JOURNAL OF SOLID STATE CHEMISTRY 15, 31C–324 (1975)

Disorder and Ionic Polarons in Solid Electrolytes*

W. J. PARDEE† AND G. D. MAHAN

Physics Department, Indiana University, Bloomington, Indiana 47401

Received October 25, 1974

The role of ion–ion repulsion and ion–phonon coupling in superionic conduction is explored. It is argued that the order–disorder phase transition is not associated with the conductivity discontinuity, but with a higher temperature second order phase transition which has been seen in some superionic conductors and which we predict for others. The specific heat, ion distribution, and conductivity are calculated.

1. Introduction

We present theoretical calculations of the specific heat, ion distribution, and ionic conductivity for the electrolyte phase of one type of solid electrolyte (*1*, *2*, *3*, *4*). We consider primarily the cation disordered halide and chalcogenide solids such as AgI (*5*), $RbAg_4I_5$ (*6*, *7*, *8*, *9*, *10*, *11*), and $AgSI_{32}$ (*12*), although our model is equally applicable to CaF_2 (*13*, *14*). Formalizing the phenomenological classification made by Rice and Roth (*15*), we will call these type I superionic conductors. Type II and type III superionic conductors are, respectively, solids of the beta-alumina group and the defect stabilized ceramic oxides. Although we are primarily considering type I, many of our considerations are applicable to type II (beta-alumina) superionic conductors. The term "superionic conductor" (*15*, *16*) was introduced because the anomalously large ionic conductivities approach those of a good liquid electrolyte (~1 Ω^{-1} cm^{-1}). Our intention here is to build on the substantial crystallographic and thermodynamic information about these materials in an effort to identify the dynamic features contributing to their special properties. The properties which we want to explain are the large ionic conductivity, the low activation energy for ionic conduction, and the incompletely understood second order phase transition within the electrolyte phase. In the remainder of the introduction, we discuss the physical foundations of our model, our methods, and our conclusions.

In surveying the available literature on phase transitions in superionic conductors, we find they commonly have two kinds of phase transition. It appears that these phase transitions fall into two categories, which we label Class I and Class II. These are, as always, apparent exceptions. We discuss them later. For the moment, we define:

Class I. These are transitions with a discontinuity in the ionic conductivity. Since this discontinuity is usually large ($\Delta \log_{10} \sigma \sim 2$), we call this the "insulator–electrolyte" phase transition. These transitions are first order, with a latent heat. They often involve a change in lattice symmetry. Examples are the 144°C transition in AgI (*5*) and the −151°C transition in $RbAg_4I_5$ (*10*, *11*). Figure 1 shows the specific heat of $RgAg_4I_5$ measured by Johnston, Wiedersich, and Lindberg (*10*).

Class II. These are second order phase transitions with a power law divergence in the specific heat. The ionic conductivity is

---

* Supported by the General Electric Co. and the National Science Foundation.

† Present address: Rockwell Science Center, Thousand Oaks, Calif. 91360.

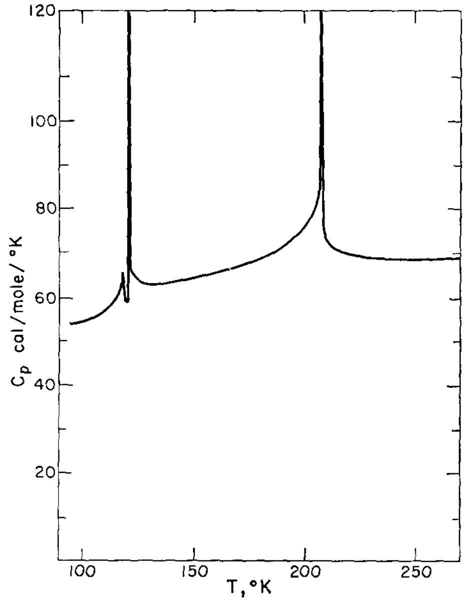

FIG. 1. The specific heat of $RbAg_4I_5$ as measured by Johnston, Wiedersich, and Lindberg (*10*). The first order transition at 121°K is an example of what we call Class I behavior. The second order transition at 209°K has a critical exponent $\alpha' = 1/16$ and is an example of Class II behavior.

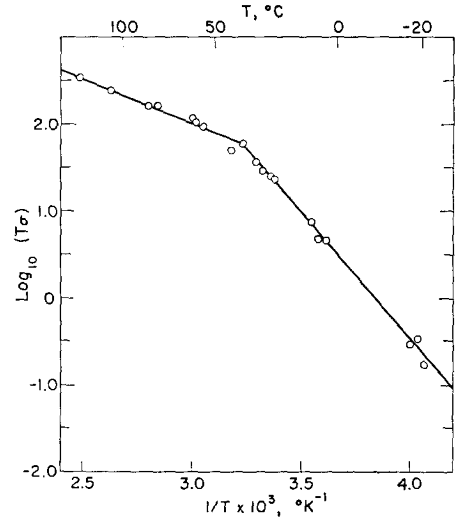

FIG. 2. The ionic conductivity of silver pyridinium iodide as measured by Geller and Owens (*8*).

continuous at this phase transition, although the activation energy for ionic conduction appears to change. Some examples are the −64°C transition in $RbAg_4I_5$ (*10, 11*), the 50°C transition in $C_5H_6NAg_5I_6$ (*8*), and the 1150°C transition in CaF_2 (*17*). The behavior is well illustrated by a plot of log ($T\sigma$) versus $1/T$, shown in Fig. 2 from the data of Geller and Owens (*8*) for silver pyridinium iodide.

We argue that the ionic order–disorder transition is the Class II transition. The presence of appreciable disorder below this transition is merely a manifestation of the slow rise of the order parameter $\xi(T)$ with decreasing temperature. The Class I transition at T_1 *is* to a partially disordered state, $\xi(T_1) < 1$, but only because perfect order occurs only for $T \ll T_2$, and generally $T_1/T_2 \geqslant 0.6$. Our model calculations for the electrolyte phase are in qualitative agreement on all experimentally observed characteristics of the Class II transitions: the specific heat, the temperature dependence of the ion distribution, and the change in activation energy. The identification of disordering with the Class II transition is in disagreement with other recent theories, so we discuss some of the evidence for our conclusion.

Silver iodide has both Class I and Class II transitions at $T_1 = 144$°C and $T_2 = 430$°C, respectively. Early workers assumed the Ag^+ disorder occurred at T_1. Perrot and Fletcher (*5*) discovered the Class II transition at 430°C, and assigned the cation disorder to it. The Class I transition appears to be mostly structural, like the transition at 137°C. Actually, the 430°C transition has a small latent heat, but we call it Class II because it appears to have most of the characteristics listed above. The cation disorder seems necessarily to be related to the 430°C transition, since there are only two kinds of ion, and the iodine ions disorder only at melting, 555°C.

The MAg_4I_5 compounds (M = Rb, K, NH_4) have both Class I and Class II transitions (*6, 9, 10, 11*). In $RbAg_4I_5$ these occur at $T_1 = -150$°C and $T_2 = -64$°C, respectively. We assign the Ag^+ disorder to the T_2 transition, since X-ray data show that the other ion species are ordered. Two recent theories (*18, 19*) ascribe the Ag^+ disorder to the transition at T_1. We believe this is incorrect, since it leaves no explanation for the Class II transition.

The fluorite structures provide a straightforward example of Class II behavior (*20*). They have only one phase transition, and it is positively identified with ionic disorder. It has exactly the Class II characteristics specified above. Although the specific heat and ionic disorder have been measured for only two materials, CaF_2 (*14*) and $SrCl_2$ (*20*), Dworkin and Bredig (*13*) have suggested that this is a general feature of all fluorite structures.

Our calculation shows that the conductivity is continuous through a Class II transition. This has not been generally recognized. For example, Wiedersich and Johnston (*11*), despite a correct treatment of the thermodynamics of the −64°C transition in $RbAg_4I_5$, *incorrectly* conclude that the "transformation is not an order–disorder reaction of the Ag^+ ions; this follows from the continuity of the conductivity through the transition." Our results show that the opposite is the case; it (probably) is an order–disorder transition because the conductivity is continuous.

We suspect that this misconception arises from the properties of Ag_2HgI_4 (*21*, *22*, *23*, *24*), the principal misfit in our classification. The phase transition at 54°C has a lambda-shaped specific heat, characteristic of a second order phase transition, but the ionic conductivity is discontinuous. The transition is order–disorder, but the three cations have only four sites. This is in marked contrast to the usual Class II transition where the cations disorder over many (~3) sites per ion. In fact, perhaps the most firmly based prediction of our model is that Ag_2HgI_4 will have a genuine Class II transition at some temperature well above 54°C. With somewhat less assurance we predict that all superionic conductors (excluding the ceramic based ones which we do not discuss) will have something like a Class II transition. The qualification is due merely to the fact that the presence of a small energy difference between sites, as seems to be the case in β-alumina (*25*), prevents the order parameter from becoming exactly zero at finite temperatures. This is much like a ferromagnet in a weak magnetic field. The theorists' idealization has no phase transition, but real magnets are little changed.

We have not been specific about the nature of the long range order. Although there are many site per conducting ion, the mutual repulsion tends to form a sublattice to separate the ions as much as possible. Since this can normally be done in at least two ways, we will generally have, say, n_1 ions on one sublattice and n_2 on another. The obvious choice for order parameter is then

$$\xi = |n_1 - n_2|/(n_1 + n_2).$$

This is the point of view we adopt in this paper. We describe the hopping ions as a lattice gas (*26*) with a repulsive interaction. We treat the thermodynamics in what is essentially a Bragg–Williams approximation (*27*), but formulated to permit short range correlations in the conductivity and the number of sites per ion to be greater than two. We caution the reader that most applications of the lattice gas model have been to systems with attractive forces, analogous to a ferromagnetic Ising model. Our model is analogous to an *anti*-ferromagnetic Ising model, and its phase diagram is quite different.

A somewhat different picture that has been frequently suggested is that the cations are arranged in ordered microdomains, and that the conduction involves a cooperative motion of an entire microdomain (*25*, *28*, *29*). Although we do not pursue this possibility here, we regard this question as open. The level of approximation used here (~Bragg–Williams) does not include such cooperative motion. However, as one improves the calculations to include more and more correlations, this model may even converge to a collective hopping picture.

No method of calculating the ionic conductivity could be found in the literature, so we invented one. This we regard as a major theoretical result of the present paper. On a more practical level, our goal is to calculate the seven experimentally accessible numbers, namely the Class II transition temperature, the left and right specific heat critical exponents, the conductivity (roughly characterized by high and low temperature activation energies and a normalization), and the site occupation probability (another activation energy, in principle), from a single set of fundamental parameters. These typically include high and low frequency dielectric constants, optical phonon frequencies, and ion–ion interaction energies. We hasten to make clear that in the approximations made here we cannot calculate critical exponents.

The physics of the conductivity calculation is quite simple. We describe it heuristically here, and we provide a careful derivation in Section 4. Although our numerical calculations are for three-dimensional networks, we can illustrate the method more clearly for a two-dimensional square lattice. Fig. 3a shows an ion hop from site A to site B. In site A it had one nearest neighbor, shown by dots, with configurational energy U, where $U > 0$ is the ion–ion nearest neighbor interaction energy. It has two neighbors in the final state at site B, so its change in energy is

$$E_f - E_i = +U + \Delta,$$

where Δ is the site energy difference. Such a transition releases an amount of energy $U + \Delta$. In an optical emission (absorption) experiment this would result in a peak at the frequency $\omega = (U + \Delta)/\hbar$. For the moment, we neglect the interaction with lattice vibrations. Then the optical absorption spectrum is just a set of discrete peaks at the energies $\Delta - nU$, where $z - 1 \geqslant n \geqslant -(z - 1)$. At site A the ion can have anywhere from zero to $z - 1$ neighbors, and likewise in the final state. The difference between the possible initial and final energies has the discrete values $\Delta - nU$, where n has the above range. Thus the simple lattice gas conductivity is of the form

$$\sigma(\omega) = \sum_{n=1-z}^{z-1} P_n \delta(\hbar\omega + nU - \Delta).$$

The probability P_n is that of finding an ion in a configuration where a hop changes its energy by nU. These are obtained by summing over all the possible configurations, two of which are shown in Fig. 3. The dc conductivity $\sigma(0)$ is proportional to the $n = 0$ amplitude (for $\Delta \sim 0$).

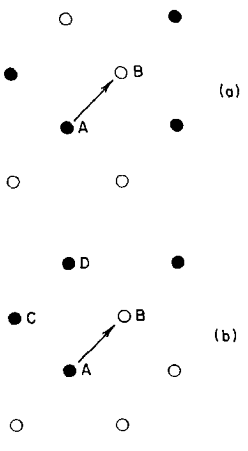

FIG. 3. Two possible nearest neighbor configurations for an ion hopping from site A to site B.

Our conductivity calculation in this paper will use a simple approximation to our general formula. The approximation is one that treats exactly the interaction of the hopping ion with its nearest neighbors before and after the hop, but includes the interaction of the neighbors among themselves only in an average sense. As a result, the probability P_n factors into initial and final configuration probabilities. Thus, if P_{im} (P_{fm}) is the probability that the initial (final) site has m neighboring sites occupied, then

$$P_n = \sum_m P_{i,m} P_{f,n+m}.$$

This approximation makes the configurations in Figs. 3a and 3b equally probable, while in reality Fig. 3b is less probable because of the repulsive interaction between C and D. This excludes collective hopping effects. The effect of including these more distant correlations is being explored, and will be reported elsewhere. We regard this as a reasonable first approximation from which we can learn a great deal. We can, in fact, draw an important qualitative conclusion without any calculation at all. The probability P_0 of a hop which doesn't change the number of neighbors will vanish exponentially (in $1/T$) as the ions become ordered at low temperature. At T_c the ions become completely disordered, so P_0 increases rapidly below T_c and is constant above T_c, in the Bragg–Williams approximation. This qualitatively explains the shape of the lattice gas conductivity shown from direct calculation in Fig. 4. This is the physical origin of the change in activation energy at the Class II phase transition.

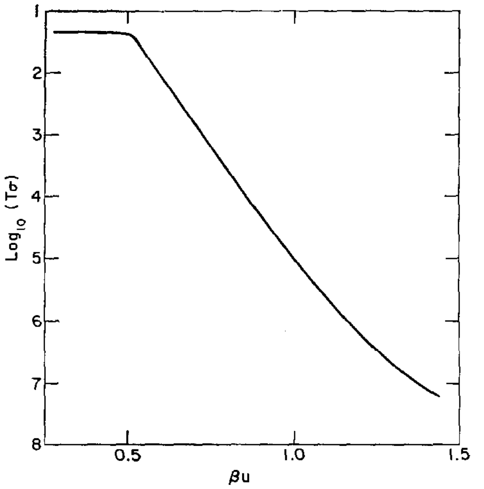

FIG. 4. Conductivity of the simple lattice gas with two sites per ion exhibiting the break in activation energy. This particular curve was done for $z = 8$, $\Delta = 0$, $U = 0.94\ \hbar\omega_{LO}$. For computational convenience λ was made small (0.5) but not zero.

The cation disorder, which we have just extensively discussed, is one of two principal features of our model. The second is the interaction of the ion current with the lattice vibrations. The transition of Fig. 3 can contribute to the dc conductivity if the excess energy $U + \Delta$ is carried away by phonons. The interaction between hopping ions and lattice vibrations is, in fact, the only contribution to the activation energy above T_c, and gives (*30*)

$$\Delta_p \simeq e^2/\pi a \ (1/\varepsilon_\infty - 1/\varepsilon_0)$$

where ε_0 and ε_∞ are the static and high frequency dielectric constants, respectively. In the exact expression for the characteristic length a is complicated, but it is on the order of the ion–ion separation. Polaron theory actually predicts a departure from the Arrenius form

$$\sigma = (c/T)e^{-A/(RT)},$$

in that the prefactor is proportional to $T^{-1/2}$ rather than T^{-1}, but this difference is difficult to detect experimentally. The point we stress is that *the low temperature region is lattice gas dominated*; *the high temperature conduction is phonon assisted hopping.*

We expect that short range correlations not included in the Bragg–Williams approximation will modify our results somewhat without, however, changing the qualitative features. In particular, we mention that reducing U lowers T_c and the activation energy below T_c, raising the conductivity. This fact may have practical use in obtaining more useful solid electrolytes.

The rest of the paper is organized as follows. The Hamiltonian is stated explicitly in Section 2. For conceptual convenience and to explore its general characteristics, we apply it to a hypothetical solid where the cations incompletely occupy a bcc lattice. In Section 3, we use the Hartree approximation to calculate the specific heat and ion distribution. We use linear response theory to obtain the conductivity as a function of temperature in Section 4. Section 5 contains a discussion of numerical results.

2. The Hamiltonian

The most striking structural characteristic of the type I superionic conductors is the availability of substantially more than one site per conducting cation. In $RbAg_4I_5$ the 16 silver ions per cell are distributed over 56 sites; in silver pyridinium iodide the 10 silver ions per cell have 34 sites available. The conducting ions are disordered, but normally not randomly distributed over the available sites. We can usually distinguish crystallographically different types of site, which we expect to differ in energy. Thus, we are led to adopt a description based on the occupation of cation sites. Let the cation sites be labeled by an index α. Each site α is either occupied ($n_\alpha = 1$) or empty ($n_\alpha = 0$). The cation distribution produces an electric field at $\mathbf{r}$ given by

$$\mathbf{E}(\mathbf{r}) = -\nabla V = -\nabla \sum_\alpha n_\alpha V_I(\mathbf{r} - \mathbf{r}_\alpha), \quad (1)$$

where V_I need not be specified now, but represents a normal Coulomb interaction.

Since the nonconducting sublattice always contains large and very polarizable anions (I^-, for example), we expect the cation hopping is strongly influenced by the lattice modes. Consider a particular longitudinal optical lattice mode with phonon operators $a_\mathbf{q}$, and a flat band $\omega(\mathbf{q}) = \omega_0$. Then the anion displacement at r_β due to this lattice mode is ($M =$ anion mass)

$$\mathbf{Q}(\mathbf{r}_\beta) = \sum_{\mathbf{q}} \hat{q}(2M\omega_0/\hbar)^{-1/2} (a_{\mathbf{q}} - a_{-\mathbf{q}}) e^{i\mathbf{q}\cdot\mathbf{r}_\beta}. \quad (2)$$

The interaction between the disordered cations and this lattice mode is

$$H_I = -\sum_{\beta} (-Ze\mathbf{Q}(\mathbf{r}_\beta))\cdot\mathbf{E}(\mathbf{r}_\beta). \quad (3)$$

We have taken the nonconducting sublattice to consist of ions with charge $-Ze$.

We expect that the cation–cation repulsion has a strong influence on the hopping. We describe it by a simple repulsive interaction between neighboring cations,

$$H_C = \sum_{\alpha\alpha'} V_{\alpha\alpha'}\, n_\alpha n_{\alpha'}. \quad (4)$$

Our basic Hamiltonian is then

$$H_0 = \hbar\omega_0 \sum_{\mathbf{q}} (a_{\mathbf{q}}{}^\dagger a_{\mathbf{q}} + \tfrac{1}{2}) + H_C + H_I. \quad (5)$$

This Hamiltonian, together with a transfer interaction to be included later, is familiar in the small polaron theory of electronic conduction in narrow band semiconductors (*31*). There, however, H_C is neglected, while here it plays a fundamental role.

For completeness, we include an outline of the standard transformation to polaron coordinates. The interaction Eq. (3) is written

$$H_I = \sum_{\mathbf{q},\alpha} (iM_{\mathbf{q}}{}^* a_{\mathbf{q}} - iM_{\mathbf{q}}\, a_{\mathbf{q}}{}^+) n_\alpha e^{i\mathbf{q}\cdot\mathbf{r}_\alpha} \quad (6)$$

with

$$M_{\mathbf{p}} = ZeN|\mathbf{q}|\,\tilde{V}(\mathbf{q})/2M\omega_0/\hbar)^{1/2} \quad (7)$$

$\tilde{V}(\mathbf{q})$ is the fourier transform of $V_I(\mathbf{r})$. Then we can complete squares to remove H_I from H_0. It becomes

$$H_0 = \hbar\omega_0 \sum_{\mathbf{q}} (A_{\mathbf{q}}{}^\dagger A_{\mathbf{q}} + \tfrac{1}{2}) + \sum_{\alpha\alpha'} U_{\alpha\alpha'}\, n_\alpha n_{\alpha'}. \quad (8)$$

We have defined the displaced phonon operators

$$A_{\mathbf{q}} = a_{\mathbf{q}} - i \sum_{\alpha} n_\alpha M_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_\alpha}/\hbar\omega_0. \quad (9)$$

The cations are now surrounded by a distorted lattice of the polarized anions, reducing their mutual repulsion to

$$U_{\alpha\alpha'} = V_{\alpha\alpha'} - \sum_{\mathbf{q}} \hbar\omega_0 \alpha(\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{r}_\alpha - \mathbf{r}_{\alpha'})}. \quad (10)$$

The coefficient $\alpha(\mathbf{q})$ is determined by calculating (in second order perturbation theory) the zero temperature phonon exchange interaction between cations. This enables us to identify

$$\alpha(\mathbf{q}) = \frac{4\pi e^2}{\hbar\omega_0 \Omega q^2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right), \quad (11)$$

where ε_0 and ε_∞ are the static and high frequency dielectric constants, respectively, and Ω is the crystal volume. Note that at long distances we would have

$$V_{\alpha\alpha'} = Ze^2/(\varepsilon_\infty r_{\alpha\alpha'})$$

and

$$U_{\alpha\alpha'} = Ze^2/(\varepsilon_0 r_{\alpha\alpha'}).$$

Of course, these expressions are wrong at short (first or second neighbor) distances.

When we introduce hopping between cation sites we will use cation creation and destruction operators; $c_\alpha{}^+$ creates a cation at site α, $n_\alpha = c_\alpha{}^+ c_\alpha$, etc. We write a simple transfer Hamiltonian

$$H' = \sum t_{\alpha\alpha'}\, c_\alpha{}^+ c_{\alpha'}. \quad (12)$$

Hermiticity requires $t_{\alpha\alpha'} = t^*_{\alpha'\alpha}$. We do perturbation theory in the small parameter $t_{\alpha\alpha'}$. We neglect H' completely in doing thermodynamic calculations, and keep 0 $(t^2_{\alpha\alpha'})$ in calculating the conductivity.

The cation operators c_α do not commute with the new phonon operators A_q. It is not difficult to show that the ionic polaron operators

$$C_\alpha = c_\alpha \exp\left\{-i \sum_{\mathbf{q}} \alpha^{1/2}(\mathbf{q})(a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_\alpha} + a_{\mathbf{q}}{}^+ e^{-i\mathbf{q}\cdot\mathbf{r}_\alpha})\right\} \quad (13)$$

commute with the A_q and satisfy the same anticommutation rules among themselves as do the c_α. The inverse of Eq. (13) is

$$c_\alpha = C_\alpha \exp\left\{i \sum_{\mathbf{q}} \alpha^{1/2}(\mathbf{q}) \times (A_{\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{r}_\alpha) + A_{\mathbf{q}}{}^+ \exp(-i\mathbf{q}\cdot\mathbf{r}_\alpha))\right\}. \quad (14)$$

These expressions will be needed in constructing the ionic current operator in Section 5.

3. Thermodynamics

We neglect the transfer interaction entirely in calculating thermodynamic quantities. In the solids of interest the conducting ions occupy perhaps only one-third of the available sites, but the average number of cations per unit volume is a constant determined by the stoichiometry. This is the physically significant constraint on our lattice gas. We impose it by using the grand canonical ensemble, choosing the chemical potential to keep the average number of cations per unit volume equal to the value given by the stoichiometry. This is a little more complicated than the simple theory of order–disorder transformations in AB alloys, although that is a special case.

It is conceptually helpful at this point to consider a hypothetical bcc sublattice of cation sites. Suppose the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ site differs in energy from the (000) site by an amount $\Delta \geqslant 0$. Let the (000) site in the α cell have occupation number $n_\alpha (= 0,1)$ and the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ site $p_\alpha = (0,1)$. Then our grand canonical Hamiltonian is

$$H_0 = \hbar\omega_0 \sum_{\mathbf{q}} (A_{\mathbf{q}}^+ A_{\mathbf{q}} + \tfrac{1}{2}) + U \sum_{\alpha,\delta} n_\alpha p_{\alpha+\delta} + (\Delta - \mu) \sum p_\alpha - \mu \sum n_\alpha \tag{15}$$

where $U > 0$ and the summation index δ runs over the eight nearest neighbors.

The phonon thermodynamics is elementary. The phonon thermodynamic potential

$$\Omega_{\text{ph}} = k_{\text{B}} T \ln (2 \sinh (\tfrac{1}{2}\beta\hbar\omega_0)) \tag{16}$$

gives the familiar Einstein specific heat,

$$C = -T\frac{\partial^2 \Omega}{\partial T^2} = \frac{\exp(\beta\hbar\omega_0)}{T^2(\exp(\beta\hbar\omega_0) - 1)^2}. \tag{17}$$

The polaron Hamiltonian is formally identical to the antiferromagnetic Ising model in a magnetic field. There is no exact calculation of the partition function even in two dimensions. In addition, the physically interesting magnetism problem is constant external field, corresponding to constant chemical potential. The constraint mentioned above,

$$\langle n_\alpha \rangle + \langle p_\alpha \rangle \equiv \bar{n} + \bar{p} = n_C,$$

corresponds to constant magnetization and cannot be normally satisfied at constant chemical potential. There is one special case where constant chemical potential and constant n_C coincide, however. For $\mu = \frac{1}{2}zU$, with z the ion–ion coordination number, the lattice gas (antiferromagnet) has a second order phase transition. *Below* the phase transition,

$$\bar{n} + \bar{p} = 1$$

is constant. The best theoretical values for the specific heat critical exponent

$$\alpha' = \lim_{T \to T_c} - d \log C_v / d \log (1 - T/T_c)$$

is thought to be exactly 1/8 (*32*). This critical exponent is known for one superionic conductor, RbAg_4I_5, and the experimental value is $\alpha' = 0.14$ (*33*). Demonstration that this value is really a consequence of our Hamiltonian awaits detailed theoretical study of RbAg_4I_5, as well as a substantial extension of Ising model "technology." We mention this as a stimulus for improvement upon the approximate methods to which we now turn.

We employ a Hartree (mean field theory) approximation for the cation occupation numbers. We replace the many body Hamiltonian Eq. (15) by two one-body Hamiltonians,

$$\begin{aligned} H_n &= n_\alpha (zU\bar{p} - \mu), \\ H_p &= p_\alpha (zU\bar{n} + \Delta - \mu). \end{aligned} \tag{18}$$

These give the coupled equations

$$\bar{p} \equiv \langle p_\alpha \rangle = (1 + \exp \beta (zU\bar{n} + \Delta - \mu))^{-1}$$

and (19)

$$\bar{n} \equiv \langle n_\alpha \rangle = (1 + \exp \beta (zU\bar{p} - \mu))^{-1}.$$

These equations are easily solved numerically to give $\bar{n}$ and $\bar{p}$ as functions of T and μ. We then solve

$$\bar{n}(\mu,T) + \bar{p}(\mu,T) = n_c \tag{20}$$

for $\mu(T,n_c)$. Knowing the chemical potential $\mu(T,n_c)$, we now know $\bar{n}(T)$ and $\bar{p}(T)$. The lattice gas specific heat is

$$\begin{aligned} C &= (d/dT)\,(zU\bar{n}\bar{p} + \bar{p}\Delta) \\ &= (zU + \Delta - 2zU\bar{p})\,(d\bar{p}/dT). \end{aligned} \tag{21}$$

We define an order parameter

$$\xi = (\bar{n} - \bar{p})/n_c. \tag{22}$$

It is obvious that for $n_c \leqslant 1$ and $\Delta > 0$,

$$\begin{aligned} \xi(T) &\to 1, \\ T &\to 0. \end{aligned} \tag{23}$$

It is not quite so obvious for $\Delta = 0$. Although the sublattices are equivalent, Eq. (19) has two solutions for average sublattice occupation. We define $\bar{p}$ to be the solution which vanishes at $T \to 0$. Of course this is precisely analogous to spontaneous magnetization.

As the temperature is increased, the entropy gained by disorder lowers the free energy more than the repulsion raises it, and $\bar{p}$ increases. For $\Delta = 0$ the order parameter vanishes as $(1 - T/T_C)^{1/2}$, a typical mean field theory phase transition. For Δ small but not zero, as seems to be the case for some real solids, the same qualitative behavior is observed, except that the order parameter becomes small but positive at the specific heat maximum. This, of course, is not really a phase transition, but the physics of interest here is very similar. Results for the specific heat and average site occupation are shown in Fig. 5.

This, we argue, is the Class II phase transition discussed in the introduction. As one cools a superionic conductor from, say, its melting point, at a temperature T_2 the mutual repulsion of the disordered ions will start to produce long range order. The transition is second order, so as the crystal is cooled further, the order parameter $\xi = (\bar{n} - \bar{p})/(\bar{n} + \bar{p})$ increases continuously. In most super ionic conductors a Class I phase transition occurs at T_1 before the perfectly ordered state ($\xi = 1$ at $T = 0$) is achieved. This is the source of confusion over whether Class I or Class II is order–disorder transition. Disorder *is* introduced at the Class I transition because $\xi(T_1) < 1$, but the order–disorder transition is at T_2 where $\xi(T_2) = 0$. This explains the entropy change

$$\Delta S \sim -k_B(\xi \ln \xi + (1 - \xi) \ln (1 - \xi))$$

at the Class I transition. For $\xi \sim 0.9$

$$\Delta S \sim 0.7 \text{ cal/(mole°K)}.$$

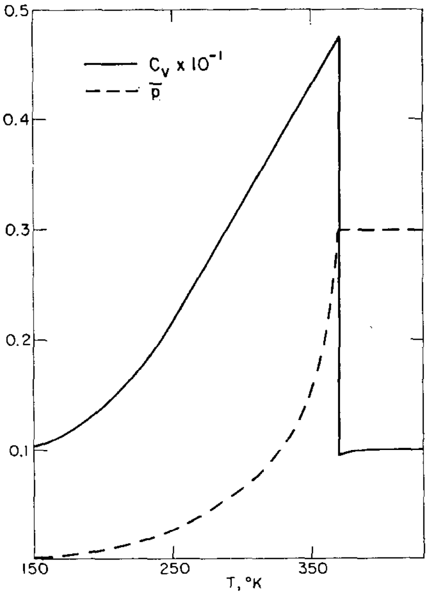

FIG. 5. Specific heat (solid curve) and fractional occupation $\bar{p}$ (dashed curve) of less occupied sublattice. Coordination number $z = 8$, $n_C = 0.6$, and $U = 1.25\ \hbar\omega_{LO}$. The energy gap $\Delta = 0$, and $\hbar\omega_{LO} = 15.4$ meV is that of the beta phase of AgI.

Silver pyridinium iodide (*7*, *8*) exhibits an apparent Class II transition at 50°C. Since its site populations have been measured over the temperature range −40 to 125°C, we discuss the relevance of our model to it. It has 10 silver ions per unit cell. At −40°C the silver ions are completely ordered, with six of them in *f* sites (tetrahedral iodine coordination) and four of them in the *c* sites with octahedral coordination. The *f* and *c* sites are not neighbors, but are connected by a total of 24 *m* sites per cell. Four *m* sites surround each *f* site at a distance of 1.6 Å. Six *m* sites surround each *c* site at a distance of 2.71 Å. The *m* sites are gradually populated as the temperature increases. We note that, experimentally, $\langle \hat{n}_f \rangle \simeq \langle \hat{n}_c \rangle = \bar{n}$. We now have the chemical potential determined by

$$\bar{n} + 2.4\,\bar{p} = 1.0.$$

This is a gross oversimplification, of course, and we make it only to point out that the data confirms our attribution of disorder to the Class II transition. Experiment is compared with this oversimplified theory in Fig. 6. Because of the naivete of the model, no effort was made to adjust the energy gap to give a detailed fit. Experimentally, the silver ions become fully ordered by −40°C without a discontinuity in the conductivity. This seems to refute recent theories (*18*, *19*) that assign the discontinuous conductivity of the Class I phase transition to a Frenkel order–disorder transition of the cations.

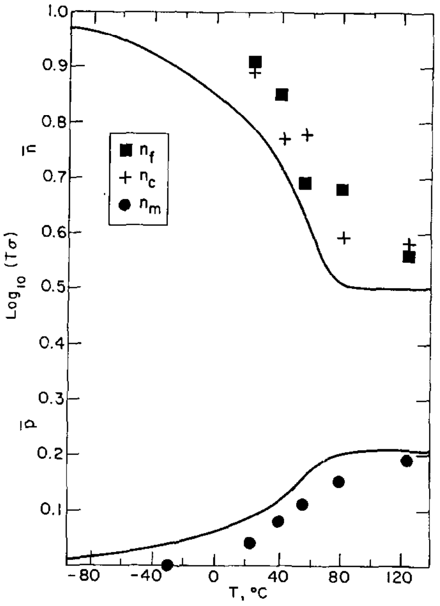

FIG. 6. Site occupation probabilities for the three kinds of site measured by Geller and Owens (8). Solid curves are those obtained from simple model $\bar{n} + 2.4\,\bar{p} = 1$. No attempt was made to fit anything except T_c.

4. Conductivity

We use a form of the Kubo formula of linear response theory to calculate the real part of the conductivity $\sigma(\omega)$. Let $J(x)$ denote the electric current operator in the Schroedinger representation. We define the temperature dependent current operator

$$\mathbf{J}(\mathbf{x}, \tau) = \exp(\tau H_0) J(\mathbf{x}) \exp(-\tau H_0) \quad (24)$$

where H_0 is the grand canonical Hamiltonian of Eq. (14). Our procedure, which requires only one integration instead of the usual two, is to calculate the current–current correlation function

$$P_{\mu\nu}(i\omega_l) = \int_0^\beta d\tau \exp(i\omega_l \tau) \operatorname{Tr}\left\{\rho \int d^3 \right. \\ \left. \times J_\nu(\mathbf{x}, \tau) J_\nu(\mathbf{0}, 0)\right\}. \quad (25)$$

The density matrix $\rho = \exp\beta(\Omega_0 - H_0)$ and the imaginary frequency $\omega_l = 2l\pi/(\hbar\beta)$, $l = 0, 1, 2, \ldots$. The thermodynamic potential $\Omega_0 = k_B T \log \operatorname{Tr} e^{-\beta H_0}$. After performing the τ integration in Eq. (25), we obtain the retarded correlation function

$$P_{\mu\nu}^R(\omega) = P_{\mu\nu}(\omega + i\delta), \qquad \delta \to 0^+. \quad (26)$$

The (real part of the) conductivity is then given by

$$\sigma_{\mu\nu}(\omega) = 1/\omega \operatorname{Im} P_{\mu\nu}^R(\omega). \quad (27)$$

The dipole moment density operator is

$$\boldsymbol{\pi}(\mathbf{r}) = e \sum_\alpha \mathbf{r}\, \delta^3(\mathbf{r} - \mathbf{r}_\alpha) c_\alpha{}^+ c_\alpha + \text{constant terms}. \quad (28)$$

We define the current operator to be the spatial average over a microscopic volume v_0 of the time derivative of π,

$$\mathbf{J}(\mathbf{r}) \equiv \langle \mathring{\boldsymbol{\pi}}(\mathbf{r}, 0)\rangle = 1/V_0 \int_{v_0} d^3\xi\, \mathring{\boldsymbol{\pi}}(\mathbf{r} + \xi, 0). \quad (29)$$

The time derivative of π is obtained by

$$\mathring{\boldsymbol{\pi}}(\mathbf{r}) = (i/\hbar)\, [H, \boldsymbol{\pi}(\mathbf{r})] = (i/\hbar)\, [H', \boldsymbol{\pi}(\mathbf{r})] \quad (30)$$

where H' is the transfer Hamiltonian of Eq. (11). The result is

$$\mathbf{J}(\mathbf{r}) = (ie/\hbar v_0) \sum_\delta t_{\alpha,\delta} \mathbf{r}_{\alpha,\delta} (c_\alpha{}^+ c_{\alpha+\delta} - c_{\alpha+\delta}{}^+ c_\alpha), \quad (31)$$

where α is the cation site nearest $\mathbf{r}$, v_0 includes only the α site and its nearest neighbors, and

$$\mathbf{r}_{\alpha,\delta} \equiv \mathbf{r}_{\alpha+\delta} - \mathbf{r}_\alpha. \quad (32)$$

We will need to express the current in terms of polaron operators C_α and phonon operators $A_\mathbf{q}$. The result is

$$\mathbf{J}(\mathbf{r}_\alpha) = (ie/\hbar v_0) \sum_\delta t_{\alpha\delta} \mathbf{r}_{\alpha\delta} (C_\alpha{}^+ C_{\alpha+\delta} X_{\alpha,\alpha+\delta} \\ - C_{\alpha+\delta}{}^+ C_\alpha X_{\alpha+\delta,\alpha}). \quad (33)$$

We have defined

$$X_{\alpha,\alpha+\delta}(\tau) = \exp\left\{ i \sum_\mathbf{q} \alpha^{1/2}(q)\, [A_\mathbf{q} \exp(-\tau\hbar\omega_0) \right. \\ \times (\exp(i\mathbf{q}\cdot\mathbf{r}_{\alpha+\delta}) - \exp(i\mathbf{q}\cdot\mathbf{r}_\alpha)) \\ + A_\mathbf{q}{}^+ \exp(\tau\hbar\omega_0)\, (\exp(-i\mathbf{q}\cdot\mathbf{r}_{\alpha+\delta}) \\ \left. - \exp(-i\mathbf{q}\cdot\mathbf{r}))] \right\} \quad (34)$$

and, of course,

$$X_{\alpha,\alpha+\delta} = X_{\alpha,\alpha+\delta}(0). \quad (35)$$

The phonon factor in the current–current correlation function can be calculated exactly. Define

$$S(\tau) = \mathrm{Tr}\{\exp\beta(\Omega_{ph} - H_{ph})\, X_{\alpha,\alpha+\delta}(\tau) X_{\alpha+\delta,\alpha}\}. \tag{36}$$

After some standard operator algebra (*34*), one obtains

$$S(\tau) = \exp\left\{-\sum_{\mathbf{q}} (2N_{\mathbf{q}} + 1)B(\mathbf{q})\right\} \times \sum_{n=-\infty}^{\infty} (N_{\mathbf{q}}/N_{\mathbf{q}} + 1)^{n/2} \exp(n\hbar\omega_0\tau) \; I_n\left(2\sum_{\mathbf{q}} (N_{\mathbf{q}}(N_{\mathbf{q}} + 1))^{1/2} B(\mathbf{q})\right), \tag{37}$$

where

$$N_{\mathbf{q}} = 1/(\exp(\beta\hbar\omega_0) - 1), \tag{38}$$

$$B(\mathbf{q}) = \alpha(\mathbf{q})|\exp(i\mathbf{q}\cdot\mathbf{r}_{\alpha\delta}) - 1|^2 \tag{39}$$

and $I_n(z)$ is the Bessel function of the first kind of imaginary argument of order n. We note that $N_{\mathbf{q}}$ is independent of $\mathbf{q}$ and define

$$\lambda_\delta = \sum_{\mathbf{q}} B(\mathbf{q}) \tag{40}$$

where the sum is over the Brillouin zone. Then Eq. (37) is succinctly written

$$S(\tau) = \exp(-\lambda_\delta \operatorname{ctnh} \tfrac{1}{2}\beta\hbar\omega_0) \sum_{n=-\infty}^{\infty} \exp \times (n\hbar\omega_0(\tau - \tfrac{1}{2}\beta)) I_n(\lambda_\delta \operatorname{csch} \tfrac{1}{2}\beta\hbar\omega_0). \tag{41}$$

To calculate $\sigma(\omega)$ we need

$$P_{zz}(i\omega) = (e^2/\hbar^2 v_0) \sum_{\delta} t_{\alpha\delta}{}^2 |\mathbf{r}_{\alpha\delta}\cdot\hat{\mathbf{z}}|^2 \times \int_0^\beta d\tau\, e^{i\omega\tau} S(\tau)G(\tau). \tag{42}$$

The polaron–polaron correlation function is

$$G(\tau) = \mathrm{Tr}\{\rho_p(C_\alpha{}^+(\tau)C_{\alpha+\delta}(\tau)C_{\alpha+\delta}^+ C_\alpha + C_{\alpha+\delta}^+(\tau)C_\alpha(\tau)C_\alpha{}^+ C_{\alpha+\delta}). \tag{43}$$

The density matrix $\tau_p = \exp\beta(H_p - \Omega_p)$ involves only the polarons' interaction. Eventually we will be forced to approximate Eq. (43), but this can be done more readily after some rearrangement. Consider first

$$G_1(\tau) = \mathrm{Tr}\{\rho_p C_\alpha{}^+(\tau)C_{\alpha+\delta}(\tau)C_{\alpha+\delta}^+ C_\alpha\}. \tag{44}$$

Note that at $\tau = 0$ this reduces to the transparent expression

$$G_1(0) = \mathrm{Tr}\{\rho_p C_\alpha{}^+ C_\alpha(1 - C_{\alpha+\delta}^+ C_{\alpha+\delta})\} = \langle n_\alpha(1 - \hat{n}_{\alpha+\delta})\rangle. \tag{45}$$

To obtain the corresponding expression for $\tau > 0$ we note that

$$\exp(\tau H_0)C_\alpha{}^+ \exp(-\tau H_0) = \exp\tau\left(U\sum_d n_{\alpha+d} - \mu_\alpha\right) C_\alpha{}^+ \tag{46}$$

and

$$\exp(\tau H_0)C_{\alpha+\delta}\exp(-\tau H_0) = \exp\tau\left(\mu_{\alpha+\delta} - U\sum_a n_a\right) C_{\alpha+\delta}. \tag{47}$$

The sums in Eq. (44) and Eq. (45) are over the nearest cation neighbors of the appropriate site, and the subscripted chemical potentials include the site energy difference Δ, $\mu_n = \mu$, $\mu_p = \mu - \Delta$. Denote the energy difference between site α and site $\alpha + \delta$ by $\Delta_{\alpha,\delta} = \mu_{\alpha+\delta} - \mu_\alpha$. Our final expression is simplified by putting a prime on the sums over nearest neighbors to denote omission of the site directly involved in the hop. Thus $\sum_d{}' \, n_{\alpha+d}$ denotes a sum over all nearest neighbors of α *except* the site $\alpha + \delta$ to which the ion hops. This gives the convenient expression

$$G_1(\tau) = \sum_{\{n\}} n_\alpha(1 - n_{\alpha+\delta}) \exp \times \left[\tau\left(\Delta_{\alpha,\delta} - U\left(\sum_a{}' n_a - \sum_d{}' n_{\alpha+d}\right)\right) + \beta(\Omega_0 - E(\{n\}))\right]. \tag{48}$$

The sum in Eq. (48) is over all configurations of the polaron lattice, and $E(\{n\})$ is the energy of each configuration. This describes a hop from site α to site $\alpha + \delta$. The other term in $G(\tau)$ is obtained by the interchange $\alpha \leftrightarrow \alpha + \delta$. This is an exact result for the correlation function $G(\tau)$. It depends on the lattice gas form of the Hamiltonian; that is, it is valid only to lowest order in the transfer interaction $t_{\alpha,\alpha'}$. However, it does not depend on the two-site model, and certainly not on the bcc lattice. We will use it as a starting point for a sort of cluster approximation, where we treat the ions nearest the hop more carefully.

We illustrate this for our hypothetical bcc cation lattice. We write a Hamiltonian for the two sites directly involved in the hop. Our approximation is

$$H = Un_\alpha p_{\alpha+\delta} - n_\alpha(\mu - (z-1)U\bar{p}) - p_{\alpha+\delta}\,(\mu - \Delta - (z-1)U\bar{n}). \quad (49)$$

Equation (49) treats the interaction between the ions on the directly involved sites exactly, while letting them interact with their neighbors only through mean field theory, The partition function Z_1 implied by Eq. (49) is

$$Z_1 = 1 + f_p + f_n + e^{-\beta U} f_p f_n \quad (50)$$

with

$$f_p = \exp \beta(\mu - \Delta - (z-1)U\bar{n}) \quad (51)$$

and

$$f_n = \exp \beta(\mu - (z-1)U\bar{p}). \quad (52)$$

We treat the uninvolved neighboring ions in the same approximation as we used for the thermodynamics; this gives a partition function

$$Z = Z_1\,(1 + e^{\beta(\mu-\Delta-zU\bar{n})})^{z-1}\,(1 + e^{\beta(\mu-zU\bar{p})})^{z-1}. \quad (53)$$

With no additional approximations we obtain

$$G_1(\tau) = (e^{-\tau\Delta}/Z_1) f_n \times \{(e^{\beta(\mu-zU\bar{p})-\tau U} + 1/e^{\beta(\mu-zU\bar{p})} + 1)\}^{z-1} \times \{e^{\beta(\mu-\Delta-zU\bar{n})+\tau U)} + 1/e^{\beta(\mu-\Delta-zU\bar{n})} + 1\}^{z-1}. \quad (54)$$

This simplifies to

$$G_1(\tau) = (e^{-\tau\Delta}/Z_1 f_n\{\bar{n}e^{-\tau U} + 1 - \bar{n}\}^{z-1} \times \{\bar{p}e^{\tau U} + 1 - \bar{p}\}^{z-1}. \quad (55)$$

The other term in $G(\tau)$ is

$$G_2(\tau) = (e^{\tau\Delta}/Z_1) f_p\,\{\bar{n}e^{\tau U} + 1 - \bar{n}\}^{z-1} \times \{\bar{p}e^{-\tau U} + 1 - \bar{p}\}^{z-1}. \quad (56)$$

Equation (55) and (56) have an intuitive interpretation. $G_1(\tau)$, of course, describes a hop from an "n" site α to a "p" site $\alpha + \delta$. Except for two correlation effects to be mentioned in a moment,

$$f_n/Z_1 \sim \bar{n}(1 - \bar{p}), \quad (57)$$

the probability that site α is initially occupied and site $\alpha + \delta$ initially empty. The other two factors are initial and final probability distributions depending on the imaginary time $t = -i\tau$. A site at $\alpha + \delta$ has probability $\bar{p}$ of being occupied and having energy $+U$ (time dependence e^{-itU}), and probability 1-$\bar{p}$ of being empty with zero energy (time independent). This suggests that the τ dependent probability distribution for the hopping ion and one neighbor in the initial state should be

$$P_i(\tau) = \bar{p}e^{-itU} + 1 - \bar{p} = \bar{p}e^{-\tau U} + 1 - \bar{p}. \quad (58)$$

This is raised to the $z - 1$ power when all neighbors are included. Thus, neglecting neighbor–neighbor correlations, one has

$$G_1(\tau) \sim \bar{n}(1 - \bar{p})\,(P_i(\tau))^{z-1}\,(P_f(\tau))^{z-1}. \quad (59)$$

Actually, Eq. (56) is a refinement over Eq. (59) in two minor respects. One of these is that the mutual repulsion tends to increase the conditional probability (that α is occupied and $\alpha + \delta$ is empty) above the random value $\bar{n}(1 - \bar{p})$, so

$$(f_n/Z_1) > (1 - f_p/(1 + f_p))\, f_n/(1 + f_n).$$

The other effect is that the average microenvironment of a *hopping* ion differs slightly from that of an average ion, in that a hopping ion has at most $z - 1$ neighbors, thus

$$\bar{n} = 1/(1 + (e^{\beta U\bar{p}}/f_n)) > 1/(1 + (1/f_n)).$$

Both correlation effects increase the conductivity, a fact which may suggest the desirability of including further correlations.

It is now straightforward to obtain the conductivity. We consider only the isotropic case, $\sigma(\omega) = \sigma_{zz}(\omega)$. Our formulas are simplified by defining the temperature dependent weights W_j,

$$W_j = \sum_{k=1-z}^{z-1} \binom{z-1}{k} \binom{z-1}{k-j} \bar{n}^k\,(1 - \bar{n})^{z-1-k} \times \bar{p}^{k-j}\,(1 - \bar{p})^{z-1+j-k}. \quad (60)$$

Terms in the summation are omitted which have a negative integar factorial in the denominator.

The weight W_j is the probability of a configuration where a hopping ion changes its number of nearest neighbors by j. Then

$$\begin{aligned}\sigma(\omega) = {} & (\pi e^2/\hbar^2 v_0)\,(1 - e^{-\beta\omega})/\omega Z_1 \sum_{\delta} t_{\delta}{}^2 \\ & \times (\mathbf{r}_{\delta}\cdot\hat{z})^2 \exp(-\lambda_{\delta}\operatorname{ctnh}\tfrac{1}{2}\beta\hbar\omega_0) \\ & \times \sum_{n=-\infty}^{\infty} \exp(-\tfrac{1}{2}n\beta\hbar\,\beta\hbar\omega_0) \\ & \times I_n\,(\lambda_{\delta}\operatorname{csch}\tfrac{1}{2}\beta\hbar\omega_0) \times \sum_{j=1-z}^{z-1} \\ & \times W_j\,(f_n\,\delta(n\hbar\omega_0 + \omega - \Delta - jU) \\ & + f_p\delta(n\hbar\omega_0 + \omega + \Delta + jU)).\end{aligned} \tag{61}$$

The observed absorption spectrum will not normally be this discrete series of infinitely sharp lines, but will be broadened into a continuum. We assume that some dispersive effect or combination of effects does broaden the spectrum into a continuum without significantly changing its envelope. We still ascribe, e.g., a lattice vibration of energy $\Delta + 5U - \hbar\omega$ to N phonons, with N the integer nearest $(\Delta + 5U - \hbar\omega)/(\hbar\omega_0)$. We accomplish this formally by converting the sum on phonon number to an integral over phonon energy, remembering to take the order of the Bessel function to be the nearest integer, thus avoiding introducing the unphysical singular behavior of Bessel functions of large negative noninteger order.

With that convention understood, we will write

$$N(j) = (\Delta + jU)/(\hbar\omega_0) \tag{62}$$

and

$$K = \omega/\omega_0. \tag{63}$$

With

$$X(j) = \tfrac{1}{2}\beta U(j - (z-1)n_c\xi) \tag{64}$$

and

$$s = \lambda\operatorname{csch}(\tfrac{1}{2}\beta\hbar\omega_0) \tag{65}$$

the frequency dependent conductivity is

$$\begin{aligned}\sigma(\omega) = {} & z\,(ta_0/2)^2\, 2\pi e^2/\hbar^2 v_0 \\ & \times \sinh\tfrac{1}{2}\beta\hbar\omega/\omega Z_1\hbar\omega_0 \\ & \times \exp[-\lambda_{\delta}\coth\tfrac{1}{2}\beta\hbar\omega_0 \\ & + \beta(\mu - \tfrac{1}{2}\Delta - \tfrac{1}{2}U(z-1)n_c)] \\ & \times \sum_{j=1-z}^{z-1} W_j\,\{e^{-X(j)}\, I_{N(j)-K}\,(s) \\ & + e^{X(j)}\, I_{N(j)+K}\,(s)\}.\end{aligned} \tag{66}$$

We consider a special case to obtain a better understanding of this expression. For $n_c = 1$ and $\Delta = 0$ we have $\mu = \tfrac{1}{2}zU$. At low temperatures

$$\bar{p} = 1 - \bar{n} = \exp(-\tfrac{1}{2}\beta zU) \tag{67}$$

and, so,

$$W_j = e^{\frac{1}{2}z\beta U}\,(j + 1 - z)\binom{2z-2}{z-1-j}. \tag{68}$$

The argument of the Bessel functions vanishes exponentially, so

$$I_n(s) \cong \lambda^n \exp(-\tfrac{1}{2}\beta n\hbar\omega_0)/n!. \tag{69}$$

The dominant term is $j = z - 1$. Collecting all the temperature dependent factors, we have

$$T\sigma(0) \cong \text{const} \times \exp(-\beta U(z-1)). \tag{70}$$

Thus at low temperatures the dc conductivity activation energy is proportional to the mutual repulsion of the hopping ions. Although we set $\Delta = 0$, the result is similar for $\Delta \neq 0$,

$$T\sigma(0) \simeq \text{const} \times \exp(-(z-1)\beta U - \beta\Delta). \tag{71}$$

The first term is much more important than the second for superionic conductors, where the site energy differences are small or zero. The activation energy is also influenced by the ion concentration, but we do not have a simple expression for $n_c \neq 1$.

At high temperatures $T > T_c$ we have

$$\bar{p} = 1 - \bar{n} = 1/2 \tag{72}$$

and

$$W_j = (1/2)^{2z-2}\binom{2z-2}{z-1-j}. \tag{73}$$

The large argument asymptotic approximation for the Bessel functions is now appropriate,

$$I_n(x) \cong e^x/(2\pi x)^{1/2}. \tag{74}$$

Then

$$T\sigma(0) \cong \text{const}\, T^{-1/2} \exp(-\beta\lambda\hbar\omega_0/4). \tag{75}$$

We see that the lattice vibrations determine the activation energy at high temperatures. The difference between the Arrhenias form (T^{-1}) and $T^{-1/2}$ is usually too small an effect to be noticeable.

The above results are for our mixed system of lattice gas plus phonons. The high and low temperature results for the lattice gas alone are different, and simpler. They are given by W_0. Thus we have from (68) and (73)

$$\begin{aligned} T \ll T_c \qquad & W_0 = e^{-1/2z\beta U(z-1)} \binom{2z-2}{z-1} \\ T > T_c \qquad & W_0 = (1/2)^{2z-2} \binom{2z-2}{z-1}. \end{aligned} \tag{76}$$

Equation (76) shows that the low temperature activation energy for the lattice gas alone is $1/2z(z-1)U$, while for the phonon plus lattice gas it is the smaller value $(z-1)U$. Thus the phonon coupling changes the activation energy, although the activation energy does not depend upon the phonon parameter. Incidently, the above results for the lattice gas explain the behavior of Fig. 4.

A central feature of our theory is that the observed activation energy Δ in good ionic conductors is caused by dynamical processes such as the cations' interaction among themselves (lattice gas) or the cation interaction with the anions (phonons). This is a considerable departure from the traditional view that there is a static barrier over which the ion hops, and Δ is the barrier height. We believe the static barrier to be totally absent in good superionic conductors. In very poor conductors, such as Cu^+ disordered salts, there may be an additional static barrier which retards conductivity, but we regard this as only a suggestion.

5. Quantitative Aspects

Most of the parameters we need, like phonon frequencies and dielectric constants, are presently unavailable for the solids of greatest interest, like $RbAg_4I_5$ or even for the electrolyte (α) phase of AgI. To obtain rough estimates we take the data for the ambient temperature (β) phase of AgI. The longitudinal optical phonon energy $\hbar\omega_{LO} = 15.4$ meV. The static and high frequency dielectric constants ε_0 and ε_∞ are, respectively, 7.0 and 4.9. The lattice constant $a_0 = 6.47$ Å. An approximate evaluation of the integral over the Brillouin zone gives for the ionic polaron (high temperature) activation energy

$$\begin{aligned} \Delta_p &= \tfrac{1}{4}\lambda\hbar\omega_{LO} \cong (e^2/\pi a)\,(1/\varepsilon_\infty) - (1/\varepsilon_0) \\ &= 0.043 \text{ eV} \end{aligned}$$

or $\lambda \cong 11.3$. The experimental activation energy is about 0.1 eV, but this is for the region below 430°C and is influenced strongly by the cation–cation interaction.

To explore our model we chose the ion–ion interaction energy U to fit the silver pyridinium iodide transition temperature (50°C). Although a more careful mean field theory treatment could easily increase the answer by a factor of two (by including the proper coordination number), one would still find, as we did, that $U \sim \hbar\omega_{LO}$. This is very small compared to $e^2/\varepsilon_0 r$. Of course the short distance interaction between the two ions is not at all like $e^2/\varepsilon_0 r$. However, one does see from comparing Fig. 7 to Fig. 2 that the low temperature activation energy implied by this U is too small. A possible explanation is that mean field theory overestimates the transition temperature, as it does in the two-dimensional case. Somewhat disturbingly, this conjecture, is not supported by available three-dimensional results. As we noted earlier, the special case

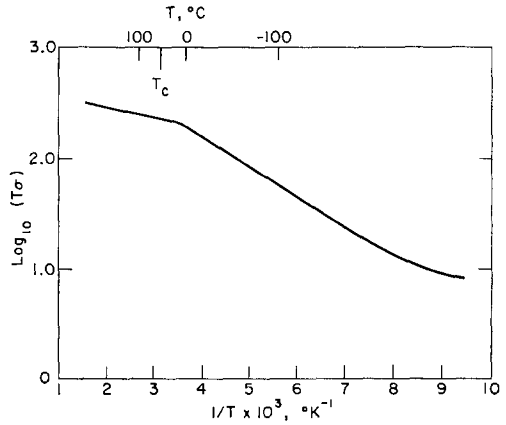

FIG. 7. Sample conductivity. The interaction energy $U = 0.94\ \hbar\omega_{LO}$ chosen to fit $T_c = 50°C$, with $\hbar\omega_{LO} = 15.4$ meV, $z = 8$, $n_c = 1.0$, $\lambda = 11.4$. The curve demonstrates the transition from lattice gas dominated hopping at low temperature to phonon-assisted hopping at high temperature.

$n_c = 1$, $T < T_c$, is analogous to an Ising antiferromagnet in zero field. This, in turn, has the same transition temperature as the ferromagnetic Ising model Numerical analysis of this problem from high temperature susceptibility series (*35*, *36*) has given $k_BT_c/U =$ 4.51 (simple cubic lattice), 6.35 (bcc lattice), and 9.83 (fcc lattice), in contrast to the mean field theory values 1.5, 2, 3, respectively. Thus the "exact" results require even smaller values of U. This comparison must be made cautiously, however. The transition temperature, in contrast to the critical exponents, is very sensitive to structure, as we see from the above. None of the simple structures above exist in actual superionic conductors. Also, in real superionic conductors $n_c \sim 0.6 < 1$, and this is not related to the available Ising results. The corresponding ferromagnetic Ising model has no phase transition at all. The antiferromagnetic Ising model does, of course, but at an unknown T_c. Mathematically, $T_c(U,n_c)$ cannot be an analytic function of both variables about $U = 0$, $n_c = 1$.

Calculation of the transfer energy t_δ is beyond the scope of this paper. It would, in any event, depend upon the detailed structure of each solid. Thus the normalization of our conductivity is arbitrary, or log $(T\sigma)$ has an unknown additive constant. Comparing our results (roughly) to the conductivity (0.29 Ω^{-1}cm^{-1}) of silver pyridinium iodide at 55°C, we find $t_\delta = 0.48\ \hbar\omega_{LO}$. This is probably too large. As we have seen, including correlations with more distant neighbors tends to increase σ, requiring a smaller t_δ. If t_δ is of this order, it may be necessary to include next order perturbation theory in both the thermodynamics and the conductivity.

There is, of course, ample room for improvement in our numerical approximations. We find it very encouraging, however, that two underlying mechanisms, the mutual repulsion of the disordered ions and the polaron interaction with the lattice vibrations, together give a unified explanation of three different kinds of experimental phenomena, the crystallography (disorder), the thermodynamics (specific heat, entropy change at the Class I transition), and the unusual behavior of the ionic conductivity.

References

1. R. T. FOLEY, *J. Electrochem. Soc.* **116**, 13C (1969).
2. B. B. OWENS, *Advan. Electrochem. Electrochem. Eng.* **8**, 1 (1971).
3. H. WIEDERSICH AND S. GELLER, "The Chemistry of Extended Defects in Non-Metallic Solids," (L. Eyring and M. O'Keefe, Eds.), North-Holland, Amsterdam (1969).
4. D. O. RALEIGH, "Solid Electrolytes," SAEST Decennial Commemorative Issue, Vol. 2, Recent Trends in Electrochemical Science and Technology, Kardikudi, India, in publication.
5. C. M. PERROTT AND N. H. FLETCHER, *J. Chem. Phys.* **48**, 2143, 2681 (1968); **50**, 2772 (1969); **52**, 3368, 3372 (1970); **55**, 4681 (1971).
6. J. N. BRADLEY AND P. D. GREENE, *Trans. Faraday Soc.* **63**, 2516 (1967).
7. S. GELLER, *Science* **157**, 310 (1967).
8. S. GELLER AND B. B. OWENS, *J. Phys. Chem. Solids* **33**, 1241 (1972).
9. B. B. OWENS AND G. R. ARGUE, *Science* **157**, 308 (1967).
10. W. V. JOHNSTON, H. WIEDERSICH, AND G. W. LINDBERG, *J. Chem. Phys.* **51**, 3739 (1969).
11. H. WIEDERSICH AND W. V. JOHNSTON, *J. Phys. Chem. Solids* **30**, 475 (1969).
12. B. REUTER AND K. HARDEL, *Naturwissenschaften* **48**, 161 (1961).
13. A. S. DWORKIN AND M. A. BREDIG, *J. Physical Chem.* **72**, 1277 (1968).
14. M. O'KEEFE, in "Fast Ion Transport in Solids," (W. Van Gool, Ed.), pp. 231–247, North-Holland, Amsterdam (1973).
15. M. J. RICE AND W. L. ROTH, *J. Solid State Chem.* **4**, 294 (1972).
16. C. W. HAAS, *J. Solid State Chem.* **7**, 155 (1973).
17. H. H. MÖBIUS, *Z. Chem.* **2**, 100 (1962).
18. M. J. RICE, S. STRASSLER, AND G. A. TOOMBS, *Phys. Rev. Lett.* **32**, 596 (1974).
19. B. A. HUBERMAN, *Phys. Rev. Lett.* **32**, 1000 (1974).
20. A. S. DWORKIN AND M. A. BREDIG, *J. Chem. Eng. Data* **8**, 416 (1963).
21. J. A. A. KETALAAR, *Trans. Faraday Soc.* **34**, 874 (1938).
22. K. W. BROWALL, H. WIEDEMEIER, AND J. S. KASPER, *J. Solid State Chem.* **10**, 20 (1974).
23. L. SUCHOW AND G. T. POND, *J. Amer. Chem. Soc.* **75**, 5242 (1953).
24. L. SUCHOW AND P. H. KECK, *J. Amer. Chem. Soc.* **75**, 518 (1953).
25. W. L. ROTH, *J. Solid State Chem.* **4**, 60 (1972).
26. H. E. STANLEY, "Phase Transitions and Critical Phenomena," Appendix A, Oxford Univ. Press, London/New York (1971).

27. R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Chap. 13, Cambridge Univ. Press, London/New York (1939).
28. Y. LeCars, J. Thery, and R. Collongues, *Rev. Int. Hautes Temp. Refract.* **9**, 153 (1972).
29. W. Van Gool and P. H. Bottelberghs, *J. Solid State Chem.* **7**, 59 (1973).
30. G. D. Mahan and W. J. Pardee, *Phys. Lett.* **49A**, 325 (1974).
31. H. G. Reik, "Polarons in Ionic Crystals and Polar Semiconductors," (J. T. Devreese, Ed.), pp. 679–714, North-Holland, Amsterdam (1972).
32. C. Domb and M. S. Green, "Phase Transitions and Critical Phenomena," p. 438, Academic Press, New York (1974).
33. W. J. Pardee and G. D. Mahan, *J. Chem. Phys.* **61**, 2173 (1974); F. L. Lederman and M. B. Salamon, *Bull. Amer. Phys. Soc. Ser. II*, **20**, 331, (1975).
34. A. Messiah, "Quantum Mechanics," North-Holland, Amsterdam, Interscience, New York (1961).
35. G. A. Baker, *Phys. Rev.* **124**, 768 (1961).
36. A. J. Gutmann, B. W. Ninham, and C. J. Thompson, *Phys. Rev.* **172**, 554 (1968).