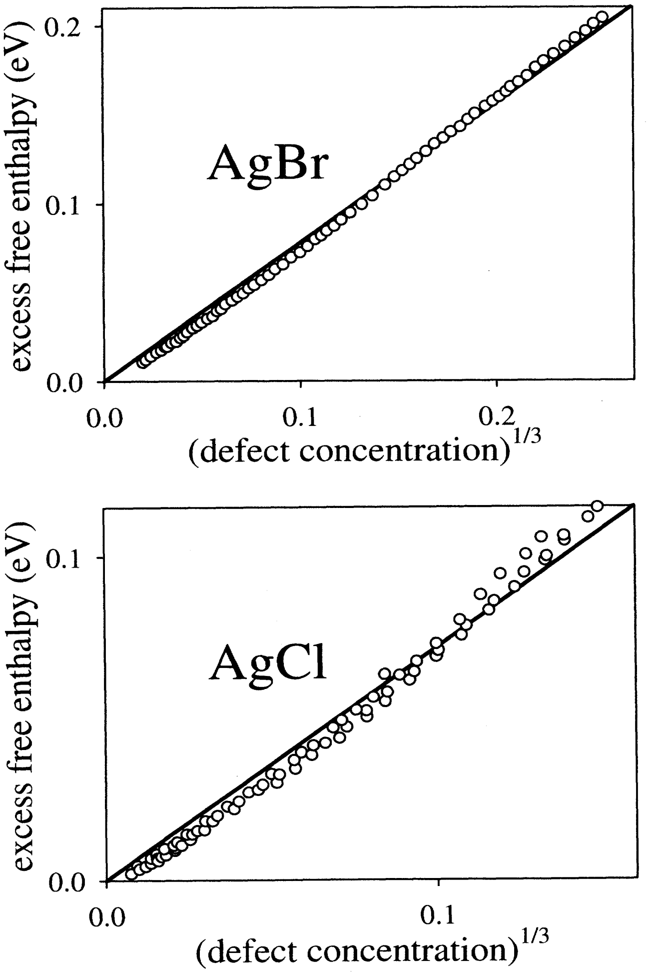

FIG. 1. Friauf's (Refs. 1, 14) excess free enthalpy data replotted versus $c^{1/3}$ reveals the validity of the cube-root law.

The total free energy of the crystal reads as follows:

$$G = G_{\text{perfect}} + c(\Delta G^0 - J'c^{1/3}) - TS_{\text{conf}}, \quad (3)$$

where

$$S_{\text{conf}} = k[c\ln g_v g_i - 2c\ln c - (\alpha_v - c)\ln(\alpha_v - c) - (\alpha_i - c)\ln(\alpha_i - c) + \alpha_v \ln \alpha_v + \alpha_i \ln \alpha_i].$$

For $J = J' = 0$ the equilibrium concentration is directly arrived at by setting $\partial G/\partial c = 0 = \mu(\hat{c})$. As a result the equilibrium defect concentration $\hat{c}$ in the low disordered state is obtained. It is explicitly given by Eq. (1). For $J' \neq 0 \neq J$ the situation is more complicated. Denoting the extreme value by c_E, the equilibrium condition results in the implicit equation, for c_E,

$$\exp\left(-\frac{\Delta G^0 - Jc_E^{1/3}}{kT}\right) = \frac{c_E^2}{g_i g_v(\alpha_i - c_E)(\alpha_v - c_E)}. \quad (4)$$

The equilibrium defect concentration $\hat{c}$ is that concentration among the set of the extreme values c_E for which the free energy is absolutely the lowest $G(\hat{c}) = \min\{G(c_{E,i})\}$. Figure 2(c) shows the graphical solution of Eq. (4) by analogy to Ref. 24. As shown in Fig. 2(a) for α's and g's = 1, Eq. (4) has one or three solutions corresponding to one minimum or two minima separated by a maximum for the concentration dependence of the total free enthalpy. The $(\Delta G^0 - Jc^{1/3})/2kT$ curve given by the dashed line in Fig. 2(c) rotates with temperature counter clockwise around the pivot point $c = \Delta H^0/J$ as indicated. The behavior is similar to, but with the slope steeper than, the linear model.[24]

There are two scenarios. One is the appearance of two minima for a relatively wide temperature range in the vicinity of phase transition. At sufficiently high temperatures the minimum at high defect concentration may become the absolute minimum and the first-order phase transition occurs with the possibility of a kinetic hysteresis. The ln (c_E) vs $1/T$ curve is shown in Fig. 2(b). It is remarkable that due to the steep dependence of G on c the high-temperature concentration is of the order of 1/2 and thus really results in a disordered state rather than in a weakly disordered interstitial crystal (see above). The other scenario is such that the absolute minimum in G continuously shifts from a low to a high defect concentration value. Consider Fig. 2(b), which refers to the first case; the concentration values of the absolute minimum show an enhancement prior to the transition compared to an Arrhenius behavior and a first-order transition at that temperature where the two minima yield the same G value [Fig. 2(a)]. In the limiting case leading to a continuous transition the $1/T$-ln(c_E) curve exhibits an inflection point with a horizontal tangent.

As shown in the Appendix the limiting case is obtained by setting the first and second derivative of $1/T = f(c_E)$

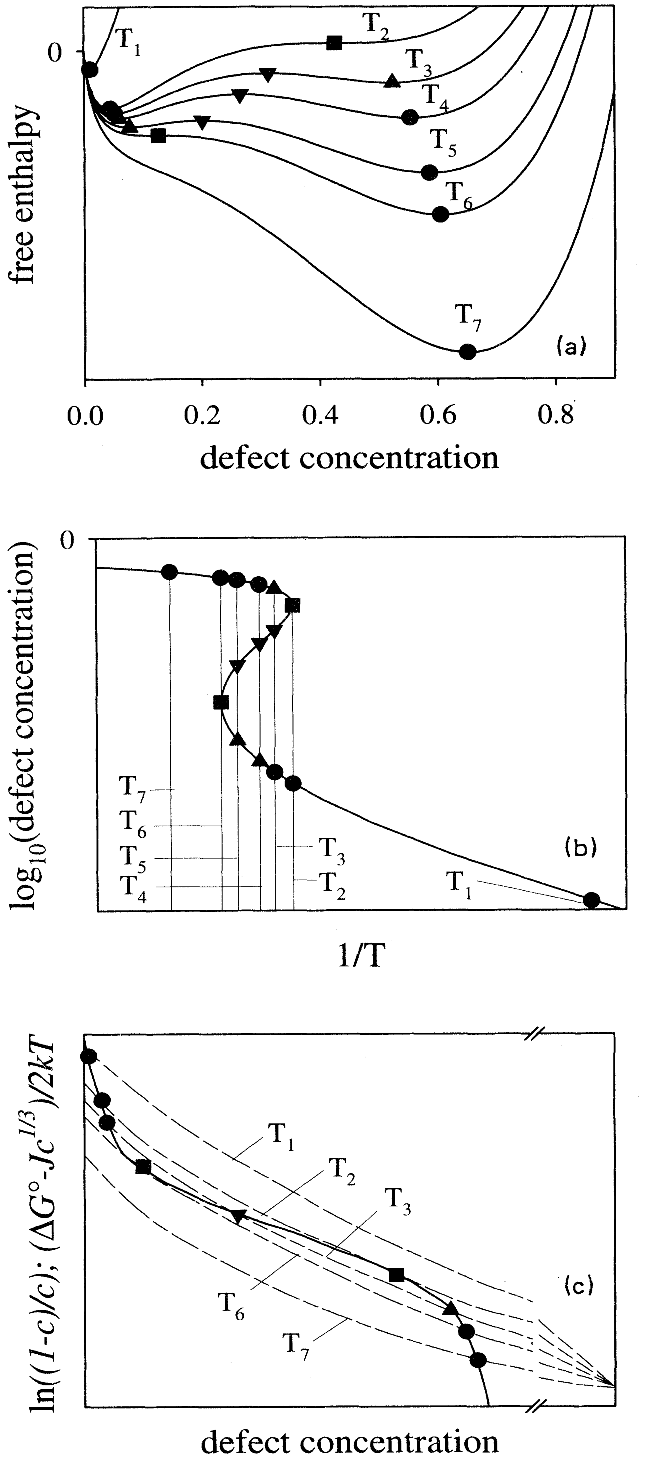

FIG. 2. (a) Two minima appear in the total free energy [Eq. (3)] as a function of defect concentration ($T_1 < T_2 < \cdots < T_7$). (b) The extreme concentrations c_E as a function of temperature. (c) Schematic representation of the graphical solution of Eq. (4) in analogy to Ref. 24. The solid line represents the term $\ln((1-c)/c) \propto \partial S_{\rm conf}/\partial c$ and the dashed lines show the term $(\Delta G^0 - Jc^{1/3})/2kT$ (circles, absolute minimum; square, degenerate case; triangle down, maximum; triangle up, relative minimum).

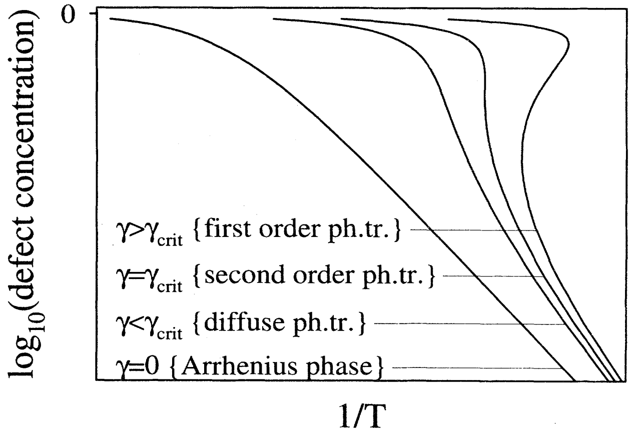

FIG. 3. Defect concentration as a function of temperature for different $\gamma \equiv J/\Delta H^0$ values. The case referring to $\gamma = \gamma_{\rm crit}$ separates the first-order transition behavior from a higher-order transition behavior. The bottom curve ($\gamma = 0$) refers to the case without interaction.

to zero. For $\alpha = 1$ we arrive at a limiting parameter ratio $\gamma_{\rm crit} \equiv (J/\Delta H^0)_{\rm crit} = 4^{1/3}/(1+\ln 3/4+\Delta S^0/8k)^{-1}$ and corresponding concentration $c_{\rm crit} = 1/4$. This is graphically shown in Fig. 3. For an arbitrary power law form for $\mu_{\rm int} \propto c^{1/m}$ the critical γ value is obtained as ($\alpha_{i,v} = 1$)

$$\gamma_{\rm crit} = \frac{(m+1)^{1/m}}{1+\frac{1}{m+1}\,(\ln m + \Delta S^0/2k)}$$

and a corresponding concentration of $c_{\rm crit} = (m+1)^{-1}$. In the case of the often-used linear model ($m = 1$) we have $\gamma_{\rm crit} = 2/(1+\Delta S^0/4k)$ and $c_{\rm crit} = 1/2$, which again points to the more realistic c values of the highly disordered phase as m increases.

IV. APPLICATION OF THE MODEL

A. Conductivity experiments: Premelting anomaly and phase transition

In the following we test the model by applying it to various Frenkel disordered materials which have different crystal structures (AgCl, AgBr: rock salt; β-AgI: wurtzite; PbF_2: fluorite), different disorder types (Ag-halide: cation disorder; PbF_2: anion disorder), and different types of phase transitions (AgI: first-order transition into the α-AgI phase exhibiting a molten Ag sublattice; AgCl, AgBr: first-order transition into the molten state; PbF_2: continuous transition into superionic state). Owing to the relationship $\sigma = \sum \sigma_j = \sigma_i + \sigma_v$, where

$$\sigma_j = z_j e c_j u_j$$

($z_j e$, charge; u_j, mobility) the conductivity is an appropriate property to check models involving defect concentrations. Two points, however, have to be borne in mind: (1) The mobility is temperature dependent via the activation thresholds $\Delta H^{\neq}$ which have to be overcome by a jump from one site to the next equivalent one, and (2) at high defect concentrations it has to be considered that a defect may be surrounded not only by regular neighboring ions and thus the mobility becomes weakly dependent on the concentration itself. A somewhat corrected expression for u_j reads

$$u_j = \frac{v_j^0(\alpha_j - c_j)}{T} \exp\left(-\frac{\Delta H^{\neq}}{kT}\right),$$

where the prefactor v_j^0 contains quantities such as jump distance, attempt frequency, and migration entropy. All quantities besides the interaction parameter J are known from the well-investigated behavior of the ionic conductivity at comparably low temperatures. Thus, the only free parameter in our analysis is J. We obtained a slightly better agreement by also adjusting the parameters v^0, ΔS^0 , ΔH^0, and $\Delta H^{\neq}$. It is very important to state that in these cases the latter parameters are found to be very close to the literature results. In the case of silver halide the interstitial defect is much more mobile than the vacancy so that we only have to deal with one defect type as long as material is intrinsic. In the case of PbF_2 there is some evidence that the situation may be more complicated in that the material changes from a vacancy to an interstitial conductor with increasing temperature in the intrinsic regime well before the premelting regime. In this case we used the low-temperature parameter set[12] to adjust J appropriately. Here we assume the vacancy to be the mobile species over the whole temperature range. For a more detailed discussion the reader is referred to a special paper on PbF_2 which we are preparing.[29]

Figure 4 shows that our results nicely describe the conductivity anomaly prior to the melting point for all the materials considered. The relevant parameters are given in Table I. It is the first time that such a quantitative agreement has succeeded. Beyond that, even the transition temperatures are predicted within an accuracy of few percent. Since in these cases structural changes are involved, a more detailed discussion is necessary (see below).

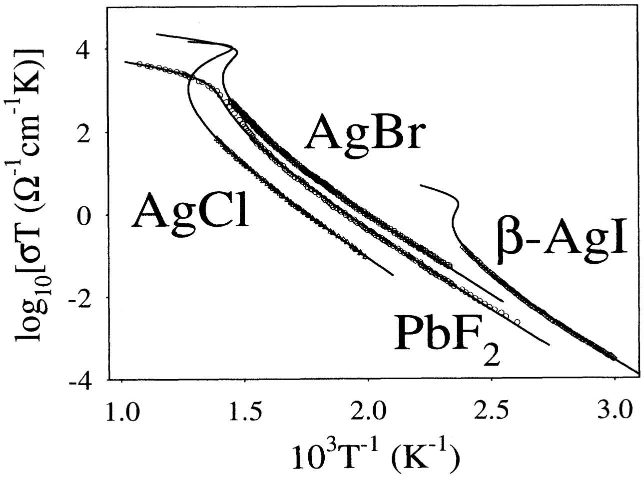

FIG. 4. Temperature dependence of conductivity. Solid lines were constructed according Eq. (4) with defect parameters from Table I. Points present experimental data according to PbF_2, Ref. 12; AgCl, Ref. 1; AgBr, Ref. 5; AgI, Ref. 8.

TABLE I. Defect thermodynamic parameters.

Compound	PbF_2[a]	AgCl[b]	AgBr[c]	β-AgI[d]
α_i, g_i	1/2, 1	2, 1	2, 1	1,1
α_v, g_v	1, 1	1, 1	1, 1	1, 1
$\Delta H^0/(\mathrm{eV})$	1.08	1.48	1.15	0.82
$\Delta S^0/k$	8.48	9.73	7.67	11.77
$J/(\mathrm{eV})$	0.75	1.03	0.803	0.497
$v_0 10^{-6}/(\frac{\mathrm{cm}^2\,K}{\mathrm{sec}\,V})$	0.088	0.030	0.164	0.004
$H^{\neq}/(\mathrm{eV})$	0.18	0.045	0.145	0.244
$\gamma = J/\Delta H^0$	0.694	0.696	0.698	0.606
γ_{crit}[e]	0.779	0.580	0.646	0.578

[a] Experimental data from Ref. 12.
[b] Experimental data from Ref. 1.
[c] Experimental data from Ref. 5.
[d] Experimental data from Ref. 8.
[e] See the Appendix.

B. Specific heat experiments

It is expected that the anomalous defect concentration in the premelting region gives rise to an anomaly in the specific heat. This has indeed been observed by different authors [AgCl (Ref. 30), AgBr (Refs. 30–33), β-AgI (Refs. 34, 35), PbF_2 (Refs. 36–38)]. We may split the specific heat at constant volume into a part stemming from phonons C_{vib} and a part stemming from the point defects C_{def}. We obtain $(\partial\Delta H^0/\partial T \simeq \partial J/\partial T \simeq 0)$

$$C_P(\hat{c}(T),T) = 3nk + \Delta H^0 \frac{\partial \hat{c}}{\partial T} - J\hat{c}^{1/3}\frac{\partial \hat{c}}{\partial T}. \tag{5}$$

In Eq. (5) the saturation limit has been used and differences between C_P and C_V have been neglected. The first point is justified by considering the low Debye temperature [AgCl, ≤ 210 K (Ref. 39), AgBr, ≤ 160 K (Ref. 40), PbF_2, ≤ 240 K (Ref. 41)] such that the Debye function $D(T/\theta_0) \simeq 1$ in the premelting range of AgCl, AgBr, and PbF_2. Corrections with respect to the second point are of the order of a few percent and may be neglected to a first approximation.

Figures 5(a), and 5(b) show experimental data for C_P of AgCl and AgBr. The solid line represents the theoretical curve by using J values from the conductivity fits. In the case of PbF_2 the experimental uncertainty is considerable. The upper line refers to the theoretical curve using $\alpha_v = 1$, $\alpha_i = 1/2$, $g_{i,v} = 1$ as done in the conductivity experiments. The lower line represents the curve by using $\alpha_v = 1\,/2$, $\alpha_i = 1/4$, $g_{i,v} = 2$. The position of the maximum is not affected. In all cases a reasonable agreement has been achieved. AgI was not considered due to unknown Debye correction at the relatively low premelting temperatures.

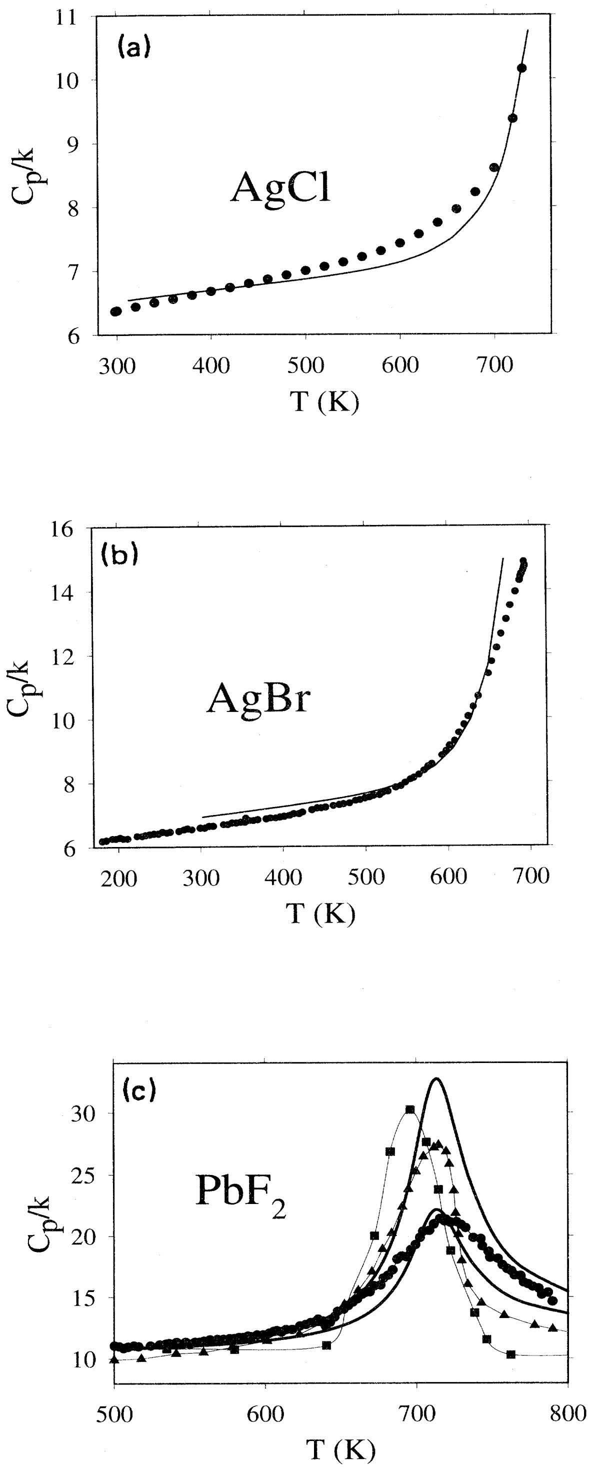

FIG. 5. The specific heat of AgCl (a), AgBr (b), PbF_2 (c). Experimental data are from AgCl, Ref. 30; AgBr, Ref. 31, Ref. 38 (PbF_2, square), Ref. 37 (PbF_2, triangle), Ref. 36 (PbF_2, circle). The lines are obtained by using the parameters of the conductivity fits (Table I). Only the lower curve in (c) was calculated using modified α and g values ($\alpha_v = 1/2$, $\alpha_i = 1/4$, $g_{i,v} = 2$). In all cases a correlation from constant volume to constant pressure has been performed [omitted in Eq. (5)].

V. DISCUSSION

It is striking that good ionic conductors which are characterized by low defect disorder enthalpies show low melting points [e.g., $T_m(\mathrm{NaCl}) = 1074$ K compared to 723 K for AgCl of the same structure]. Obviously, the reason leading to a facilitated formation of defects is also responsible for the low disorder temperature. This may indicate that a zero-J phase is not realistic and supports in a qualitative respect the idea of "critical" defect concentration close to the melting point.[42] These aspects are highly supported by empirical rules connecting defect properties to the melting points, such as Tamann's thumb rule that solid state reactions (actually diffusion) proceed in reasonable times at temperatures higher than 2/3 of the melting point or the impressive relationships between melting points and disorder enthalpies.[43]

In the present paper a quantitative description has been achieved by using a simple and effective cube-root law indicating that the defect-defect interaction can be described in a mean sense by considering an effective defect sublattice. Since the agreement achieved is completely sufficient in view of the experimental error, a more refined treatment taking into account volume changes, variation of the mobility, the inclusion of Debye-Hückel effects, and others requires a higher experimental accuracy. There are indications that the effective exponent in a log-log plot may be somewhat higher than $c^{1/3}$, but this is probably an overestimation of the experimental accuracy. It has already been stated that analogous laws are found in liquid electrochemistry and semiconductor physics to describe carrier-carrier interactions.[44,45] Also, such a law has been observed for the concentration dependence of the defect association energy in CeO_2.[46] It is probable that the correlation discussed above may also apply to frequently observed anomalies in the atomic self-diffusion of metals prior to the melting point.[47–49]

In order not to lose the phenomenologic generality, at this stage, we do not intend to discuss the cube-root law on a microscopic level, i.e., to specify the type of interaction. It can, however, be figured that long-range interactions may scale with the mean carrier-carrier distance.[50]

Again in an effective sense we may estimate that the energy of the crystal is obtained by superimposing a defect lattice of a mean lattice constant a_{def} to the perfect lattice (lattice constant a). We are well aware of the fact that this is an effective mean field argument, since we are not assuming ordering effects. On the other hand, however, March and Tosi[51] have indeed shown that the Madelung energy of a molten salt in which ions may be assumed to be more or less randomly distributed is similar to the Madelung energy of the respective crystal. Since for the materials under investigation μ_{int} and ΔH^0 are, for a first approximation, via the inverse dielectric constant[52] proportional to the Madelung energy of the defect lattice and to the Madelung energy of the perfect lattice, respectively, in this extremely rough approach $\gamma c^{1/3}$ is proportional to $(z_{\mathrm{def}}^2 \zeta_{\mathrm{def}} a_{\mathrm{def}}^{-1})/(z^2 \zeta a^{-1})$ (where z is the charge, ζ the Madelung constant) and thus — for the cases considered — $\gamma \sim \zeta_{\mathrm{def}}/\zeta$. Also in the asymmetrical compound PbF_2 this is a reasonable approximation since effects concerning charges and effects stemming from the more complicated relation between $a, a_{\rm def}$, and c partly compensate. In this case ζ is the reduced Madelung constant. It is very encouraging that the γ values in Table I indeed turn out to be approximately of the order of 1 independent of the material considered. Even the fact that the γ values are slightly lower than unity may be understood in this way for AgCl and AgBr, for which reliable data are available. The empirical ratio of lattice enthalpy and the product of ε and $\Delta_F H^0$ is not unity but rather 0.7[52]. On the other hand we have to consider the factor of 4/3 when transforming Gibbs energies into chemical potentials. Altogether a value $\gamma < 1$ would demand a Madelung constant for the defects lattice which is somewhat lower than that of the crystal lattice. Interestingly, indeed such a lower value has been suggested by March and Tosi[51] as the "liquid Madelung constant." However, due to the crudity of the model, we consider the success of such refinements probably accidental.

Moreover, the proportionality of J and ΔH^0 emphasizes that the pure Arrhenius crystal is unrealistic, that the defects necessarily interact, and that easily disordering crystals (generally good ionic conductors) necessarily exhibit low melting points.

As shown above, not only the premelting behavior but also the phase transition temperature can be described for the Frenkel and anti-Frenkel disordered AgCl, AgBr, AgI, and PbF_2. Since in the case of PbF_2 the structure does not change, the presuppositions of the model are best fulfilled and the agreement achieved is very important. Moreover, the agreement also is surprisingly good for AgI where a first-order transition occurs to the α-AgI phase exhibiting a different structure. It even succeeds for the melting processes in the case of AgCl, and AgBr. At best it could be expected that the disorder model described gives an upper limit of the phase transition. If the agreement is not accidental, we have to assume that the major reason for the relative lowering of the free enthalpy of the actual high-temperature phase is based on the same grounds which are responsible for the defect-defect interaction. Or more precisely, the structural changes of the hypothetical disordered solid high-temperature phase into the real high-temperature phase, i.e.,

$$\text{AgI (hypothetical disordered } \beta\text{-phase)} \rightleftharpoons \text{AgI } (\alpha\text{-phase})$$

$$\text{AgBr (hypothetical disordered rock-salt structure)} \rightleftharpoons \text{AgBr (liquid)},$$

are, at the transition point, not accompanied by a major free enthalpy change any more. This is definitely not true at temperatures well beyond T_c. This hypothesis may be checked in more detail by computer experiments and more advanced theories of liquids. There is also the possibility of a compensation effect between the consequence of the neglect of the real structure of the high-temperature phase and an overestimation of the free enthalpy value in the low-temperature state by neglecting structural modifications in the low-temperature phase. The effect of the J term (compared to the ideal Arrhenius phase where $J = 0$) on the $G(T)$ curve of the phase is mainly to stabilize a disordered high-temperature (HT) phase and to reduce drastically the transition point compared to the zero-J phase. Owing to the large steepness of the $G(T)$ curve for the HT phase, the transition acts not very sensitively on the variation of the defect formation parameters. Thus an overestimation of the free enthalpy for the HT phase does not result in a large error with respect to the temperature. A fact that is puzzling us in this context is that the calculated free enthalpy of the virtual phase is lower than actual values given in the literature. How far this is affecting the concept or how far experimental errors are important has to be further clarified.

Since (homogeneous) doping substantially changes the carrier concentrations, the experimentally observed changes of the phase transition temperature with the doping concentrations is qualitatively understandable. A more quantitative approach is being prepared for PbF_2.[29]

As shown in Ref. 53, large deviations of the ionic point defect concentrations from the bulk values may also occur in boundary regions. As a consequence, surface premelting and also surface phase transitions may occur even under conditions where the bulk is not yet affected. Thus, interactions among chemical excitations may be the reason for such phenomena observed in $CsHSO_4$.[54,55] Also phenomena such as amorphization in composite electrolytes ("heterogeneous doping"),[56] phase transitions in thin films, or grain boundary melting may be — at least partly — traced back to these grounds. As already mentioned, an analogous interaction effect in semiconductors is the band narrowing due to the interaction of the electronic carriers. In light of these considerations it is very tempting to explain the effect of surface metalization and surface melting very recently found[57] in Ge (111) in the same way. The analogous behavior is augmented by the fact that the band narrowing effect has been shown to follow a cube-root law in different cases.

VI. CONCLUSIONS

We have shown for various Frenkel disordered materials that a cube-root term in the chemical potential of the defects is able to describe quantitatively the anomalous defect concentration at high temperatures below the transition to a sublattice-disordered or totally disordered (molten) state. Even the transition temperature (PbF_2: continuous solid/solid; AgI: first-order solid/solid; AgBr, AgCl: first-order solid/liquid) can be predicted nicely. We have given a necessary criterion for the limiting case of a second-order transition. These considerations do not only have an impact on the relationship between the molten state and point defect disorder in the low-temperature phase, but are also relevant for the discussion of solid solutions, the occurrence of nonlinear kinetics, and the discussion of phase transitions at interfaces. There is no doubt that the given treatment has neglected different important features, such as structural changes or the appearance of additional defect types (e.g., Schottky disorder, etc.). However, a simplified lattice model reproduces the fact that the effective chemical interaction potential is $\sim -\Delta H^0 c^{1/3}$.

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APPENDIX: CRITERION FOR SECOND-ORDER PHASE TRANSITIONS IN A POWER LAW MODEL

Generalizing $c^{1/3}$ to $c^{1/m}$, Eq. (4) can be recast as

$$\eta(\xi) = \frac{L(\xi)}{\xi^{1/m}\gamma - 1},$$

where $\eta = \Delta H^0/kT$, $\xi = c_E$, $\gamma = J/\Delta H^0$, and

$$L(\xi) = \ln \frac{\xi^2}{(\alpha_i - \xi)(\alpha_v - \xi)} - \Delta S^0/k.$$

The limiting case from a first-order to a higher-order transition is obviously characterized by $\eta' = \eta'' = 0$. Writing $\eta' \equiv u/v$ we have

$$u = \gamma \xi^{1/m} \left[m - \frac{L(\xi)}{\frac{\alpha_i}{\alpha_i - \xi} + \frac{\alpha_v}{\alpha_v - \xi}} \right] - m$$

and

$$v = m\xi \frac{\left(\xi^{1/m}\gamma - 1\right)^2}{\left(\frac{\alpha_i}{\alpha_i - \xi} + \frac{\alpha_v}{\alpha_v - \xi}\right)}.$$

Thus, a necessary condition for a first- or second-order transition is ($u = 0$)

$$\gamma \xi^{1/m} \left[m - \frac{L(\xi)}{\frac{\alpha_i}{\alpha_i - \xi} + \frac{\alpha_v}{\alpha_v - \xi}} \right] = m. \tag{A1}$$

For $\gamma = J = 0$ obviously no solution exists (no interaction), whereas for $\gamma \to \infty$ the bracketed term needs to be zero. The second derivative $\eta'' = \frac{vu' - uv'}{v^2}$ at the ξ value at which η' vanished, reduces to $\eta'' = v/u'$. The critical case demands $\eta'' = 0$ with the consequence that

$$u' = \gamma \xi_{\text{crit}}^{1/m} L(\xi_{\text{crit}}) \times \left\{ \begin{array}{r} m\xi_{\text{crit}} \left[\frac{\alpha_i}{(\alpha_i - \xi_{\text{crit}})^2} + \frac{\alpha_v}{(\alpha_v - \xi_{\text{crit}})^2} \right] \\ - \left[\frac{\alpha_i}{(\alpha_i - \xi_{\text{crit}})} + \frac{\alpha_v}{(\alpha_v - \xi_{\text{crit}})} \right] \end{array} \right\} = 0. \tag{A2}$$

We arrive at the ξ_{crit} value given by the cubic equation. The ξ_{crit} value is obtained by setting the bracketed term in Eq. (A2) to zero. The general solution is too clumsy to be given here. For the special case that $\alpha_i = \alpha_v = 1$ we simply find

$$\xi_{\text{crit}} = \frac{1}{1+m}.$$

Inserting ξ_{crit} into Eq. (A1) yields for $m = 3$ the critical γ value

$$\gamma_{\text{crit}} = \frac{4^{1/3}}{1 + \ln 3/4 + \Delta S^0/8k}.$$

The other solution of Eq. (A2), viz., $\xi^{(2)} = \exp(\Delta S^0/k)/[1 + \exp(\Delta S^0/k)]$ and $\gamma^{(2)} = \exp(-\Delta S^0/k) + 1$, can be discarded since the denominator v vanishes too.

In order to calculate γ_{crit} for $\alpha_i \neq \alpha_v$ Eq. (A2) has been solved for the specific materials considered (see Table I).

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