Thermoelectric Power of Superionic Conductors*

S. M. GIRVIN

Physics Department, Indiana University, Bloomington, Indiana 47401

A technique for the calculation of the thermoelectric power in many-particle systems exhibiting hopping conduction is presented. It is shown that the combination of thermopower and conductivity data provides very useful information about the microscopic nature of the ion hopping process in solid electrolytes. There are two main qualitative features of the transport data. In most systems the heat of transport (determined from the thermopower) and the activation energy for conduction are nearly equal, and in systems exhibiting lattice gas order–disorder transitions, these parameters may change across the phase boundary. An extended polaron lattice gas model is presented which is consistent with these features of the data and which allows a determination of the relative strengths of static barrier and polaron effects on the hopping. The results of the model suggest that polaron coupling is relatively small in most materials except for those based on organic halides.

I. Introduction

Superionic conductors are solid electrolytes which are characterized by rather unusual transport properties. The conductivities of these materials approach those of liquid electrolytes and in addition, they exhibit very large thermoelectric powers (*1*). There has been some confusion in the literature concerning the thermopower of superionic conductors and it is the purpose of this paper to attempt to clear up this confusion and to present a theory for the thermopower of the lattice gas model (*2–5*). A comparison is made between this theory and the free ion model (*6*). It is shown that the thermopower provides extremely useful information about the microscopic nature of ionic hopping in solid electrolytes.

The first point of possible confusion is the sign convention. We define the thermopower,

S, of a material by the equation

$$\nabla\phi = S\nabla T, \qquad (1)$$

where ϕ is the electrochemical potential induced by the applied temperature gradient, ∇T. With this convention (see the Appendix) the thermopower typically has a sign opposite that of the charge of the mobile species (in simple systems).

The equations of irreversible thermodynamics (*7, 8*) establish that the thermopower is given by

$$S = -Q/(qT) + H, \qquad (2)$$

where q is the charge of the mobile ion species, Q is the so-called heat of transport, and H is a correction term due to electrode contact potential effects. In thermoelectric cells with reversible electrodes it appears that H may be safely assumed to be temperature independent (*1, 8*). Since observed thermopowers have a temperature dependence consistent with Eq. (2), the heat of transport may be un-

ambiguously deduced from thermopower measurements. One striking feature of the data is that in most systems the heat of transport is nearly equal to the activation energy for conduction. This observation provides an important clue to the nature of particle transport in electrolytes. The microscopic theory of superionic transport properties is at a very rudimentary stage and so a first-principles calculation of the heat of transport in real systems is presently impossible. It is possible, however, to compare the predicted value of the heat of transport and the activation energy of conduction for the various phenomenological models currently in use.

2. Models

Two types of rather different models have been proposed. The free ion model emphasizes the interaction between the mobile ions and the background lattice and the kinetic energy aspects of the problem by postulating the existence of an energy gap, ε_0, in the ion density of states. Conduction occurs via the excitation of ions from localized states at zero energy into "continuum" states above the gap. The lattice gas model takes the opposite view and emphasizes the potential energy aspects of the problem. The ion–ion Coulomb interaction is represented by a nearest-neighbor interaction on the lattice and ionic motion is allowed through a phenomenological hopping term. The kinetic energy and the static part of the background potential are otherwise ignored. Both these models predict an activated form for the conductivity which is in agreement with experiment. The lattice gas model appears to describe correctly the thermodynamics of the nonstructural order–disorder phase transitions found in superionic conductors and in addition correctly predicts a change in the activation energy at the phase boundary (4, 5). The thermopower offers another point on which these two models may be compared.

3. Free Ion Thermopower

Since the free ion model ignores correlations among the particles, its transport properties are conveniently studied from the Boltzmann equation point of view. The modified transport equation proposed by Rice and Roth is not the standard one [compare Rice and Roth (6, Eqs. (2.12)–(2.18)) with Ziman (9, Eq. (7.76))] because of the special statistical nature of the free ion states. This modification results in a positive sign for the thermopower, contrary to experiment. The Rice and Roth claim of agreement with the data is in error because they have misquoted the sign convention used by Takahashi (10). This discrepancy is easily remedied by assuming an ordinary free ion theory in which the usual transport equation is obeyed. Then following the method of reference (6) one finds that at low temperatures the heat of transport is simply equal to the band gap, ε_0, which in turn is equal to the activation energy for conduction, E_a. Thus one obtains

$$S = -E_a/(qT), \qquad (3)$$

in agreement with the data. It should be remarked that one could equally well formulate a "free hole" theory which would yield a positive thermopower. Such a theory would be applicable to ordinary defect ionic conduction for systems in which the vacancy mobility is much higher than the interstitial mobility and (as seen in the following sections) to lattice gas systems at high concentration.

4. Lattice Gas Thermopower

There has not previously been available a theory for the thermopower in systems with hopping conduction in which the interaction among the particles is important. We therefore present a calculation of the thermopower for the lattice gas model. Like the calculation of the conductivity (4, 5), this is complicated by the particle interactions. We must therefore

give up the Boltzmann equation point of view and turn to the Kubo formalism.

The Hamiltonian for the lattice gas model which includes ionic polaron effects (4, 5) is

$$H = \sum_i h_i, \qquad (4)$$

with

$$h_i = \frac{U}{2} \sum_\delta n_{i+\delta} n_i - \frac{t}{2} \sum_\delta (c^\dagger_{i+\delta} c_i + c^\dagger_i c_{i+\delta})$$
$$+ \hbar\omega b^\dagger_i b_i + i\lambda n_i(b^\dagger_i - b_i). \qquad (5)$$

The sum in Eq. (5) is over nearest-neighbor sites, $c^\dagger_j$ creates a particle on site j, n_j is the number operator for site j, and $b^\dagger_j$ creates a local phonon excitation on site j. The parameter U controls the ion–ion interaction, t controls the hopping, and λ determines the ion–phonon interaction. For simplicity the phonons have been taken to be dispersionless and interact with the ions only locally.

The Kubo formalism requires a knowledge of various flux operators. The current operator may be determined by the following. The polarization operator, P, is given by

$$\mathbf{P} = \sum_j q n_j \mathbf{R}_j, \qquad (6)$$

where q is the ionic charge and $\mathbf{R}_j$ is the position of the jth site. The current is defined by

$$\mathbf{J} = \dot{\mathbf{P}}, \qquad (7)$$

$$\mathbf{J} = (i/\hbar) [H, \mathbf{P}]. \qquad (8)$$

Evaluation of Eq. (8) yields

$$\mathbf{J} = \frac{iqt}{\hbar} \sum_{j\delta} \delta c^\dagger_{j+\delta} c_j. \qquad (9)$$

Likewise the energy flux operator is defined by

$$\mathbf{J}_E \equiv \sum_j \mathbf{R}_j \frac{i}{\hbar} [H, h_j]. \qquad (10)$$

Let

$$\mathbf{J}_E = \mathbf{J}_U + \mathbf{J}_{PH}, \qquad (11)$$

where $\mathbf{J}_U$ is the energy flux in the absence of phonon coupling and $\mathbf{J}_{PH}$ is the additional flux

due to the phonon coupling. Evaluation of Eq. (10) yields (for a lattice with cubic symmetry)

$$\mathbf{J}_U = \frac{iUt}{\hbar} \sum_{j\mu} \boldsymbol{\mu}\{(n_{j+2\mu} + n_{j-\mu})c^\dagger_{j+\mu} c_j$$
$$+ \frac{1}{2} \sum_{\delta \neq \pm\mu} (n_{j+\mu+\delta} + n_{j+\delta})c^\dagger_{j+\mu} c_j\}, \qquad (12)$$

and

$$\mathbf{J}_{PH} = -(E_B/q)\,\mathbf{J}, \qquad (13)$$

where E_B is the polaron binding energy given by

$$E_B = \lambda^2/\hbar\omega. \qquad (14)$$

It should be noted that Eq. (12) only gives the component of the energy flux which is parallel to the particle flux and that since all calculations will be restricted to lowest order in t, a term in t^2 has been dropped from $\mathbf{J}_U$. $\mathbf{J}_U$ essentially measures the average number of bonds that move with the hopping particle. The reason for the factor of $\frac{1}{2}$ in the second term of Eq. (12) can be understood from Fig. 1. The center of gravity of the bond in configuration (a) moves twice as far as it does for the configuration shown in (b).

Now that the flux operators have been established, we may proceed to the Kubo formulas for the transport coefficients (11, 12). The conductivity is determined by the
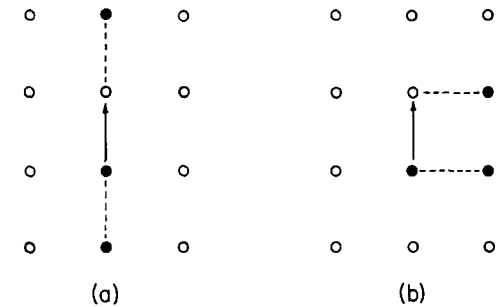

FIG. 1. Two typical hops allowed in the absence of phonon coupling. The energy flux, $\mathbf{J}_U$ associated with the hop illustrated in (a) is twice as great as that for the hop shown in (b) because of the different configurations of the neighbors.

retarded current–current correlation function which may be obtained by analytic continuation of the Matsubara $(13, 14)$ function

$$\sigma(\omega) = (-i/\hbar\omega)\, G(-i\omega + \delta), \qquad (15)$$

where

$$G(\omega_n) \equiv \int_0^{\hbar\beta} d\tau \exp(i\omega_n \tau) g(\tau), \qquad (16)$$

and $g(\tau)$ is the current–current correlation function in the Matsubara representation

$$g(\tau) = (1/dV)\, \langle T_\tau\, \mathbf{J}(\tau) \cdot \mathbf{J} \rangle. \qquad (17)$$

The volume of the system is V, d is the dimensionality, and T_τ is the time ordering operator. We define a second correlation function by

$$\sum (\omega) \equiv (-i/\hbar\omega)\, G_Q(-i\omega + \delta), \qquad (18)$$

where

$$G_Q(\omega_n) \equiv \int_0^{\hbar\beta} d\tau \exp(i\omega_n \tau) g_Q(\tau), \qquad (19)$$

and

$$g_Q(\tau) \equiv (1/dV)\, \langle T_\tau\, \mathbf{F}(\tau) \cdot \mathbf{J} \rangle, \qquad (20)$$

The heat flux operator, $\mathbf{F}$, is defined by

$$\mathbf{F} \equiv \mathbf{J}_E - \mu\mathbf{J}, \qquad (21)$$

where μ is the chemical potential. The heat of transport is given by

$$Q = q \sum (0)/\sigma(0). \qquad (22)$$

We see from the above that the heat of transport is simply the ratio of two correlation functions—the heat flux–current and the current–current functions.

4a. Special Cases

The required correlation functions are in general difficult to evaluate exactly. It is therefore useful to consider some special cases in which the physics involved in Eq. (22) is not obscured by technical details. If it happens that the heat flux is simply proportional to the particle flux so that

$$g_Q(\tau) = (\Delta/q)\, g(\tau), \qquad (23)$$

then Eq. (22) is easily evaluated and one finds for the heat of transport

$$Q = \Delta. \qquad (24)$$

The physical meaning of this result is that each particle carries a well-defined amount of energy with it when it hops. This is of course precisely the case for the free ion model at low temperatures where Δ is determined by the energy gap, ε_0.

Under certain circumstances, Eq. (23) also holds for the lattice gas model. For example, within the framework of the mean field approximation, the number operators in Eq. (12) may be replaced by their expectation values and one obtains

$$\mathbf{J}_U = (zUc/q)\, \mathbf{J}, \qquad (25)$$

where z is the lattice coordination number and c is the concentration. The heat of transport is then given by the very simple expression

$$Q = (zUc - E_B - \mu). \qquad (26)$$

Equation (26) becomes exact in the limit of $c \to 1$ or $c \to 0$. It is also exact for $c = 0.5$ since it correctly predicts that Q vanishes for a half-filled band as a consequence of particle–hole symmetry (15).

In general, Eq. (26) can be expected to be valid at high temperatures $(kT > U)$ but not at low temperatures. As pointed out by Kwak and Beni (17), the chemical potential is proportional to kT at high temperatures and so dominates over the U term in Eq. (26). At low temperatures, correlation effects will be the controlling factor. A good treatment of these correlations is difficult; however, an exact low-temperature expansion of the thermopower can be made.

Consider the case of no phonon coupling $(\lambda = 0)$. Since we are working only to lowest order in the transfer term, every ion jump must exactly conserve energy. The phonon reservoir is not available to supply or absorb energy, which means that a hopping ion cannot change the number of neighbors it has. At some critical temperature, T_c, the lattice gas

undergoes an order–disorder phase transition and, as noted in (4), the probability of an ion being able to hop without changing its number of neighbors vanishes exponentially in $(1/T)$ if the concentration is such that the ions become perfectly ordered at low temperatures. This means that the conductivity will have the usual activated form. The activation energy and its relation to the thermopower may be obtained by the following argument. Suppose that the lattice gas has some concentration, c, and is in a fully ordered state at zero temperature, which is characterized by the fact that every particle has l_1 of its nearest-neighbor sites occupied and every empty site has l_2 of its nearest-neighbor sites occupied. The state of the system at low but nonzero temperatures may be considered to be the $T = 0$ state with a certain number of defects. It is the mobility of these defects which is responsible for the conduction. The energy of formation of a defect consisting of a particle on what should be an empty site is

$$F_2 = Ul_2 - \mu, \qquad (27)$$

while the energy of formation of a defect consisting of a particle missing from what should be an occupied site is

$$F_1 = -Ul_1 + \mu, \qquad (28)$$

The condition that there be equal numbers of such defects (to maintain the correct particle concentration),

$$(1 - c) \exp(-\beta F_2) = c \exp(-\beta F_1), \qquad (29)$$

determines the chemical potential

$$\mu \simeq \tfrac{1}{2}\{U(l_2 + l_2) - kT \ln((1 - c)/c)\}. \qquad (30)$$

The conductivity, σ, is determined by the concentration of each type of defect and their diffusion coefficients, D_1 and D_2:

$$\sigma = q^2\beta\{cD_1 \exp(-\beta F_1) + (1 - c) D_2 \exp(-\beta F_2)\}. \qquad (31)$$

Equation (23) is satisfied for each type of

charge carrier so that the heat of transport is given by

$$Q = \{-F_1 cD_1 \exp(-\beta F_1) + F_2(1 - c) D_2 \exp(-\beta F_2)\}/(\sigma/q^2\beta). \qquad (32)$$

The relative minus sign enters because the particle and hole defects have opposite charges. This means that the sign of the thermopower is not necessarily given by the sign of the charge of the mobile ion species and that the magnitude of the heat of transport satisfies

$$|Q| \leqslant (\partial \ln(\sigma/\beta))/\partial\beta. \qquad (33)$$

For the special case in which the conductivity is dominated by only one type of defect, one has

$$Q = \pm E_a, \qquad (34)$$

where E_a is the activation energy for conduction and $(+/-)$ refers to (particle/hole) defects being dominant. An example of a model situation in which this condition holds is provided by the planar triangular (pt) and the fcc lattices at a concentration of $\tfrac{2}{3}$ (or $\tfrac{1}{3}$). The low-temperature pt phase is ordered[1] as shown in Fig. 2a. Each particle has $l_1 = 3$ neighbors and each hole has $l_2 = 6$ neighbors. As can be seen from Fig. 2b, particle defects have zero mobility since they are completely surrounded by other particles. This means that the conduction is entirely by hole defects and Eq. (34) becomes exact at low temperatures. The heat of transport is then given by[2]

$$Q = -E_a = -\tfrac{1}{2}(3U + kT \ln 2). \qquad (35)$$

The mean field result is different:

$$Q = -\tfrac{1}{2}(U + kT \ln 2), \qquad (36)$$

showing the importance of correlations at low temperatures. For a concentration of $\tfrac{1}{3}$, Q has the same magnitude but opposite sign since the

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[1] This structure would actually require next-nearest-neighbor forces in order to be stable at finite temperatures.

[2] Note that the terms in the chemical potential proportional to kT contribute to H and not Q in Eq. (2).
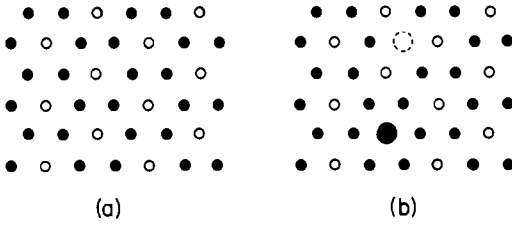
(a)   (b)

FIG. 2. (a) Structure of the low-temperature phase of the pt lattice at a concentration of two-thirds. (b) Illustration of a particle defect and a hole defect. Note that the presence of a particle defect still does not permit any particles to hop without changing their number of neighbors. There are, however, three possible hops allowed for the hole defect.

conduction is due only to particle defects. This situation is actually realized in Na$^+$ β-alumina (16). There is a stoichiometric excess of sodium ions which forms an ordered two-dimensional pt superlattice at low temperatures. Unfortunately there do not appear to be any thermopower data available for this material. In addition it is not clear how applicable this simple model is since the actual lattice gas concentration is only approximately $\frac{1}{3}$ and the ordering is very gradual with temperature (indicating that the thermodynamics of the system is more complex than that of the simple lattice gas model).

Recall that the above results were obtained for the case of no phonon coupling. As previously noted, the addition of phonon coupling introduces a contribution, $\mathbf{J}_{PH} = -(E_B/q)\mathbf{J}$ to the heat flux, $\mathbf{F}$, in Eq. (21) but this is exactly canceled out by the associated reduction in the chemical potential by E_B, the polaron binding energy. Thus the phonon coupling modifies the thermopower only indirectly through its effect on the $\langle \mathbf{J}_U(\tau) \cdot \mathbf{J} \rangle$ correlation function. As noted in (4), this effect is quite small at low temperatures so that Eq. (34) remains valid even in the presence of phonon coupling. At high temperatures the lattice gas disorders and the conductivity become dominated by the phonon coupling. This is most simply illustrated by the case $U = 0$, $\lambda \neq 0$, which is easily solved. Since $U = 0$,

we have

$$\mathbf{F} = -(E_B/q)\mathbf{J} - (\mu/q)\mathbf{J}, \qquad (37)$$

$$\mathbf{F} = (kT/q)\ln((1-c)/c)\mathbf{J}. \qquad (38)$$

The thermopower is then given by

$$S = -(k/q)\ln((1-c)/c), \qquad (39)$$

We thus see that at high temperatures the thermopower saturates at a fixed value and is no longer correlated with the activation energy (4, 5) for conduction, which is $E_B/2$. This is a crucial point and we return to it in the later sections.

4b. The General Case

We have investigated several cases in which the evaluation of the required correlation functions was simplified by a proportionality between the heat flux and the particle flux. We now consider what steps can be taken toward a solution of the general case. Mahan (5) has shown that the calculation of the dynamics involved in the conductivity may be reduced to the evaluation of certain static lattice gas correlation functions. A similar procedure is employed here to find the heat of transport.

We begin by making the usual canonical transformation to displaced phonon coordinates:

$$b_i^\dagger = B_i^\dagger + i(\lambda/\hbar\omega)\, n_i, \qquad (40)$$

$$c_i^\dagger = \exp\left[i(\lambda/\hbar\omega)\,(B_i^\dagger + B_i)\right] a_i^\dagger. \qquad (41)$$

Substitution of the definitions of $\mathbf{F}$ and $\mathbf{J}$ into Eq. (20) yields (for $\tau > 0$)

$$g_Q(\tau) = (NqUt^2a^2/\hbar^2 dV)\,\alpha(\tau)\,\delta(\tau)\,K_Q(\tau), \qquad (42)$$

where a is the lattice constant and

$$\alpha(\tau) \equiv \left\langle \exp\left[i(\lambda/\hbar\omega)\,(B_i^\dagger(\tau) + B_i(\tau))\right] \right. \\ \left. \exp\left[-i(\lambda/\hbar\omega)\,(B_i^\dagger + B_i)\right]\right\rangle, \qquad (43)$$

$$\delta(\tau) \equiv \left\langle \exp\left[-i(\lambda/\hbar\omega)\,(B_i^\dagger(\tau) + B_i(\tau))\right] \right. \\ \left. \exp\left[i(\lambda/\hbar\omega)\,(B_i^\dagger + B_i)\right]\right\rangle, \qquad (44)$$

$$K_Q(\tau) \equiv$$

$$\sum_\mu \left\langle \left[(n_{j+2\mu} + n_{j-\mu}) + \frac{1}{2} \sum_{\delta \neq \pm\mu} (n_{j+\mu+\delta} + n_{j+\delta}) \right] \right.$$

$$\left. \times a_{j+\mu}^\dagger(\tau) a_j(\tau) a_j^\dagger a_{j+\mu} \right\rangle. \qquad (45)$$

The phonon correlation functions are standard (5). The particle correlation function, K_Q, will be evaluated only to lowest order in t (5) so that the hopping term is dropped when $a_i^\dagger(\tau)$ is evaluated:

$$a_i^\dagger(\tau) = \exp\left[\sum_v \left(\frac{U\tau}{\hbar} \right) n_{i+v} \right] a_i^\dagger. \qquad (46)$$

The number operators may be removed from the exponential so that

$$a_i^\dagger(\tau) = \left\{ \prod_v (1 + n_{i+v}(\exp(U\tau/\hbar) - 1)) \right\} a_i^\dagger. \qquad (47)$$

Equation (45) may now be written

$$K_Q(\tau) =$$

$$\sum_\mu \left\langle \left\{ (n_{j+2\mu} + n_{j-\mu}) + \frac{1}{2} \sum_{\delta \neq \pm\mu} (n_{j+\mu+\delta} + n_{j+\delta}) \right\} \right.$$

$$\times \left\{ \prod_{v \neq -\mu} \left[1 + n_{j+\mu+v} \left(\exp\left(\frac{U\tau}{\hbar} \right) - 1 \right) \right] \right\}$$

$$\times \left\{ \prod_{v' \neq \mu} \left[1 + n_{j+v'} \left(\exp\left(\frac{-U\tau}{\hbar} \right) - 1 \right) \right] \right\}$$

$$\left. \times n_{j+\mu}(1 - n_j) \right\rangle. \qquad (48)$$

This has the general form

$$K_Q(\tau) = \sum_{m=-(z-1)}^{(z-1)} a_m \exp\left(\frac{mU\tau}{\hbar} \right), \qquad (49)$$

where the coefficients a_m are linear combinations of various static correlation functions of the form $\langle n_i n_j \ldots n_k \rangle$. A similar set of coefficients is required for the conductivity correlation function. Once the coefficients a_m have been obtained it is an easy matter to perform the necessary time integrations and evaluate Eq. (22) for the heat of transport. The required coefficients may be exactly evaluated in one and two dimensions using the known Ising model correlation functions (5). This has
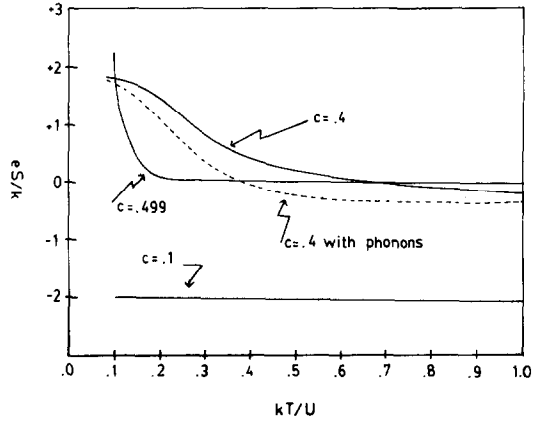

FIG. 3. Plot of the (dimensionless) thermopower, eS/k, vs the (dimensionless) temperature, kT/U, for the one-dimensional lattice gas at three different concentrations. The thermopower is antisymmetric about concentration $\frac{1}{2}$ and the effect of phonon coupling is important only for concentrations away from 0, $\frac{1}{2}$, and 1.

been done for the one-dimensional case with and without coupling to the phonons (which were, for simplicity, treated classically). The results are displayed in Fig. 3.[3] The thermopower in the absence of polaron coupling has the same form as that obtained by Kwak and Beni (17) for the one-dimensional Hubbard model.

Note that coupling to the phonons reduces the magnitude of the thermopower at intermediate temperatures. This is caused by the fact that without phonons a hopping particle cannot change its number of neighbors. Thus if a hop from site i to $i + 1$ is to contribute to the energy transport, both $i - 1$ and $i + 1$ must be occupied. With phonon coupling only one of those two sites need be occupied. Hence the average number of bonds carried along with the hopping particle is decreased. This reduces the heat of transport and hence the thermopower. This feature of the dynamics is important in solid electrolytes and may also be of relevance to the TTF–TCNQ system to which the Hubbard model calculations of Kwak and Beni (17) were applied.

[3] The calculation leading to the results displayed in Fig. 3 is very similar to a calculation recently published by Hinklemann (35).

The simple one-dimensional model discussed above does not have an order–disorder phase transition and thus the thermopower is a smooth function of temperature. It is clear, however, that in higher dimensions the change in the static particle correlation functions across the phase boundary will result in a change in the heat of transport just as the activation energy for conduction changes (5). This phenomenon is observed in Ag_2HgI_4, which has a first-order lattice gas phase transition (18) at a critical temperature $T_c = 52°C$. The heat of transport and the activation energy for conduction are both discontinuous at the phase boundary (19, 20).

5. Summary of Model Results

We now review what has been learned in the above simple model calculations and consider the relevance of the models to the experimental situation. There are two important qualitative features of the data. The first is that in a wide variety of systems the heat of transport is nearly equal to the activation energy for conduction. The free ion model was found to fulfill this condition in a natural way since a single parameter, ε_0 (the energy gap), determines both the activation energy for conduction and the heat of transport. The lattice gas model does not do as well on this point. It was found that at low temperatures

$$|Q| \lesssim E_a, \qquad (50)$$

with equality obtained only under special circumstances. Indeed for concentration $\frac{1}{2}$, the heat of transport was found to vanish at all temperatures independent of E_a. At high temperatures E_a is controlled by the polaron energy, E_B, but the heat of transport was found to be essentially independent of this parameter. Thus it appears that the free ion model is more successful than the lattice gas model in this regard.

The second important qualitative feature of the data is that in systems which undergo order–disorder phase transitions, the heat of transport changes across the phase boundary. The first-order phase transition in Ag_2HgI_4, for example (18), does not involve any significant structural change in the anion sublattice. Only the cation lattice gas order parameters change across the phase boundary. Since the free ion model ignores interactions (and correlations) among the particles, it cannot explain the change in E_a and Q in this phase transition. On the other hand, the lattice gas model can explain not only the very existence of this phase transition (and the fact that it is first order (18)) but also the change in E_a and Q across the phase boundary. Hence the lattice gas model is distinctly more successful than the free ion model in this regard.

It is clear from these findings that neither model gives a complete description of transport in solid electrolytes. Each model emphasizes a different subset of terms in the total Hamiltonian and so a synthesis of appropriate features from both of them is necessary in order to achieve a theory which is consistent with the data. The lattice gas model already correctly describes the equilibrium statistical mechanics of the problem. It can also properly describe the dynamics, provided that we add to it one feature extracted from the free ion model—the static potential acting on the mobile ions due to the background lattice. We develop this extended lattice gas model in the next section.

6. Extended Lattice Gas Model

The lattice gas Hamiltonian used in the previous sections is formally identical to (and indeed was motivated by) the usual electronic polaron Hamiltonian. However, the physics involved in the hopping term is not the same in these two models. Recall that in the electronic polaron problem one considers a tight binding band made up of states localized in potential wells. Since the electron mass is so much less than the masses of the atoms in the lattice, it is generally safe to assume that the electronic excitation energies are very large on the scale

of phonon energies. One therefore need consider only the ground-state electronic band. A second consequence of the light electron mass is that the electronic wavefunction is imperfectly localized in a given potential well and so overlaps its neighbors. The hopping parameter t is determined by this overlap and is a measure of the kinetic energy required to completely localize an electron on one site.

This description is not valid in the present problem. The masses of the mobile ions are of the same order as the masses of the atoms in the background lattice. Hence the scale of excitation energy for an ion in a potential well is one phonon energy. In addition the overlap between low-energy states on neighboring sites is essentially zero. Thus the hopping term in the lattice gas model is purely phenomenological in nature and represents the average rate of hopping due to thermal fluctuations. The parameter t may therefore be temperature dependent (5). In order to improve the model this hopping term must be treated in more detail.

In contrast to the conclusions of (5) we assume that a substantial part of the activation energy for conduction is due to a static barrier between sites. This means that on each site there is a potential well of depth W of the order of 0.1 eV. A particle in one of these wells may be in one of several vibrational states labeled by a new quantum number σ. The LO phonon energy, $\hbar\omega_{LO}$, is typically of the order of 15 meV so that there are roughly $(W/\hbar\omega_{LO}) \sim 6$ possible vibrational states. This internal degree of freedom was previously ignored but will now play a central role. Hopping is postulated to occur only after a particle has been excited to a high vibrational state, the low-lying states being too localized. This feature is reminiscent of the energy gap postulated in the free ion model.

One is thus led to a Hamiltonian for the extended lattice gas model:

$$H = \sum_i h_i, \qquad (51)$$

$$h_i \equiv \frac{U}{2} \sum_{\delta,\sigma,\sigma'} n_{i+\delta,\sigma} n_{i,\sigma'} + \hbar\omega b_i^\dagger b_i$$
$$+ \lambda \left(\sum_\sigma n_{i,\sigma} \right)(b_i^\dagger + b_i) + \sum_\sigma \varepsilon_\sigma n_{i,\sigma} + T_i, \qquad (52)$$

$$T_i \equiv -\frac{1}{2} \sum_{\delta,\sigma,\sigma'} \{ t_{\sigma\sigma'} c_{i+\delta,\sigma}^\dagger c_{i,\sigma'} + \text{h.c.} \}, \qquad (53)$$

where h.c. indicates Hermitian conjugate. A great many possible effects are still neglected in this Hamiltonian. In particular, the coupling between the vibrational states σ and the phonons in the background lattice is probably quite large and may be important in controlling the conductivity (21). This model is proposed simply because it is the minimum extension of the lattice gas model which is consistent with both conductivity and thermopower measurements.

If there are M vibrational levels ranging in energy from zero to W and if $t_{\sigma\sigma'} = t\delta_{\sigma,M}\delta_{\sigma',M}$, then the transport calculations proceed exactly as before. For most systems thermopower data are available only for the high-temperature disordered phase where the particle hopping is controlled by the static barrier and the polaron coupling. Neglecting correlations in the disordered phase, one finds that the static and dynamic barriers simply add in their effect on the conductivity so that the activation energy is given by

$$E_a \simeq W + E_B/2. \qquad (54)$$

As noted previously the dynamic barrier does not contribute to the heat of transport, so that

$$Q \simeq W. \qquad (55)$$

At sufficiently high temperatures there will be significant corrections of order kT to the above equations. The neglect of these corrections is not a good approximation in many systems (1); however, the rudimentary nature of the present model and the uncertainties in the measured quantities do not justify their inclusion.

Combining the above equations yields a basic result of the model,

$$Q = E_a - E_B/2, \qquad (56)$$

from which one sees that the observed correlation in E_a and Q is now explained if W is the dominant term in the activation energy. This suggests that E_B is of the order of kT or less in many systems. Shahi (1) has pointed out that Q seems to correlate best with $E_a - kT$. Since most disordered systems have been studied at roughly similar temperatures, this may simply indicate that $E_B \sim 2kT$ in these systems. Measured values of Q and $E_a - kT$ taken from Shahi's compilation are shown in Table I. There are two major exceptions to the general trend in Table I. As noted in (22), $[(CH_3)_4N]_2Ag_{13}I_{15}$ and $[(C_2H_5)_4N]_2Ag_{13}I_{15}$ have heats of transport of 0.115 and 0.150 eV, respectively, while their activation energies are 0.17 and 0.24 eV. These materials are otherwise similar to $RbAg_4I_5$ and so the discrepancy is somewhat surprising (22). It was proposed in (22) that this effect is due to some (unexplained) temperature dependence in the number of mobile ions. The present model suggests, however, that the difference between E_a and Q may simply be the result of a particularly large value of the polaron binding energy in these materials (perhaps due to the

polarizability of the organic groups). The heats of transport are similar to those of the other silver conductors, indicating that the static barrier heights are similar. The activation energies for conduction are larger because of the increased dynamic barrier. If this is a correct interpretation of the physics involved, then the above consideration will be an important factor in the search for useful new materials based on organic complexes.[4]

6a. Additional Considerations

There are two more points worth noting concerning the extended lattice gas model. The first is that the additional degree of vibrational freedom in this model will be reflected in the Raman and infrared spectra. The rate at which particles hop will determine the phase coherence time for the vibrations of the mobile atoms. As pointed out in (23) for classical particles diffusing in a periodic potential, the density–density correlation function is oscillatory for short times but diffusive in nature for long times. This is believed to explain the observed increase with temperature in the width of the phonon line in the ir and Raman spectra. Thus the extended lattice gas model reflects this additional qualitative feature of the physics of solid electrolytes.

The second point worth noting is that the cation hopping process typically involves the passage of an ion from one site to another through an energetically unfavorable region. The barrier height is controlled by the position of the cage ions, which are themselves vibrating. This may be described by supposing that for small displacements of some generalized coordinate, X, the barrier height is given by

$$W = W_0 + \lambda X, \qquad (57)$$

where W_0 and λ are constants. The effect of fluctuations in X may be approximately

TABLE I

Material	Q (eV)	$E_a - kT$ (eV)	Ref.
α-AgI	0.052	0.051	(33)
β-AgI	0.351	0.38	(33)
α-Ag$_2$HgI$_4$	−0.322	0.33	(20)
α-Ag$_2$HgI$_4$	0.402	—	(19)
β-Ag$_2$HgI$_4$	−0.764	0.58–0.81	(20)
β-Ag$_2$HgI$_4$	~0.0	—	(19)
KAg_4I_5	0.088	0.095–0.10	(34)
$RbAg_4I_5$	0.086	0.074–0.11	(34)
$RbAg_4I_5$	0.078	—	(25)
$NH_4Ag_4I_5$	0.058	0.095	(19)
$NH_4Ag_4I_5$	0.093	—	(25)
$Ag_6I_4WO_4$	0.138	0.16	(8)
$[(CH_3)_4N]_2Ag_{13}I_{15}$	0.115	0.17	(22)
$[(C_2H_5)_4N]_2Ag_{13}I_{15}$	0.150	0.24	(22)

[4] Takahashi (27) has recently reported (32) values for E_a and Q in high-conductivity silver and copper conductors which contain various organic halides. Most of these materials show $E_a > Q$, indicating substantial polaron coupling.

considered by defining a thermal-averaged barrier height, $\bar{W}$, by

$$\exp(-\beta\bar{W}) = \langle\exp(-\beta W)\rangle. \quad (58)$$

Evaluating $\langle\exp(-\beta\lambda X)\rangle$ for a harmonic oscillator of energy $\hbar\omega$ yields (24)

$$\bar{W} = W_o - (\beta\lambda^2/4)\coth(\beta\hbar\omega/2). \quad (59)$$

For $kT \gg \hbar\omega$ this is approximately

$$\bar{W} = W_o - \lambda^2/(2\hbar\omega). \quad (60)$$

Thus the fluctuations in the cage ion positions simply renormalize the barrier height without adding new terms to the Hamiltonian. This is of course only an approximate result since the cation vibration frequency is on the same scale as the frequency of the cage vibrations so that the two motions may be strongly coupled (21). Whether or not this coupling produces only a simple renormalization of the parameters is not clear. These details of the dynamics are among the factors which must be considered in going beyond the present model.

7. Summary

The microscopic theory of transport in solid electrolytes is at a rudimentary stage. Various phenomenological models have been developed to explain separate facets of the data but if further progress is to be made a unified theory must be developed. It was shown in this regard that the combination of thermopower and conductivity information provides some extremely useful clues about the nature of the ion hopping process. The technique for calculation of the thermopower in many particle systems exhibiting hopping conduction was established on the microscopically rigorous basis of the Kubo formalism and was illustrated with several model calculations.

The extended lattice gas model was proposed as the simplest model consistent with the main qualitative features of both the conductivity and thermopower data. Most materials have a heat of transport Q and an activation

energy for conduction E_a which are approximately equal. This implies within the context of the model that the primary source of the activation energy is the static barrier between sites and not the polaron coupling. The unexpectedly large difference between E_a and Q in the two organic-based compounds which have been studied suggests that the polaron coupling is exceptionally large in these materials. Another important feature of the data is the change in E_a and Q across an order–disorder phase boundary. The model successfully explains the thermodynamics of the phase transition and these changes in the transport parameters.

The present state of the theory is at best semiquantitative. Still further details of the hopping dynamics must be included in the Hamiltonian and higher-order hopping terms considered in the evaluation of the required correlation functions before a quantitatively accurate theory can be obtained. Progress will be swifter if more and better measurements of E_a and Q over the widest possible temperature ranges become available. It would be particularly useful to fill the void in data on the low-temperature ordered phases of various systems which to date have been largely ignored. It would also be of interest to have further studies of the organic-based materials in order to see if the difference between the heat of transport and the activation energy is in fact due to polaron coupling as indicated in the present model.

Appendix

There has been some confusion in the literature regarding sign conventions. Most authors (6, 8, 19, 25–31) use the convention defined by Eq. (1), which will be referred to as the standard convention. Rice and Roth (6) predict a positive sign for the thermopower in their free ion model. Their claim of agreement with Takahashi's measurements (10) is in error because they have misquoted his sign convention (27). Browall and Kasper (20)

obtain a negative sign for the thermopower of Ag_2HgI_4, in agreement with the earlier measurement of Magistris *et al.* (*19*); however, the latter use the standard convention (*30*), while Browall and Kasper do not (*31*). The two measurements also disagree considerably on the magnitude of the heat of transport in the low-temperature β phase. It would be extremely useful to have new measurements performed on this material in order to resolve this ambiguity. Good thermopower data for Ag_2HgI_4 are especially important because of the unique properties of this material. It exhibits a pure lattice gas order–disorder phase transition which has a latent heat (*18*), and in addition it is the only one of the standard silver conductors which has a lattice gas concentration exceeding $\frac{1}{2}$ (*1, 18*).

Acknowledgments

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