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Defects and the first-order phase transitions in AgI

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The various defect theories of the β-α transition in AgI and many other type-I fast-ion conductors are criticized. Because the symmetries of the two phases are quite different, they are thermodynamically independent and an order-disorder transition in the β phase does not entrap the β-α transition. It is shown by a model-free theory and experimental data that there is no critical value in the defect concentration. Rather, this varies along the length of the phase boundary. These ideas are illustrated in the very case of AgI, along its rocksalt–α-phase boundary which traverses a diffuse fast-ion transition in the rocksalt phase.

Recently, Shahi and co-workers[1,2] have suggested that the first-order β-to-α transition in AgI at 420 K is driven by a critical concentration of defects in the β phase. The α phase is a fast-ion conductor or solid electrolyte in which the cation sublattice is diffusive while the anions remain localized in a bcc lattice. According to many who espouse the defect model,[1-5] this highly defective α phase is anticipated in the lower-temperature β (wurzite) phase by the high density of Frenkel defects. As the transition temperature is approached, the concentration of defects either diverges[3-5] or approaches a critical level.[1,2] In each of these theories, it is implied that this behavior is general in its applicability to a number of type-I fast-ion transitions in the scheme of Boyce and Huberman.[6]

I submit, however, that the above notions are not valid, neither in general nor in the specific AgI system for which they were developed. The two phases in question have quite different symmetries, no similarity exists even in their short-range order, and consequently they are thermodynamically independent. The equilibrium transition point on an isobar occurs just where the Gibbs free energies of the two phases happen to be equal. Three situations illustrated in Fig. 1 may be envisaged. The temperature dependence of the Gibbs free energy is shown schematically for the defect-free β phase (β-β) and for the α phase (α-α). As the negative slope at any point is, by definition, the state entropy, these curves have negative gradient, as shown, and have a small negative curvature due to the temperature dependence of the entropy. The point of intersection is the transition temperature and the discontinuous decrease in gradient is the transition entropy. Lines 1, 2, or 3 describe the perturbed free energy when the β phase has a fast-ion diffuse transition well below, near, or well above the β-α transition, respectively. The decrease in slope around the diffuse transition is by definition the excess entropy and, most important, the effect of the fast-ion transition is to displace the β-α transition to higher temperature.

We note first of all that Cava and Rietman,[7] in detailed and very careful ionic conductivity measurements on single crystals close to the β-α transition, find no evidence for pretransition behavior. This suggests that case 3 is the relevant one, particularly as ionic conductivity directly probes the defect density. To this we may add that a constant-stress molecular-dynamics simulation[8] of AgI allows one to superheat the β phase with no anomaly near the thermodynamic transition point. Likewise, only when supercooled to 300 K does the α phase display a diffuse fast-ion transition to nonsuperionic α-AgI. This is the true order-disorder precursor to the fast-ion α phase. Nonetheless, for the purpose of investigating the proposal of Shahi and co-workers, let us admit the possibility that case 2 pertains so that the defect density grows dramatically in the vicinity of the phase transition. Two important points must be noted. First, even if the defect growth runs away to first order so that the knee in curve 2 undergoes a discontinuous change in slope, the point where it cuts the α-phase curve is quite arbitrary, i.e., an order-disorder transition in the β phase does not entrap the β-α transition and cannot be said to drive it. Second, were case 2 to prevail, rather than being driven by a well-

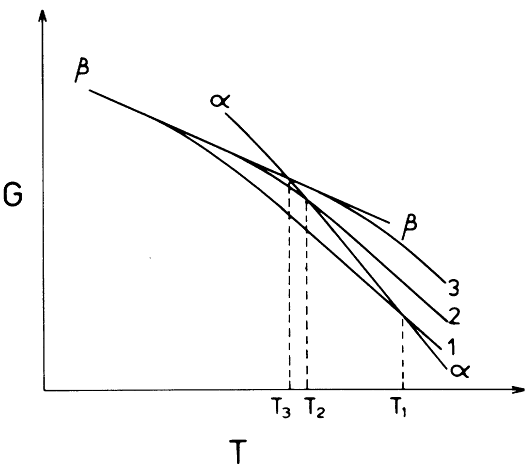

FIG. 1. Schematic diagram of the temperature dependence of the Gibbs free energy of the α phase (α-α) and the defect-free β phase (β-β). Curves 1, 2, and 3 denote the free energy where a diffuse fast-ion transition occurs well below, near, or well above the β-α transition. The transition temperatures T_1, T_2, and T_3 are noted.

defined critical concentration of defects, the β-α transition temperature can be seen to vary linearly with defect concentration along the transition boundary. This point requires some development.

Consider, for initial simplicity, just one defect species with thermal formation enthalpy h_f and formation entropy s_f with Gibbs free energy of formation $g_f = h_f - Ts_f$ which in general is a function of the defect density n. The total free energy is

$$G = G_\beta + ng_f(n) - TS_c(n) \ , \tag{1}$$

where G_β is the defect-free Gibbs function for the β phase and S_c is the configurational entropy of the distribution of defects. At equilibrium, G is stationary in the density n, so that

$$G = G_\beta + T(nS_c' - S_c) - n^2 g_f' \ , \tag{2}$$

where the prime denotes derivative with respect to n. In the vicinity of the order-disorder process H_β and S_β are weak functions of temperature and pressure in comparison with the second and third term in Eq. (2). So also are H_α and S_α in the α phase. Thus we take $\Delta H_0 = H_\alpha - H_\beta$ and $\Delta S_0 = S_\alpha - S_\beta$ to be constants. The equilibrium transition occurs at T_t, given by

$$\Delta H_0 - T_t \Delta S_0 = T_t(nS_c' - S_c) - n^2 g_f' \ . \tag{3}$$

Now consider the variation in T_t and n along the phase boundary. Let the zero suffix and superfix denote the zero-pressure values; then

$$(T_t^0 - T_t)[\Delta H_0 + n_0^2 g_f'] \\ = (n - n_0)(T_t^0 S_c'' - 2g_f' - n_0 g_f'')n_0 T_t^0 + \cdots \ . \tag{4}$$

Thus to first order in $n - n_0$, the shift in transition temperature is linear in the shift in defect density. If there is a single critical defect concentration the transition temperature must not shift with pressure. The fact that it does, and markedly so ($dT/dp = -15.7$ K/kbar),[9] implies that the concentration varies along the boundary. The above argument is model free in that neither the defect nor the concentration dependence of its formation energy is specified. Our only assumption is that, where case 2 of Fig. 1 prevails, ΔH_0 and ΔS_0 are weak functions of temperature and pressure in comparison with the defect terms. Inclusion of the variation in ΔH_0 and ΔS_0 simply adds the Clausius-Clapeyron term $T_t(p - p_0)\Delta V_0$ on the right-hand side of Eq. (4). Were this to dominate in general, our argument may break down but this amounts to saying that the defects contribute negligibly to the total free energy and case 3 prevails as we have already proposed.

Moreover, the sign of the variation is opposite to that which is observed. Consider, specifically, $g_f' \sim 0$ (as in the early stage of divergence) and the configurational entropy of n defects distributed over N lattice sites:

$$S_c = k \ln[N!/n!(N-n)!] \\ = kN \ln[N/(N-n)] - kn \ln[n/(N-n)] \ , \tag{5}$$

so that Eq. (3) becomes

$$T_t^{-1} \Delta H_0 - \Delta S_0 = -nk \ . \tag{6}$$

Consider now the total pressure derivative along the phase boundary

$$[T_t^{-2} \Delta H_0 - k(\partial n/\partial T)_p](dT_t/dp) = k(\partial n/\partial p)_T \ . \tag{7}$$

As the first term in square brackets is more than six times the second ($\sim nh_f T_t^{-2}$) the sign of the slope of the transition boundary is given by the sign of $(\partial n/\partial p)_T$ which is positive due to the negative formation volume.[9,10] In fact, the boundary slope is negative.[11] The above model may readily be generalized with the same conclusion to the actual case of a vacancy and interstitial defect.

Shahi, Weppner, and Rabenau[2] used for their arguments the data of Weiss, Jost, and Oel[12] on the depression of the β-α transition temperature with Pb^{2+} doping. They deduced a critical defect density of about 0.8 mole%. In fact, these data argue rather firmly against the transition being driven by a critical defect density. They estimate the intrinsic defect concentration at T_t at $\sim 0.8\%$, but then the depression continues to grow monotonically with Pb^{2+} concentration, C, up to 5 mole%. They invoke 80% impurity-vacancy binding to account for the difference. We can easily calculate the free defect densities from the original data and we will see that, with doping, they rise well above the intrinsic density at the transition. Moreover, we will see as predicted by Eq. (4) that the transition-point depression is linear in the defect concentration.

It is important first of all to establish mobilities and to use data from the one conductivity study rather than draw from various sources where the absolute conductivities differ. Shahi *et al.*[2] give two sets of interstitial and vacancy mobilities μ_i and μ_v. The first of these, based on the data of Weiss *et al.*,[12] are

$$\mu_i = 0.042 \exp[-(0.27 \text{ eV})/kT] \ , \\ \mu_v = 3.68 \exp[-(0.43 \text{ eV})/kT] \ , \tag{8}$$

and these yield $\mu_i(420 \text{ K}) \sim \mu_v(420 \text{ K}) \sim 2.5 \times 10^{-5}$ $\mathrm{cm^2 V^{-1} s^{-1}}$ at the intrinsic transition. Below the transition the interstitial defect becomes the more mobile of the two. We consider that Eq. (8) well represents the data of Weiss *et al.* Note, for example, that at small doping they observe a relative conductivity minimum below 400 K. Lidiard[13] gives for this

$$(\sigma/\sigma_0)_{\min} = 2\sqrt{\phi}/(1+\phi), \quad \phi = \mu_i/\mu_v \ , \tag{9}$$

from which we deduce from their data $\phi(323 \text{ K}) = 3.3$, $\phi(343 \text{ K}) = 2.6$, $\phi(363 \text{ K}) = 2.0$, and $\phi(383 \text{ K}) = 1.4$. These results agree with Eq. (8) and we note that the minimum disappears close to the transition point so that $\mu_i \sim \mu_v$ there. The alternative set of mobilities quoted by Shahi *et al.* has μ_v a factor of 6 lower at the transition and is quite inconsistent with the relative conductivity minimum observed by Weiss *et al.*

We may proceed now to calculate vacancy and interstitial concentrations, x_v and x_i, from the same conductivity data. The intrinsic conductivity at T_t is about 2.5×10^{-4}

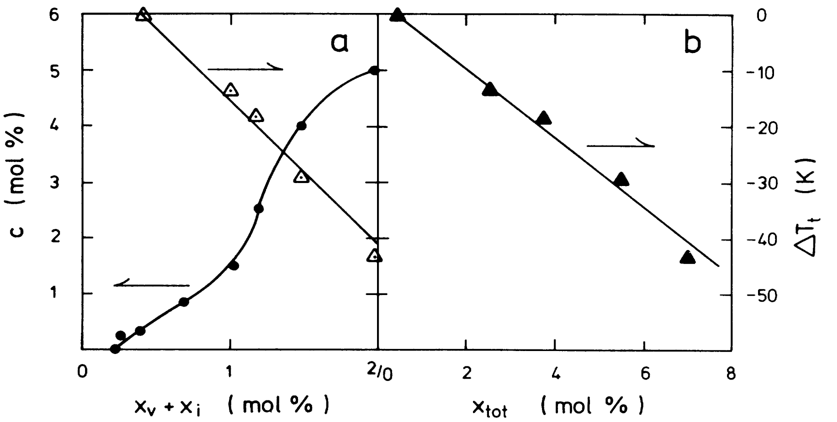

FIG. 2. (a) The concentration c of Pb^{2+} and the depression ΔT_t in transition temperature as functions of vacancy plus interstitial concentration $x_v + x_i$ deduced at $T_t(c)$ from conductivity data of Ref. 9. (b) The depression ΔT_t is also plotted (filled triangles) as a function of total defect concentration $x_{tot} = x_v + x_i + c$.

S/cm so that $x_i \sim x_v \sim 0.21\%$, giving a total intrinsic defect concentration of 0.42%, the so-called critical concentration. For Pb^{2+} dopant levels from 1.5% to 5% the conductivity at T_t is well into the extrinsic region and therefore governed by free, unassociated vacancies only. Using the conductivities at the impurity-dependent transition temperatures quoted by Weiss *et al.* and the above vacancy mobility, the free-vacancy concentrations at $T_t(c)$ are calculated and shown in Fig. 2(a). Both dopant levels c and the transition depression ΔT_t are shown in Fig. 2. At the highest concentration $x_v \sim 2\%$, well above the "critical concentration," and moreover the total defect concentration of x_v free vacancies, x_i interstitial defects, x_v free impurities, and $c - x_v$ impurity vacancy dipoles is $(2+0.02+2+3)\% = 7.02\%$. Clearly there is no critical concentration and the transition point depression simply varies linearly with defect concentration as indicated in Eq. (4). This is a simple consequence of the defects perturbing the total free energy of the β phase. Note that the alternative vacancy mobility quoted by Shahi *et al.* yields x_v $(c = 5\%) = 14.7\%$ at the transition. This is impossibly high as, in the extrinsic region, $x_v \leq c$ due to dipole association.

Figure 2(b) also shows the total defect concentration $x_{tot} = x_i + x_v + c$ to illustrate linearity of ΔT_t in x_{tot} also. Neither of these plots rigorously represents the true dependence since each defect kind occupies a different free-energy level. Nevertheless, by extrapolating back to zero defect density we may deduce that the defect-free transition temperature lies between 2.5 and 11 K above the intrinsic transition temperature and closer to the latter than the former.

All this goes to show that the β-α transition is not driven by a critical concentration of defects in the β phase nor by an intrinsic divergence of Frenkel defects. The combined weight of evidence is persuasive. We have drawn from the anomaly-free conductivity data of Cava and Rietman,[7] computer simulation in the metastable superheated region,[8] model-free defect calculations, and the impurity depression of the transition temperature. This argument is completed by considering the higher-pressure rocksalt-α-phase boundary. This actually is cut by a diffuse fast-ion transition in the rocksalt phase[14] in contrast to the defect model[1-5] which would have both of these transitions running parallel to each other. Rather, on increasing pressure from 0.4 to 1.0 GPa the status evolves from case 3 in Fig. 1 with a defect density in the rocksalt phase of less than 10^{-4}, to case 1 where the defect density is a few percent. Of course, the diffuse fast-ion transition inevitably perturbs the phase boundary,[15] but in no way can the rocksalt-α transition be said to be driven by a critical concentration of defects.

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