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On the Necessity for Invoking a Free-Ion-Like Model for the Super Ionic Conductors

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Rice and Roth's free-ion-like model of ionic conduction relates the oscillator frequency, the hopping length, the migration activation energy, and the mass of the jumping ion. They applied their formula to atomic self-diffusion in metals and interpreted the agreement of the calculated oscillator frequencies and the observed Debye frequencies as evidence for the validity and uniqueness of their model. However, an expression of the same form can be derived for a simple harmonic oscillator hopping type model, and therefore the necessity for invoking a free-ion-like model is questionable.

The analysis of Rice and Roth (*1*) of the ionic conduction parameters of compounds in each of the three groups of highly conducting "super" ionic conductors provides a useful basis for understanding the similarities and differences in conduction mechanisms. For example, the agreement of the parameters obtained for the ionic components of molten metals with those obtained for the silver halides and chalcogenides and the β-aluminas lends further justification for describing the disordered cations in these ionic conductors as being in a liquid-like state (*2*, *3*).

Rather than using a conventional hopping model, Rice and Roth (*1*) introduced a free-ion-like model to describe the translational state in which the ion moves from one localized state to another. In this excited state, the ion of mass M is assumed to propagate with a velocity v_m and an energy $\varepsilon_m = \frac{1}{2}Mv_m^2$. The energy spectrum of these elementary excitations is assumed to be continuous for energies $\varepsilon_m \geqslant \varepsilon_0$ (where ε_0 is a characteristic "energy gap") and to vanish for $\varepsilon_m < \varepsilon_0$. The excited ion interacts with the rest of the solid, thereby losing energy and returning to a localized state. A lifetime τ_m characterizes the transitory existence of the ion in the mth state and an ionic mean-free path l_m is introduced through the relation $l_m = v_m \tau_m$.

Rice and Roth (1) proceed to calculate the transport coefficients using a Boltzmann transport equation. In the low-temperature limit in which $\varepsilon_0/kT \gg 1$, their result for the ionic conductivity becomes

$$\sigma = \frac{1}{3}\frac{(Ze)^2}{kT} n v_0 l_0 e^{-\varepsilon_0/kT} \qquad (1)$$

where Ze is the charge of the ion, n is the number of potentially mobile ions per unit volume and ε_0, v_0, l_0, and τ_0 characterize the free-ion-like state at the energy gap ε_0. As they point out, this result closely resembles the Arrhenius expression for the "hopping" model of ionic conductivity, which may be written as

$$\sigma = \frac{1}{3}\frac{(Ze)^2}{kT} n a_0{}^2 \nu_0 e^{-E/kT} \qquad (2)$$

where a_0 is the "hopping" distance, ν_0 the ionic oscillator frequency, and E the migration activation energy and indeed, they state that for the conventional hopping mechanism these two expressions are equivalent. The energy gap ε_0 is identified with E, the mean-free path l_0 with a_0, and the inverse lifetime $1/\tau_0$ with ν_0.

Rice and Roth (*1*) claim, however, that one aspect of the free-ion-like model, i.e., the free-ion-like relation $\varepsilon_m = \frac{1}{2}Mv_m^2$, has no counterpart in the conventional hopping model. They

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proceed to use this expression to derive the relationship

$$\nu_0 = \frac{1}{a_0}\left(\frac{2E}{M}\right)^{1/2}, \qquad (3)$$

which they treat as a prediction of the free-ion-like model. They apply this formula to the case of atomic self-diffusion in metals; the transport mechanism is presumed to be by means of vacancies. They choose the hopping distance a_0 to be the nearest neighbor distance and use the activation energy E determined by experiment. They find excellent agreement between the ν_0 calculated from Eq. (3) and the observed Debye frequencies and consider this "to constitute fairly satisfactory evidence for the basic validity of the free-ion-like relation between ε_m and v_m."

However, a result of the form of Eq. (3) can be obtained for a "hopping" model using a classical harmonic oscillator approximation for the localized oscillating state. When the ion achieves a critical amplitude of oscillation, it "hops" to a nearby vacant localized state. Consider the case of two neighboring lattice sites a distance a_0 apart, one containing a migrating ion, the second empty. Assume identical harmonic oscillator potentials at each site as shown in Fig. 1a. The oscillator frequency ν for the ion at Site 1 is given by the usual expression

$$\nu = \frac{1}{2\pi}\left(\frac{k}{M}\right)^{1/2}, \qquad (4)$$

where k is the force constant and M the mass of the ion. The energy ε of the ion is

$$\varepsilon = \tfrac{1}{2}kA^2, \qquad (5)$$

where A is the amplitude of oscillation. Knowledge of the energy of the oscillator for a given

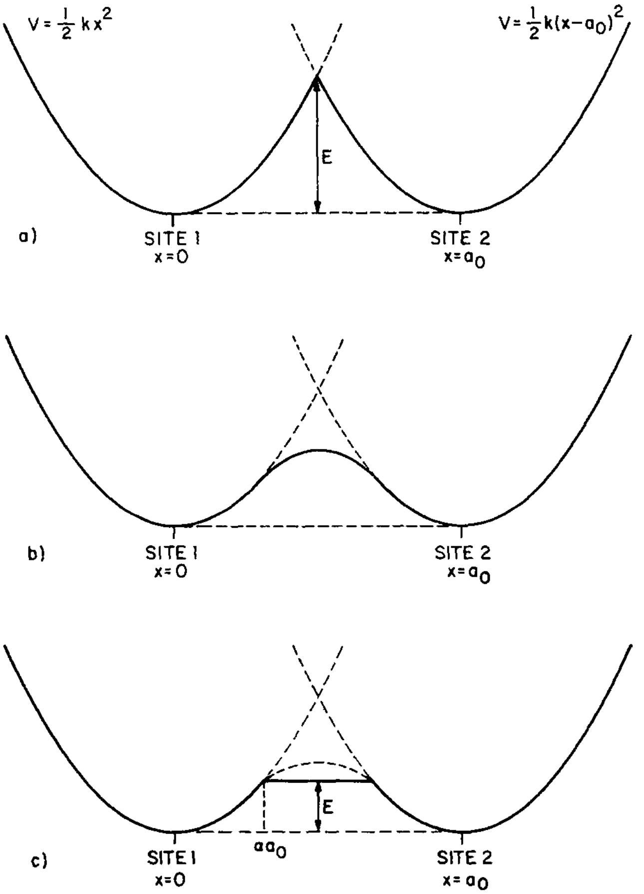

FIG. 1. Simple harmonic oscillator potentials as approximations for the localized oscillatory state of a hopping model. (a) Simple harmonic oscillator potentials; (b) more "realistic" potential; (c) approximation to "realistic" potential.

amplitude of oscillation thus gives us a way of estimating the effective force constant and in turn enables us to calculate ν. Thus from Eqs. (4) and (5) we find the relationship

$$\nu = \frac{1}{2\pi A}\left(\frac{2\varepsilon}{M}\right)^{1/2}. \qquad (6)$$

The similarity of Eqs. (3) and (6) is clear. From Fig. 1a, we can find the amplitude necessary for the ion to have sufficient energy, the activation energy E, to "hop" to Site 2. This critical amplitude is obviously $a_0/2$ so that

$$\nu = \frac{1}{\pi a_0}\left(\frac{2E}{M}\right)^{1/2}. \qquad (7)$$

Thus the ν's calculated from Eq. (7) are about one-third those found by Rice and Roth [Eq. (3)].

A more realistic potential is that shown in Fig. 1b. For simplicity we approximate this potential by the one shown in Fig. 1c for which the critical amplitude is αa_0. For this case Eq. (6) becomes

$$\nu = \frac{1}{2\pi\alpha a_0}\left(\frac{2E}{M}\right)^{1/2}. \qquad (8)$$

The value of α will depend on the particular model. If we choose $\alpha = 0.16$ so that $2\pi\alpha = 1$, Eq. (8) becomes identical to the free-ion-like model result, Eq. (3). For fcc metals, $\alpha = 0.16$ corresponds to a critical amplitude of $0.29r$, where r is the atomic radius. (For bcc metals, $\alpha = 0.16$ corresponds to a critical amplitude of $0.28r$.) It is interesting to note that this is very close to the critical amplitude of $0.275r$ which Achar invoked in his reaction coordinate calculation (*4*) in order to obtain agreement between his calculated motion energy and the observed diffusion activation energy for the seven fcc metals he considered.

To summarize, there is no need to invoke a free-ion-like model. A simple harmonic oscillator "hopping" type model can be used to obtain a relationship between ν, E, M, and a_0 which is identical in form to that obtained from the free-ion-like model. A reasonable choice of a critical amplitude of oscillation results in frequencies identical to those obtained from the free-ion-like model. If one wishes to make one further identification between the two models, one can interpret the velocity v_m of the free-ion-like model as the maximum velocity of the ion undergoing oscillation, i.e., the velocity at zero displacement.

Finally, one can question whether the calculated oscillator frequency for these metals should be expected to be identical to the Deby frequencies. The effective oscillator frequency should be related to the frequencies of those phonon modes with the proper phase and polarization to maximize the probability of a "hop." The Debye frequency is defined such that the acoustic mode branches of lower velocity are more heavily weighted. Since the metals considered by Rice and Roth (*1*) have transverse velocities which are about half the longitudinal velocities, it is the tranverse modes which essentially determine the Debye frequency. Even within a transverse branch there is anisotropy so that some modes are weighted more heavily than others. The oscillator and Debye frequencies will be the same order of magnitude and perhaps even bear a relatively constant relationship to one another for the fcc metals (*4*), but, in view of the differences in the physical significance of these quantities, it is difficult to argue that the two frequencies "should" be identical. Equality of the two seems fortuitous.

References

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