Cooperative Phenomena in Solid Electrolytes

B. A. Huberman
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 27 September 1973)

A theory of cooperative effects in ionic solids is presented, which points to the ionic carrier density as the main source of the anomalous behavior found in solid electrolytes. Depending on the parameter values, it predicts either an exponential increase of the conductivity with temperature, or a discontinuous change of the conductivity with an associated peak in the excess specific heat. The predicted behavior corresponds to that found in most solid electrolytes, particularly $RbAg_4I_5$.

A number of ionic solids, notably $RbAg_4I_5$, AgI, and some trifluoride compounds,[1] display anomalously high conductivities, which in some cases are comparable to those of ionic melts. These so-called solid electrolytes display some unusual characteristics: a large cation (anion) disorder at high temperatures, an essentially rigid crystal framework provided by the anion (cation) lattice, and cation diffusion coefficients typical of those found in liquids. A remarkable feature encountered in many of these compounds, as illustrated in Fig. 1, is that the high conductivities they display are achieved via sharp discontinuities as a function of temperature, with associated entropy changes comparable to those of melting. These facts, coupled to the existence of singularities in their excess specific heat, raise some doubt as to whether attempts based on pure transport considerations[2] can be successful in explaining the observed behavior.

I wish to present here a theory of cooperative effects in ionic solids which points to the ionic carrier density as the main source of the anomalous discontinuities found in many solid electrolytes. Although the underlying assumptions are simple, the predicted behavior corresponds to that found in a wide class of ionic conductors, and their thermodynamic properties follow in a straightforward way.

In this model, we assume the ground state of an ionic solid to be a perfectly ordered crystal with no defects present and with a given number of interstitial sites available per ion. As the temperature increases, the system exhibits disorder by forming Frenkel pairs[3] which contribute to the ionic conductivity as

$$\sigma = e^2 N \bar{n}_i(T) \mu_i(T). \tag{1}$$

Here N is the total number of ions, e their charge, $\bar{n}_i$ the fractional number of cations in interstitial sites, and μ_i their mobility given by

$$\mu_i(T) = \nu_0 f a^2 \exp(-\beta E_m)/k_B T, \tag{2}$$

where a is the jump distance of the diffusing ion, f is the correlation factor,[4] E_m the activation enthalpy of motion, ν_0 a constant with dimensions of frequency that encompasses the cation entropy[5] and its vibration frequency in the potential well, and $\beta = (k_B T)^{-1}$. In calculating the activation energy for Frenkel-pair formation, we will take into account the screened interaction between the atom at an interstitial site and the vacancy. This attractive interaction, proportional to $\bar{n}_i^2$, renders the total activation energy excitation-num-

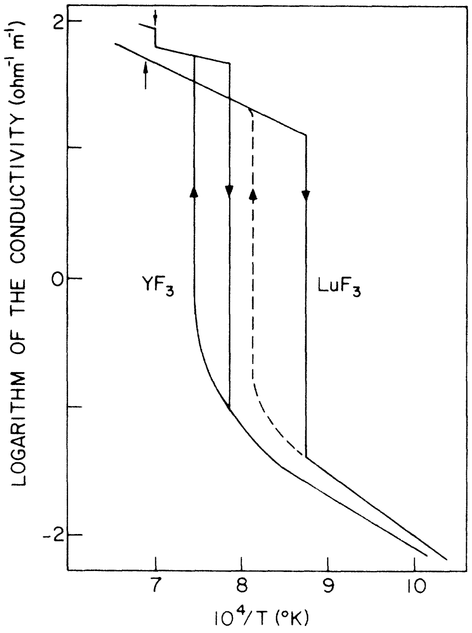

FIG. 1. The logarithm of the specific conductivities of YF_3 and LuF_3 as a function of reciprocal temperature, after O'Keeffe, Ref. 1. The arrows indicate the melting points of the two salts.

ber dependent, and the trial free-energy density can then be written as

$$\mathfrak{F} = U_i n_i - U n_i^2 + 2k_B T[n_i \ln n_i + (1-n_i)\ln(1-n_i) + \tfrac{3}{2} n_i \ln\Gamma], \tag{3}$$

where U_i is the activation energy for promoting an atom into an interstitial site, and U is the attractive pair interaction. The factor $\Gamma = \omega'/\omega$, which is the ratio of the localized interstitial phonon frequency to that of the lattice, accounts for the change in the elastic constants an atom undergoes as it goes into an interstitial site. Equation (3) describes a perfectly ordered crystal at $T=0$ provided that $U_i > U$. By minimizing Eq. (3) one obtains

$$n_i = \{\Gamma^{3/2} \exp[\tfrac{1}{2}\beta(U_i - 2n_i U)] + 1\}^{-1}. \tag{4}$$

Equation (4) admits at most three solutions for given values of the parameters, and the equilibrium configurations $n_i = \bar{n}_i$ are the ones that produce an absolute free-energy minimum at a given temperature. Depending on the values of U_i, U, and Γ, two types of behavior are found, as illustrated in Fig. 2, where is plotted $\log\bar{n}_i$ as a function of $1/T$ for $\Gamma = 0.5$. Curve *a* ($U_i = 3U$) shows a modified exponential increase of $\bar{n}_i$ as a function of temperature with no discontinuities present, a behavior that corresponds to simple ionic transport. Curve *b* ($U_i = 1.15U$) shows an exponential increase of n_i marked with a sharp discontinuity in the ionic carrier density at a critical temperature, the magnitude of the discontinuity depending on the value of U_i/U. This critical behavior is due to the existence at a given temperature of two equal free-energy minima for different values of $\bar{n}_i$, signaling the onset of a first-order transition with hysteresis present.[6] Beyond this temperature the cation sublattice is completely disordered.

The excess specific heat, which is given by

$$\Delta C = T\,dS/dT, \tag{5}$$

can be calculated using the fact that $\bar{n}_i$ corresponds to a free-energy minimum and that

$$(\partial S/\partial n_i)_{n_i=\bar{n}_i} = -(\partial^2\mathfrak{F}/\partial T\,\partial n_i)_{n_i=\bar{n}_i}. \tag{6}$$

One then obtains

$$\Delta C = T(\partial^2\mathfrak{F}/\partial n_i^2)_{n_i=\bar{n}_i}(\partial\bar{n}_i/\partial T)^2. \tag{7}$$

By use of Eqs. (3) and (4) and after some algebra, the excess specific heat can be written as

$$\Delta C = k_B^2 T\left[2k_B T\bar{n}_i(1-\bar{n}_i) - 2U\bar{n}_i^2(1-\bar{n}_i)^2\right]\left(\frac{\ln^2(1-\bar{n}_i)/n_i}{U_i + 3\ln\Gamma - U\bar{n}_i - U\bar{n}_i(1-\bar{n}_i)\ln(1-\bar{n}_i)/\bar{n}_i}\right)^2. \tag{8}$$

The results of Eq. (8) for $T < T_0$ for the parameter values given in Fig. 1 ($U_i = 1.15U$, $\Gamma = 0.5$) are shown in Fig. 3 where the background Debye contribution has been subtracted. As expected from phase transition behavior, ΔC shows a sharp increase as the critical temperature is approached, in agreement with what is observed in $RbAg_4I_5$ at 121°K.[7]

Two points are worth noting concerning the results we have just obtained: (a) the role played by the phonon entropy Γ, which amounts to a temperature-dependent renormalization of the activation energy U_i, and (b) the fact that for $U=0$ Eqs. (3) and (4) reproduce the classical result of ionic conductivity, with U_i playing the role of activation enthalpy.

The general behavior shown in Figs. 2 and 3 is observed in solid electrolytes like $RbAg_4I_5$ and LuF_3, which show a sudden increase in their conductivities at a critical temperature and, associated with it, a narrow peak in their excess specific heat. Above this transition the conductivity continues to increase in a thermally activated way and most likely mobility considerations such as tunnel formation[2] are responsible for the seemingly low motion enthalpies observed. Although one is reminded of the difficulty in isolating reliable values for both the activation energy U_i and phonon frequencies, a choice of $U_i = 0.3$ eV and $\Gamma = 0.5$ gives for the $RbAg_4I_5$ transition ($T_c = 121$°K) $U = 0.25$.

In conclusion, I have shown that the anomalous behavior in the conductivity found in most solid electrolytes can be explained in a natural way by using a model of lattice defects which allows for first-order transitions in the lattice order parameter to take place, with a consequent in-

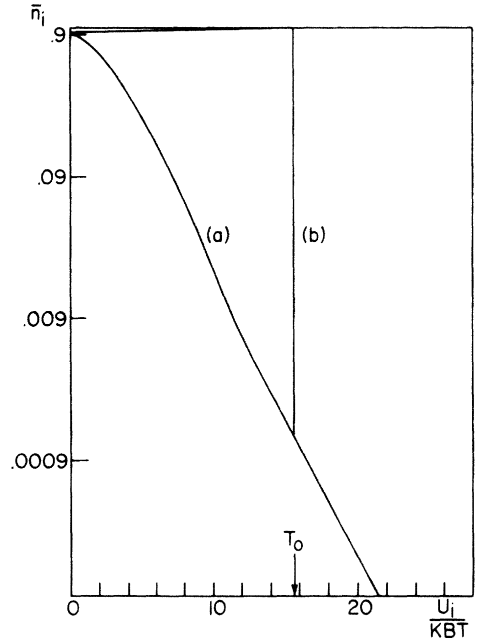

FIG. 2. The number of ionic carriers as a function of U_i/T for $\Gamma=0.5$. Curve a corresponds to $U_i=3U$ and curve b corresponds to $U_i=1.15U$. T_0 denotes the critical temperature at which a first-order transition takes place.

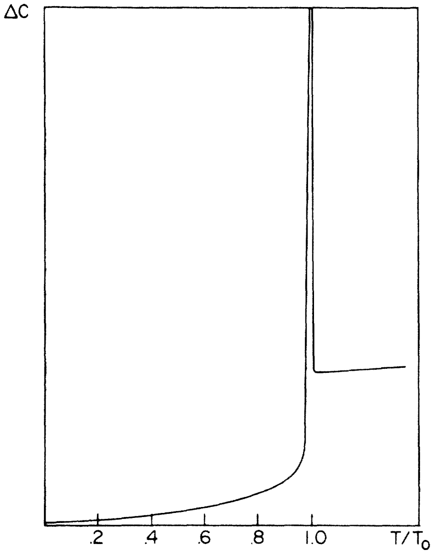

FIG. 3. The excess specific heat, in arbitrary units, as a function of T/T_0 for $U_i=1.15U$ and $\Gamma=0.5$. The Debye contribution has been subtracted.

crease in the number of ionic carriers. In this model both the phonon entropy and the attractive pair interaction play a central role in determining whether the transition to a disordered state takes place in a continuous or abrupt way. I have not included ion-ion interactions nor considered the detailed multiplicity of available sites per ion.[8] These effects will add to a more precise description of the properties of solid electrolytes away from the transition but do not change the main predictions of the model. Nevertheless, this simple model predicts the general behavior found in most solid electrolytes and provides a physical framework for the understanding of both their transport and thermodynamic properties.

In elaborating these ideas, I have benefited from discussions with R. M. Martin, R. M. White, and W. Streifer. Their comments are appreciated.

---

[1] See for instance H. Widersich and S. Geller, in *The Chemistry of Extended Defects in Non-Metallic Solids*, edited by L. Eyring and M. O'Keeffe (North-Holland, New York, 1970), p. 629; M. O'Keeffe, Science 180, 1276 (1973).

[2] W. H. Flygare and R. A. Huggins, J. Phys. Chem. Solids 34, 1199 (1973), and references contained therein.

[3] Although we have chosen Frenkel-pair formation for the sake of simplicity, more complicated situations can be incorporated in this model by the use of appropriate constraints in the free energy.

[4] The correlation factor will differ from unity if consecutive jumps of the diffusing entity are not independent.

[5] A. B. Lidiard, in *Encyclopedia of Physics*, edited by S. Flügge (Springer, Berlin, 1957), Vol. XX, p. 246.

[6] I.e., a secondary free-energy minimum persisting in a temperature range around T_0.

[7] W. V. Johnston, H. Wiedersich, and G. W. Lindberg, J. Chem. Phys. 51, 3739 (1969).

[8] For a detailed treatment of the effects of such interactions, see H. Wiedersich and W. V. Johnston, J. Phys. Chem. Solids 30, 465 (1969).