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Ionic Transport in Super Ionic Conductors: a Theoretical Model

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Ionic solids exhibiting exceptionally high levels of ionic conductivity are found among the cation disordered ionic compounds of the silver halide–chalcogenide type, the various cation substituted beta aluminas, and certain defect-stabilized ceramic oxides. We present in this paper a theoretical model for ionic transport phenomena in such "super" ionic conductors. The model is based on the hypothesis that there exists in the ionic conductor an energy gap ϵ_0 above which ions of mass M, belonging to the conducting species, can be thermally excited from localized ionic states to free-ion like states in which an ion propagates throughout the solid with a velocity v_m and energy $\epsilon_m = \frac{1}{2}Mv_m^2$. On account of the interaction with the rest of the solid such an excited free-ion like state is supposed to have a finite life-time τ_m. On the basis of a postulated Boltzmann transport equation for the thermal occupations of the various free-ion like states, simple expressions are derived for the ionic conductivity σ, thermal conductivity K_I, and thermoelectric power Q. The theoretical result for Q is well substantiated by available experimental data. The result for σ may be used to deduce empirical values for the characteristic "mean-free path", $l_0 = v_0 \tau_0$, of the free-ion like state excited at the gap entry ϵ_0. The characteristic life-time τ_0 could be deduced in principal from measurements of the frequency dependent ionic conductivity $\sigma(\omega)$ which, according to the model, should be of the Drude type.

Section 1. Introduction and Summary

There is at present considerable experimental and technological interest in the properties and understanding of solids of exceptionally high ionic conductivity (*1*). Such solids, examples of which we shall present below, exhibit ionic conductivities that can be as large as inverse ohm-centimeters at temperatures ranging from a little above room temperature to ceramic temperatures of the order of 1800°K. Because in almost all cases the high ionic conductivities of these solids are achieved with a negligible degree of electronic conductivity†, there has been much interest in their possible utilization as solid electrolytes for various battery and fuel cell systems (*1*, *2*). These highly ion conducting solids, which may perhaps be aptly called "super" ionic conductors, can be broadly divided into three main groups. These are: (a) the ionic compounds of the type typified by the cation disordered phases of the silver halides and chalcogenides, (b) the isomorphous series of hexagonal compounds exhibiting the so called beta-alumina structure, and (c) the defect stabilized ceramic oxides of the calcium fluoride structure. Examples of the first type of super ionic conductor are

α-Ag^*I
α-Ag_2^*S
α-Ag_2^*Te
α-Ag_2^*Se
α-Cu^*I
α-Cu_2^*Se
α-Ag_3^*SI
α-$Ag_3^*HgI_4$
Na_2^*S
Ag_3^*SBr
$Ag_4^*HgSe_2I_2$
$RbAg_4^*I_5$ ($Rb \rightarrow K$, Cs, NH_4)

The beta-alumina compounds comprising the second group are:

$$A_2^*O \cdot nM_2O_3 \begin{cases} A^* = Na^*, Rb^*, Ag^*, K^*, Li^*, Tl^*. \\ M = Al, Ga, Fe^{3+}. \\ n = 5\text{–}11 \text{ (integer).} \end{cases}$$

Some members of the defect-stabilized ceramic oxide group (c) are the following:

$$CaO \cdot AO_2^* \ (A = Zr, Hf, Th, Ce).$$
$$M_2O_3 \cdot ZrO_2^* \ (M = La, Sm, Y, Yb, Sc).$$

In each of the above chemical formulas the conducting cation or anion species has been indicated by the use of an asterisk.

The ionic compounds belonging to the first group can be structurally characterized as having a

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† Except for α-Ag_2, α-Ag_2Se and α-Cu_2Se which have high electronic conductivity: see P. Junod, *Helv. Phys. Acta*, **32**, 601 (1960).

relatively rigid crystalline framework composed of the nonconducting ionic species, with the conducting cation species distributed in a statistically disordered fashion among the available sites offered by the rigid nonconducting framework. There are usually several, and sometimes many, possible sites per conducting cation. As was first recognized by Strock (*4*) in 1934, the exceptionally high ionic conductivities of these solids result from the almost liquid-like state of the disordered cation species. An excellent general discussion of this group of solids has been given recently by Wiedersich and Geller (*5*). In the beta-alumina group of ionic compounds (*6*) cation conduction $(A^+)^*$ takes place in planes which separate the nonconducting crystalline spinel-blocks of the beta-alumina structure. The conducting plane is characterized by a two-dimensional hexagonal array of O^{2-} anions, with the ions $(A^+)^*$ distributed in a random fashion over the two-dimensional manifold of possible cation sites defined by the fixed anion network. Thus, the essence of the cation disorder that is responsible for the high ionic conductivity of these solids may be regarded as a two-dimensional counterpart of that found prevalent in the first group of ionic solids. In the third group of ionic conductors, anion $(O^{2-})^*$ transport is animated by a relatively large and fixed number of $(O^{2-})^*$ vacancies produced by the stabilizing agent on account of the requirement of overall charge neutrality (*7*). For example, in the case of $CaO \cdot ZrO_2^*$, known in the literature as *calcia stabilized zirconia*, we may write the explicit chemical formula $Ca_x^{2+}Zr_{1-x}^{4+}O_{2-x}^{2-*}$, where x denotes the fractional concentration of Ca. Thus, in this example, the addition of the stabilizing Ca introduces a fixed concentration of $x/2$ vacancies in the anion $(O^{2-})^*$ component (typically $0.1 \lesssim x \lesssim 0.2$). The study of ionic conductivity in this group of compounds has been particularly interesting from the standpoint of observing the phenomenon as a function of the fixed vacancy content (*8*).

The super ionic conductors presented in the foregoing text are different in several respects from the well-known conventional ionic conductors. Firstly, of course, there is the vast difference in the magnitude of the ionic conduction involved. For example, taking an extreme case, the ionic conductivity of the super ionic conductor $RbAg_4I_5$ (*9*, *10*) at 250°K is some 17 orders of magnitude larger than that of NaCl at the same temperature (*5*). It is notable that in contrast to the case of conventional ionic conductors, the large conductivities of the super ionic conductors are attained at relatively small fractions of their melting points, and with correspondingly low activation energies for ionic transport. Figure 1 shows the dependence of ionic conductivity on temperature for some typical super ionic conductors. Figure 2 shows the same data[1] as a function of the homologous temperature. Another major difference, connected with the high level of ionic conductivity, is the fact that the number of

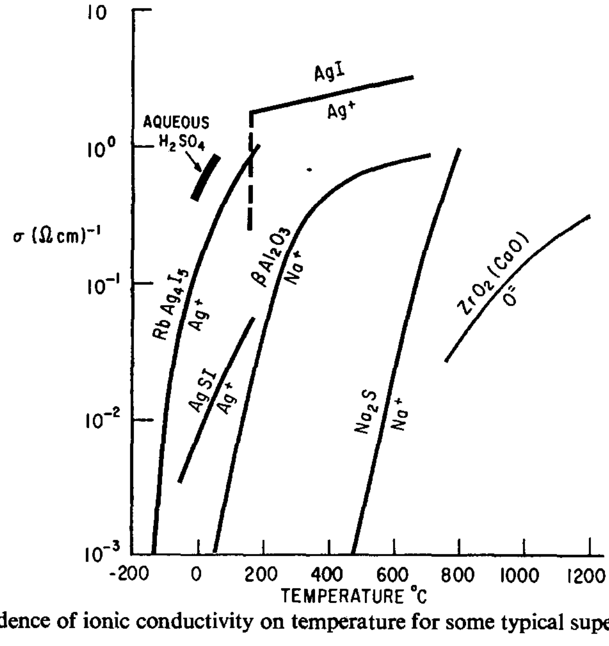

FIG. 1. The dependence of ionic conductivity on temperature for some typical super ionic conductors.

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[1] We would like to thank Dr. Westbrook for supplying us with Figs. 1 and 2. Data for these figures are taken from the appropriate references given in Tables II–IV.

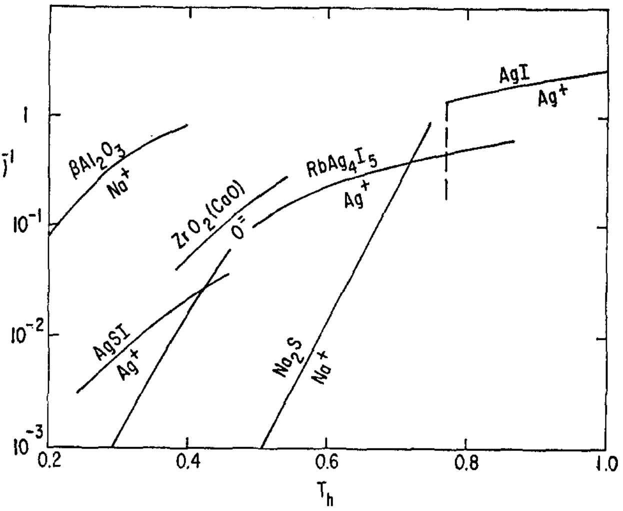

FIG. 2. The ionic conductivity versus homologous temperature T_h.

potentially mobile ionic species, or "carriers", in the super ionic conductors is both large and fixed, independent of the absolute temperature. In the conventional ionic conductors, the number of potential carriers is small and usually temperature dependent (Schottky or Frenkel defects are thermally activated) (*11*). Another, and potentially exciting difference, is that in some of the super ionic conductors, most notably in those belonging to the stabilized ceramic oxide group, it appears possible that the mobile ionic carrier is transported in a cooperative fashion over "mean-free paths" that are typically many interionic distances (*12*, *13*). The effective ionic mean-free path for ionic charge transport in the conventional ionic conductors is, of course, the interionic hopping distance.

As in the case of the conventional ionic conductors, the underlying physical mechanism of ionic transport in the super ionic conductors is that of the thermal excitation of an ion from a localized oscillatory state to a state in which the ion moves translationally through the solid to some other available localized state situated at some finite distance from the locality of its initial state. Up to the present time, the ionic conductivity resulting from this mechanism has been generally discussed in terms of the conventional hopping formalism (*11*). Thus, an Arrhenius type of formula for the ionic conductivity is considered, the pre-exponential factor of which is proportional to the product of the square of some mean hopping distance, $\bar{a}$, and some mean local ionic oscillator frequency $\bar{\nu}$. While this type of discussion is probably in many cases qualitatively valid, it is in practice rather unsatisfactory from the point of view of obtaining relevant information from experiment. For example, although an Arrhenius formula accounts in a natural way for the exponential temperature dependence of the observed conductivity, it cannot be used to deduce empirical values of say the mean hopping distance, $\bar{a}$, since knowledge of the other key phenomenological parameter, $\bar{\nu}$, is quite unknown. Also, for the super ionic conductors, it is not entirely clear how one should further develop the Arrhenius theory of ionic conductivity in order to discuss, on a microscopic basis, other ionic transport effects such as, for example, thermoelectricity, thermal diffusion, and ionic response to a time-dependent electromagnetic field. For these reasons there has been very little theoretical discussion of general ionic transport phenomena published on the high ionic conductivity field.

It is the purpose of the present paper to present a model theory of ionic transport processes in the super ionic conductors which affords a general treatment of the various transport phenomena and, within the confines of the model, allows the key phenomenological parameters of the theory to be obtained from experiment in an unambiguous way. In contrast to the approach used in the conventional theory of ionic conduction (*11*), special emphasis is placed in the present theory on the actual translational motion of the conducting ion during passage between initial and final localized states in the solid.

The basic idea which constitutes the framework of the present model is an attempt to regard the state of translational motion of a thermally excited ion as a well-defined elementary excitation of the solid. Specifically, it is postulated that in such an excited state the conducting ion, of mass M, propagates through the solid in a free-ion like manner with a well-defined velocity $\mathbf{v}_m$ and energy $\epsilon_m = \frac{1}{2}M\mathbf{v}_m^2$. The energy spectrum of these elementary excitations is assumed to be continuous for all energies ϵ_m greater than, or equal to, some characteristic threshold energy, ϵ_0, and to vanish for any $\epsilon_m < \epsilon_0$. The "energy gap" ϵ_0 is to be interpreted as a measure of the binding energy of the localized ion. The transport mechanism, then, is depicted here as the thermal excitation of ions, belonging to the conducting species, from localized ionic states to a spectrum of free-ion like states existing above a specific energy gap ϵ_0.

Once a localized ion has been excited to a free-ion like state it cannot, of course, be expected to remain indefinitely in this state because of the retarding effect of its interaction with the rest of the solid. Eventually these interactions cause the propagating ion to decay into some available localized state within the solid. In order to represent the effect of these interactions in the present model we ascribe to each free-ion state a phenomenological life-time τ_m. Thus, if an ion is initially excited from some localized state to a free-ion like state of energy $\epsilon_m(\geqslant\epsilon_0)$, the ion is considered to remain in this specific state for a characteristic time τ_m before decaying to some other localized state. In this way a concept of an ionic mean-free path is introduced. Such a quantity may be taken to be $l_m = \mathbf{v}_m\tau_m$ for an ion propagating in the free-ion like state of energy ϵ_m.

The ideas of the model just presented may be very conveniently expressed in terms of a Boltzmann transport equation formulism for the thermal occupation of the free-ion like states. This formulism is presented in Section 2 where general expressions are obtained for the various linear ionic transport coefficients. Here, an explicit function for the spectrum of the free-ion like states is obtained from a simple statistical mechanical argument. In the limit that $\epsilon_0 \gg k_BT$, where k_B denotes Boltzmann's constant, the ionic transport coefficients may be expressed in terms of the mean-free path l_0 $(=\mathbf{v}_0\tau_0)$ and velocity $\mathbf{v}_0 = \sqrt{2\epsilon_0/M}$ of the free-ion like state at the gap energy ϵ_0. In Section 3 these expressions are discussed from an experimental standpoint. The theoretical expression for the ionic conductivity is used to deduce empirical values of l_0 and $\mathbf{v}_0$ from the observed ionic conductivities of the super ionic conductors. For the purposes of comparison, this procedure is also applied to the current experimental data on ionic self-diffusion in molten metals. On the basis of this analysis the super ionic conductors are classified according to whether ionic transport is associated with mean-free paths of the order of an interionic distance or with mean-free paths of the order of many interionic distances. One theoretical prediction of the model, relating the ionic thermoelectric power (Peltier coefficient) in a simple way to the energy gap ϵ_0, is very well substantiated by the available experimental data for this transport property.

An important theoretical prediction, closely related to the underlying ideas of the present theoretical model, is that the ionic conductivity should have a definitive frequency dependence. In Section 4, it is shown that the frequency dependence of the ionic conductivity should be of the Drude type, a dependence well known in the electron theory of metals (*14*). The experimental observation of this frequency-dependent ionic conductivity would provide a direct measurement of the fundamental free-ion like life-time τ_0. Some representative calculations of the effects of the frequency-dependent ionic conductivity on the electromagnetic absorption and reflection coefficients of a super ionic conductor are made. A deduction of the free-ion life-time τ_0 from such experiments would also be of importance from the standpoint of an independent confirmation of the possible existence of large free-ion like mean-free paths.

The present paper is concluded by a brief discussion in Section 5 of the connection of the present theory with the conventional hopping theory.

Section 2. The Transport Theory

A. Formal Specification of the Model

The essence of the theoretical model of ionic transport processes outlined in the introduction is the assumption that there exists in the ionic conductor an energy gap, ϵ_0, above which ions of mass M, belonging to the conducting species, can be thermally excited from localized ionic states to free-ion like states in which an ion propagates throughout the solid with a velocity $\mathbf{v}_m$ and energy $\epsilon_m = \frac{1}{2}M\mathbf{v}_m^2$. On account of the interaction with the rest of the solid, such an excited free-ion like state is supposed to have a finite life-time τ_m.

A theory of ionic transport processes based on these simple ideas may be very conveniently developed in terms of the thermal occupations, n_m, of the various free-ion like states. Specifically, let $n_m/4\pi$ denote the probability that an ion has been thermally excited to a free-ion like state of energy $\epsilon_m(\geqslant\epsilon_0)$ in which it propagates through the conductor within the solid angle $d\Omega$. The direction of propagation is $\mathbf{v}_m/|\mathbf{v}_m|$. We shall assume in the present treatment that the propagation velocity, $\mathbf{v}_m$, and hence the energy ϵ_m, is independent of the direction of propagation. The total number of thermally excited free-ion like states per unit volume, N, may be written as

$$N = \frac{1}{\Omega}\sum_m \int \frac{d\Omega}{4\pi} n_m, \qquad (2.1)$$

where Ω denotes the volume of the conductor, and the sum in (2.1) is over all possible free-ion energy states ϵ_m. The question of the actual spectrum of such states will be discussed shortly. For sufficiently small values of n_m we shall assume that at a finite temperature T the Gibbs free energy of the conductor may be expanded according to

$$\begin{aligned} G &= G_0 + \Delta H - T\Delta S \\ &= G_0 + \sum_m \int \frac{d\Omega}{4\pi} \epsilon_m n_m - \\ &\quad k_B T \sum_m \int \frac{d\Omega}{4\pi}(n_m - n_m \log n_m), \qquad (2.2) \end{aligned}$$

where G_0 denotes a constant independent of n_m and k_B denotes Boltzmann's constant. Minimization of (2.2) with respect to n_m yields the equilibrium thermal occupation

$$n_m{}^0 = e^{-\epsilon_m/k_B T}. \qquad (2.3)$$

With regard to the question of the spectrum of the free-ion like states, let us define the function $g(\epsilon_m)$ such that $g(\epsilon_m)\delta\epsilon_m$ gives the number of free-ion like states per unit volume available in the solid with energies between ϵ_m and $\epsilon_m + \delta\epsilon_m$. The summation over the states m may then be replaced by an integral according to

$$\frac{1}{\Omega}\sum_m \to \int_0^\infty g(\epsilon_m)\, d\epsilon_m. \qquad (2.4)$$

We shall refer to $g(\epsilon_m)$ as "the density of states function." In terms of $g(\epsilon_m)$, (2.1) becomes

$$N = \int_0^\infty d\epsilon_m g(\epsilon_m) \int \frac{d\Omega}{4\pi} n_m.$$

Since ϵ_m has been assumed to be independent of direction, we have at equilibrium,

$$N_0 = \int_0^\infty d\epsilon_m g(\epsilon_m) e^{-\epsilon_m/k_B T}. \qquad (2.5)$$

An explicit expression for $g(\epsilon_m)$ may be obtained from the following argument. Firstly, the postulate of the energy gap implies that we take $g(\epsilon_m) = 0$ for all $\epsilon_m < \epsilon_0$. For $\epsilon_m \geqslant \epsilon_0$, we note that the number of free-ion like states thermally excited at equilibrium per unit volume with energies lying between ϵ_m and $\epsilon_m + \delta\epsilon_m$ is

$$\delta N_0 = g(\epsilon_m) e^{-\epsilon_m/k_B T} \delta\epsilon_m, \qquad (2.6)$$
$$(\epsilon_m \geqslant \epsilon_0).$$

Let the number of potentially mobile ionic species per unit volume in the conductor be denoted by n. Now it follows from a well-known equilibrium statistical mechanical argument that the probability for a localized atom to be found in *any* energy state greater than ϵ is the Boltzmann factor $e^{-\epsilon/k_B T}$. Thus, the number of ions per unit volume lying in energy states between ϵ and $\epsilon + \delta\epsilon$ at equilibrium is

$$\delta N(\epsilon) = (n/k_B T)\, e^{-\epsilon/k_B T}. \qquad (2.7)$$

Since the present model assumes that the free-ion like states originate from the thermal excitation of ions of the conducting species from their localized states in the conductor, we may identify (2.7) with (2.6) for $\epsilon \geqslant \epsilon_0$ and hence obtain the desired expression for $g(\epsilon_m)$. Thus, the density of states function will be taken as

$$\begin{aligned} g(\epsilon_m) &= 0, &\quad \epsilon_m &< \epsilon_0 \qquad (2.8) \\ g(\epsilon_m) &= n/k_B T, &\quad \epsilon_m &\geqslant \epsilon_0. \end{aligned}$$

Substituting (2.8) into (2.5) we see that the total number of free-ion like states thermally excited per unit volume at equilibrium is

$$N_0 = n\, e^{-\epsilon_0/k_B T}. \qquad (2.9)$$

In the nonequilibrium state n_m may be a function of both the time t and position $\mathbf{r}$. Explicitly, let $n_m(\mathbf{r}, t)$ denote the value of the thermal occupation of the free-ion like state of energy ϵ_m at time t in the vicinity of a point $\mathbf{r}$ within the conductor. The ionic current at the point $(\mathbf{r}, t)$ will be given by

$$\mathbf{i}(\mathbf{r}, t) = Ze \int_0^\infty d\epsilon_m g(\epsilon_m) \int \frac{d\Omega}{4\pi} \mathbf{v}_m n_m(\mathbf{r}, t), \qquad (2.10)$$

where Ze denotes the charge carried by an ion belonging to the conducting species. The heat, or enthalpy, current, $\mathbf{J}_H$, furnished by the free-ion like states is likewise (cf. 2.1)

$$\mathbf{J}_H(\mathbf{r}, t) = \int_0^\infty d\epsilon_m g(\epsilon_m) \int \frac{d\Omega}{4\pi} \epsilon_m \mathbf{v}_m n_m(\mathbf{r}, t). \qquad (2.11)$$

At equilibrium n_m is given by (2.3) and the corresponding equilibrium charge and heat fluxes, (2.10) and (2.11), vanish.

We may now define the postulate concerning the finite life-time τ_m of the free-ion like state. This postulate is defined by the assumption that for small departures from equilibrium the rate of change of the thermal occupation of the free-ion like states is governed by a Boltzmann transport equation of the form

$$[\partial n_m(\mathbf{r},t)/\partial t + \mathbf{v}_m \cdot [\partial n_m(\mathbf{r},t)/\partial \mathbf{r}] = -[n_m(\mathbf{r},t) - n_m{}^0]/\tau_m. \quad (2.12)$$

The left-hand side of this equation describes the evolution of $n_m(\mathbf{r},t)$ due to the free propagation of the free-ion like state, while the right-hand side represents the decay of the state on account of its interaction with the rest of the solid. The characteristic life time τ_m of the free-ion like state will be assumed to be independent of the direction of propagation and to depend only on the energy of the state ϵ_m. The transport equation (2.12) completes our formal specification of the present model.

B. Formal Expressions for the Transport Coefficients

The transport properties of interest will be the ionic conductivity, σ, the free-ion like contribution, K_I, to the total thermal conductivity K of the conductor, and the ionic thermoelectric power, or Peltier coefficient, Q. In the absence of an electronic component of transport, the linear isotropic macroscopic transport relations for the conductor will be

$$\mathbf{i} = \sigma \mathbf{E} \quad (2.13)$$

$$\begin{aligned} \mathbf{J} &= -K_L \nabla T + \mathbf{J}_H \\ &= -(K_L + K_I)\nabla T \qquad \text{(zero ionic current)} \quad (2.14) \end{aligned}$$

$$\mathbf{E} = -Q\nabla T \qquad \text{(thermoelectric field, zero ionic current)}, \quad (2.15)$$

where K_L denotes the lattice contribution to the total thermal conductivity and $\mathbf{J}$ denotes the total heat flux. The above transport coefficients may be calculated within the framework of the present formalism by following the procedure of treating the Boltzmann transport equation well known in the electron theory of metals (*15*).

In the presence of a weak stationary electric field $\mathbf{E}$ and small uniform temperature gradient ∇T, the free-ion like occupations may be expanded as

$$n_m(\mathbf{r}) = n_m{}^0(\mathbf{r}) + \delta n_m, \quad (2.16)$$

$$n_m{}^0(\mathbf{r}) = \exp\{-[\epsilon_m + Ze\phi(\mathbf{r})]/k_B T(\mathbf{r})\}. \quad (2.17)$$

Here, $\phi(\mathbf{r})$ is the electric field potential, $\mathbf{E} = -\partial\phi/\partial\mathbf{r}$, and (2.17) is the equilibrium thermal occupation appropriate for the locality $\mathbf{r}$. The temperature of this locality is denoted by $T(\mathbf{r})$, and it is understood that $\delta n_m \ll n_m{}^0(\mathbf{r})$. Substituting (2.16) into the transport equation (2.12), and setting $\partial n_m/\partial t = 0$, we obtain the steady state solution:

$$\delta n_m = n_m{}^0 \tau_m \mathbf{v}_m \cdot [Ze\mathbf{E} + (\epsilon_m/T)\nabla T]/k_B T. \quad (2.18)$$

We have assumed $Ze\phi(\mathbf{r}) \ll \epsilon_m$ and have retained only those terms in δn_m that are of first order in either $\mathbf{E}$ and ∇T. The ionic current may now be calculated by substituting (2.10) and (2.18) into (2.10). Recalling that the equilibrium current vanishes, we have

$$\mathbf{i} = \boldsymbol{\sigma} \cdot \mathbf{E} + \boldsymbol{\sigma}_T \cdot \nabla T, \quad (2.19)$$

where $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}_T$ are in general, the tensors:

$$\boldsymbol{\sigma} = \frac{(Ze)^2}{k_B T} \int_0^\infty d\epsilon_m g(\epsilon_m) \int \frac{d\Omega}{4\pi} n_m{}^0 \tau_m \mathbf{v}_m \mathbf{v}_m, \quad (2.20)$$

$$\boldsymbol{\sigma}_T = \frac{Ze}{k_B T^2} \int_0^\infty d\epsilon_m g(\epsilon_m) \int \frac{d\Omega}{4\pi} n_m{}^0 \tau_m \epsilon_m \mathbf{v}_m \mathbf{v}_m. \quad (2.21)$$

Under isotropic conditions, we may take one-third of the traces of (2.20) and (2.21) to obtain the isotropic transport coefficients. The isotropic conductivity is

$$\sigma = \tfrac{1}{3}\,[(Ze)^2/k_B T]\,\langle \mathbf{v}_m l_m \rangle, \quad (2.22)$$

where we have defined the average

$$\langle f_m \rangle = \int_0^\infty d\epsilon_m g(\epsilon_m) f_m e^{-\epsilon_m/k_B T}, \quad (2.23)$$

for any function, f_m, of the energy ϵ_m. We have introduced the "mean-free path"

$$l_m = \mathbf{v}_m \tau_m \quad (2.24)$$

for the free-ion like state of energy ϵ_m. The thermoelectric power Q follows from equating (2.19) to zero and use of the definition (2.15);

$$Q = (1/ZeT)(\langle v_m \epsilon_m l_m \rangle / \langle v_m l_m \rangle). \quad (2.25)$$

The calculation of the isotropic ionic conductivity, K_I, follows in a similar manner from (2.18), (2.16), (2.11), and its definition (2.14). The result is

$$K_I = \frac{\langle \epsilon_m{}^2 v_m l_m \rangle}{3k_B T^2} \left\{ 1 - \frac{\langle \epsilon_m v_m l_m \rangle^2}{\langle v_m l_m \rangle \langle \epsilon_m{}^2 v_m l_m \rangle} \right\}. \quad (2.26)$$

C. Explicit Expressions for the Transport Coefficients

We now employ the specific form (2.8) for the density of states function $g(\epsilon_m)$ in order to obtain explicit results for the various transport properties.

The problem reduces to the evaluation of the averages of the type (2.23) over the free-ion like states. With the aid of (2.8) the average (2.23) is

$$\langle f_m \rangle = \frac{n}{k_B T} \int_{\epsilon_0}^{\infty} d\epsilon_m \, e^{-\epsilon_m/k_B T} f(\epsilon_m).$$

For small $(k_B T/\epsilon_0)$ we may write, after a repeated integration by parts, the expansion

$$\langle f_m \rangle = nf(\epsilon_0)\, e^{-\epsilon_0/k_B T}\{1 + C_1(k_B T/\epsilon_0) + \ldots \\ C_N(k_B T/\epsilon_0)^N + \ldots\}, \qquad (2.27)$$

where the coefficients C_N are defined by

$$C_N = [\epsilon_0{}^N/f(\epsilon_0)]\,[d^N f(\epsilon)/d\epsilon^N]_{\epsilon=\epsilon_0}. \qquad (2.28)$$

In the limit that $\epsilon_0 \gg k_B T$, we have

$$\langle f_m \rangle = nf(\epsilon_0)\, e^{-\epsilon_0/k_B T} \qquad (k_B T \ll \epsilon_0). \quad (2.29)$$

It is seen from the definition of $\langle f_m \rangle$ that this result could be formally interpreted in terms of an effective density of states function of the form

$$g_{\text{eff}}(\epsilon_m) = n\delta(\epsilon_m - \epsilon_0). \qquad (2.30)$$

At temperatures for which $(k_B T/\epsilon_0)$ is not small the correction terms of the expansion (2.27) must be considered. However, the calculation of the various dimensionless expansion parameters (2.28), appropriate for the ionic transport coefficients, will require a knowledge of the energy dependence of the ionic mean-free path, $l(\epsilon_m)$, in the region of ϵ_0. More specifically the energy dependence of τ_m is required since l_m may be written as $l_m = (\sqrt{2\epsilon_m/M})\tau_m$. Unfortunately, this information is not specified by the present theory. For this reason we shall in the following part of this paper generally restrict our attention to the low-temperature limit $\epsilon_0/k_B T \ll 1$, where this information is not required.

With (2.29) the general expression (2.22) for the ionic conductivity reduces immediately to the result

$$\sigma = \tfrac{1}{3}[(Ze)^2/k_B T]\, n v_0 l_0\, e^{-\epsilon_0/k_B T}, \qquad (2.31)$$

where l_0 and v_0 denote, respectively, the mean free path and velocity of the free-ion like state excited at the gap energy ϵ_0. In terms of the life-time τ_0 of this state (2.31) may be reexpressed as

$$\sigma = \tfrac{2}{3}[(Ze)^2/k_B TM]\, n\epsilon_0 \tau_0\, e^{-\epsilon_0/k_B T}. \qquad (2.32)$$

The general expression (2.25) for the thermoelectric power, Q, reduces to the particularly simple form

$$Q = (k_B/Z\mathrm{e})\cdot(\epsilon_0/k_B T). \qquad (2.33)$$

On applying (2.29) to evaluate the various averages in the general result (2.26) for the thermal conductivity, K_I, however, we obtain the result

$$K_I = 0. \qquad (2.34)$$

This result is not surprising. As we pointed out above in writing (2.30), the low-temperature limit $k_B T \ll \epsilon_0$ implies that only the free-ion like states excited at the gap energy ϵ_0 are effective in ionic transport. In this case, it follows that the heat flux (2.11) contributed by the free-ion like states is proportional to the ionic current (2.10). However, the thermal conductivity is defined under conditions of vanishing ionic current [cf. (2.14)]. Hence, if the ionic current is zero, the heat current carried by the free-ion like states must also be zero. A finite thermal conductivity, K_I, will be obtained, however, at finite values of $k_B T/\epsilon_0$. In order to calculate this quantity to the first (nonvanishing) order in $k_B T/\epsilon_0$, the second term of the expansion (2.27) must be retained when evaluating the various averages of (2.26). On doing this we find

$$K_I = (\alpha/2)\, n k_B v_0 l_0 (\epsilon_0/k_B T)\, e^{-\epsilon_0/k_B T}, \quad (2.35)$$

where we have defined

$$\alpha = 1 + (2\epsilon_0/3l_0)\,[dl(\epsilon)/d\epsilon]_{\epsilon=\epsilon_0}. \qquad (2.36)$$

Equations (2.31), (2.33) and (2.35) are the main results of this section. The theory of transport processes developed in this section may be easily reformulated for the case where ionic transport is confined to a two-dimensional plane. As was mentioned in the introduction, such a situation is encountered in the beta-alumina family of ionic conductors. If we denote by n_A the number of potentially mobile ions per unit area in a conducting plane of such a solid, and by b the distance between adjacent parallel planes, then it may be shown that in place of the result (2.31) we have

$$\sigma_{\|} = \tfrac{1}{2}[(Ze)^2/k_B T]\,(n_{\mathrm{A}}/b)\, v_0 l_0\, e^{-\epsilon_0/k_B T} \quad (2.37)$$

for the ionic conductivity parallel to a plane direction. The result (2.33) for the thermoelectric power is left unchanged for a temperature gradient applied parallel to the conducting planes. Finally, $K_I(\|)$ is obtained from (2.35) by the replacement of n by $\tfrac{2}{3}n/b$.

Section 3. Discussion and Application to Experiment

The result (2.31) for the ionic conductivity is

$$\sigma = \tfrac{1}{3}[(Ze)^2/k_B T]\, n v_0 l_0\, e^{-\epsilon_0/k_B T}, \qquad (3.1)$$

where

$$l_0 = v_0 \tau_0, \qquad v_0 = \sqrt{2\epsilon_0/M} \qquad (3.2)$$

denote, respectively, the velocity and mean-free path of the free-ion like state excited at the gap energy ϵ_0. τ_0 denotes the life-time of this state and n the number of potentially mobile ionic species per unit volume. Since n, Ze, and M are assumed known for a given super ionic conductor the result (3.1) specifies the ionic conductivity in terms of two basic parameters of our theoretical model, namely, ϵ_0 and τ_0. In the spirit of the theoretical model, ϵ_0 and τ_0 are to be regarded as constants which characterize a particular ionic conductor. The temperature dependence of σ predicted by (3.1) is that of the observed Arrhenius type so that a plot of $\log(\sigma T)$ *vs.* $1/T$ yields a straight line whose slope and intercept are determined, respectively, by ϵ_0 and by the appropriate pre-exponential factor in (3.1). Thus, empirical values of ϵ_0 and τ_0, and hence of l_0 and v_0, may be obtained from the observed ionic conductivity data if n, Ze, and M are known. Later in this section, an attempt will be made to deduce such empirical values for various super ionic conductors.

The result (2.33) for the ionic thermoelectric power predicts that this quantity is inversely proportional to the absolute temperature T, the coefficient of proportionality being essentially governed by the magnitude of the energy gap ϵ_0. Also, the *sign* of the ionic thermoelectric power is determined by the sign of the charge of the conducting ionic species. The observed values Q_{obs} of the ionic thermoelectric power should thus follow the law

$$ZeTQ_{\text{obs}} = \text{const.} = \epsilon_0. \tag{3.3}$$

Since the value of the constant ϵ_0 can be obtained from independent measurements of the temperature dependence of the ionic conductivity,

$$\epsilon_0 = \frac{-d(\log T\sigma)}{d(1/k_B T)}, \tag{3.4}$$

a direct experimental test of the theoretical prediction (3.3) is possible. Takahashi et al. (*16*) have recently measured the homogeneous ionic thermoelectric powers of a series of super ionic conductors belonging to the silver halide type. These conductors are listed in the first column of Table I. Indeed Takahashi observes that the magnitude of Q is proportional to T^{-1} and that the sign* of the thermoelectric power is positive, corresponding to the positive charge of the silver cation. The observed values of the constant $ZeTQ_{\text{obs}}$ appropriate for each conductor are shown in the second column of Table I. The corresponding values of ϵ_0, deduced by Takahashi from independent measurements of the ionic conductivity on the same specimens, are shown in the third column of the Table. We see that the theoretical prediction (3.3) is very well substantiated by Takahashi's measurements.

TABLE I

Test of the Theoretical Relation (3,3) of the Text for the Silver Compounds Studied Experimentally by Takahashi

Super ionic conductor	$ZeTQ_{\text{obs}}$ (eV)	ϵ_0 (eV) Deduced from conductivity
$KAg_3^*I_4$	0.092	0.095
$RbAg_4^*I_5$	0.078	0.098[a]
$NH_4Ag_4^*I_5$	0.093	0.095
$Ag_2^*HgI_4$	0.61	0.69
$Ag_2^*Hg_{0.25}S_{0.5}I_{1.5}$	0.15	0.14
$Ag_4^*HgSe_2I_2$	0.17	0.15
$Ag_{1.1}^*Hg_{0.3}Se_{1.4}I_{0.9}$	0.11	0.10
$Ag_{1.5}^*Hg_{0.25}Te_{0.35}I_{0.9}$	0.14	0.17

[a] In recent pressure work on $RbAg_4I_5$, Bundy et al. (*38*) have deduced $\epsilon_0 = 0.08$ at room pressure.

An experimental test of (3.3) for the conductors belonging to the other groups of super ionic conductors does not seem possible at the present time owing to the lack of suitable experimental data on the ionic thermoelectric power. Pizzini et al. (*17*) have recently measured the thermoelectric powers of various stabilized zirconia compounds, but unfortunately in these measurements it does not seem possible to separate out the required homogeneous thermoelectric power from the inhomogeneous contribution resulting from the ionization reactions at the measuring electrodes. We have not been able to locate measurements of Q for the beta-alumina group of conductors. Such measurements would be of particular interest in the present context.

In the absence of radiative heat transfer, the total thermal conductivity K of a super ionic conductor will be

$$K = K_L + K_I,$$

where K_L denotes the usual lattice contribution (phonon transport) and K_I denotes the contribution (2.35) arising from the free-ion like states. Using the result (2.31) for the ionic conductivity, we may write K_I in the form

$$K_I = \sigma T L_I, \tag{3.5}$$

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* Takahashi et al. (*16*) actually report negative values for the thermoelectric powers. This is because these authors have employed the definition $\mathbf{E} = Q\nabla T$ rather than the conventional definition $\mathbf{E} = -Q\nabla T$.

TABLE II

FREE-ION LIKE PARAMETERS FOR THE SUPER IONIC CONDUCTORS OF THE SILVER HALIDE AND CHALCOGENIDE TYPE

Super ionic conductor	n (10^{22} cm^{-3})	ϵ_0 (eV)	v_0 (10^5 cm sec^{-1})	τ_0 (10^{-13} sec)	l_0 (Å)	r_0 (Å)	Reference to data
α-Ag^*I	1.57	0.10	0.42	5.2	2.2	1.97	(*26*)
α-Ag_2^*S	3.44	0.11	0.44	6.4	2.8	1.67	(*27*)
α-Ag_2^*Se	3.23	0.10	0.42	4.4	1.85	1.70	(*27*)
α-Ag_2^*Te	2.82	0.14	0.50	4.0	2.0	1.78	(*28*)
Na_2^*S ($T \lesssim 520°C$)	1.43	0.77	2.56	0.98	2.5	2.24	(*29*)
Na_2^*S ($T \gtrsim 520°C$)	1.43	1.66	3.73	1.8×10^5	6.7×10^5	2.24	(*29*)
α-Ag_3^*SI	2.41	0.08	0.38	1.5	0.56	1.81	(*30*)
β-Ag_3^*SI	2.55	0.21	0.61	0.98	0.60	1.78	(*30*)
Ag_3^*SBr	2.70	0.28	0.70	1.3	0.93	1.75	(*30*)
$RbAg_4^*I_5$	1.13	0.10	0.42	3.1	1.3	2.03	(*10*)
α-$Ag_2^*HgI_4$	0.77	0.77	0.84	11.4	96	2.07	(*31*)

where L_I defines an "ionic Lorentz number"

$$L_I = (9\alpha L_0/2\pi^2 Z^2)(\epsilon_0/k_B T), \qquad (3.6)$$

in which L_0 denotes the Sommerfeld electron Lorentz number $L_0 = (\pi^2/3)(k_B{}^2/e^2) = 2.45 \times 10^{-8}$ v^2/°K^2. The temperature dependence of K_I is the same form as σ, whereas it is well known (*18*) that K_L follows the law $K_L \propto T^{-1}$. Thus the temperature dependence of the total thermal conductivity should follow the law

$$TK = \text{const.} + \text{const. } e^{-\epsilon_0/k_B T}.$$

The magnitude of K_I, however, is probably too small for it to be practically separated from the dominant lattice thermal conductivity K_L. Taking $\sigma \sim 1\ \Omega^{-1}$ cm^{-1}, $\epsilon_0 \sim 0.15$ eV, $Z = 1$, and $\alpha \sim 1$ as typical values for the most highly conducting super ionic conductors, we have

$$K_I \sim 0.2 \times 10^{-4}\ \text{W cm}^{-1}\ {}^\circ\text{K}^{-1},$$

which compares with values of K_L of the order of 10^{-2} W cm^{-1} °K^{-1} (*18*) at temperatures at which ionic conductivities of the order of 1 Ω^{-1} cm^{-1} are achieved. Thus although the temperature dependence of K_I is distinctive, its magnitude relative to K_L is expected to be too small to be observed experimentally.

We now return the topic of our discussion to the ionic conductivity. As a function of temperature the observed ionic conductivity data can always be fitted to an Arrhenius relation of the form $\sigma(T) = (\sigma_0/T)e^{-E/k_B T}$, where σ_0 and E are constants. According to the theoretical result (3.1), and the definitions, (3.2), we have

$$E = \epsilon_0, \quad \text{and} \quad \sigma_0 = \tfrac{4}{3}[(Ze)^2/k_B M]\, n\epsilon_0\tau_0. \qquad (3.7)$$

For the beta-alumina family of ionic conductors, for which ionic conductivity is restricted to a parallel series of two-dimensional planes, the appropriate formula for σ_0 is

$$\sigma_0 = [(Ze)^2/k_B M](n_A/b)\,\epsilon_0\tau_0, \qquad (3.8)$$

which follows from the result (2.37) of the preceding section. Thus if Z, M, and n, or n_A/b, are known, empirical values of the basic theoretical parameters, ϵ_0 and τ_0, and hence, in view of (3.2), v_0 and l_0, may be deduced from the observed conductivity data. Tables II–IV show the results of such analysis applied to a selection of super ionic conductors belonging to the three groups of conductors outlined in Section 1. The first column of each table indicates the particular ionic conductor and the second the assumed value of n, or of n_A, where appropriate. The next four columns show, respectively, the deduced values of ϵ_0, v_0, τ_0, and l_0. The sixth column of each table lists an interionic distance, r_0, typical of the particular conductor, with which the deduced value of l_0 may be compared. In Table II, r_0 has been chosen as the mean interionic radius

$$\tfrac{4}{3}\pi r_0{}^3 = 1/N_I,$$

where N_I denotes the *total* number of ions per unit volume of the conductor. In Table III, which deals with the beta-alumina series, r_0 has been defined according to

$$\pi r_0{}^2 = 1/N_A,$$

where N_A denotes the total number of ions per unit area of the conducting mirror plane. In Table IV, which studies the defect-stabilized oxides, r_0 is the O^{2-} nearest-neighbor distance in the calcium

TABLE III

FREE-ION LIKE PARAMETERS FOR THE BETA-ALUMINA FAMILY OF SUPER IONIC CONDUCTORS

Super ionic conductor	n_A[a] (10^{14} cm^{-2})	ϵ_0 (eV)	v_0 (10^5 cm sec^{-1})	τ_0 (10^{-13} sec)	l_0 (Å)	r_0[a] (Å)	Reference to data[b]
$(Li^+)^*$-beta	4.5	0.38	3.2	0.46	1.5	1.97	(*6*)
$(Na^+)^*$-beta	4.5	0.17	1.2	0.5	0.6	1.97	(*19*)
$(K^+)^*$-beta	4.5	0.23	1.1	0.23	0.25	1.97	(*6*)
$(Rb^+)^*$-beta	4.5	0.31	0.84	0.15	0.13	1.97	(*6*)
$(Ag^+)^*$-beta	4.5	0.18	0.56	1.4	0.8	1.97	(*19*)
$(Tl^+)^*$-beta	4.5	0.36	0.58	0.57	0.33	1.97	(*19*)

[a] An average conducting plane containing 1.22 cations per planar cell has been assumed for all the beta-aluminas.

[b] For Li^+, K^+, and Rb^+ betas, tracer diffusion data was converted to conductivity data on the assumption that the Nernst–Einstein relation is modified by a correlation factor equal to 0.6 as experimentally verified by Whittingham and Huggins (*19*) for Na^+, Ag^+, and Tl^+ betas.

fluoride structure. Finally, in the last column the number of the reference to the experimental conductivity data is given.

In obtaining the results shown in Table II for the super ionic conductors of the silver halide and chalcogenide type, the assumption was made that n, the number of potentially mobile ionic species per unit volume, is to be identified with the total number of cations per unit volume belonging to the disordered conducting species. Thus, for example, in $RbAg_4I_5$ all of the silver cations have been assumed to be potential carriers. The results in Table II for this group of conductors show that ϵ_0 is typically of the order of tenths of electron volts, and that τ_0 is of the order of an inverse oscillator frequency, i.e., a few times 10^{-13} sec. The free-ion like velocity v_0 is typically of the order 0.5×10^5 cm sec^{-1} with the corresponding mean-free path, l_0, of the order of a mean interionic radius, r_0. We should perhaps stress here that the deduced values of τ_0 and l_0 are subject to an appreciable amount of uncertainty in the extraction of the pre-exponential factor σ_0 from the observed conductivity. Also, it is not always certain that *all* of the ions of the conducting species participate in the conduction process, as assumed here. The tabulated values of τ_0 and l_0 should, therefore, only be taken to be indicative of the correct order of magnitudes. Two ionic conductors listed in Table II, α-Ag_2HgI_4 and the higher temperature phase of Na_2S, do, however, exhibit mean-free paths that are orders of magnitude larger than a typical interionic distance, and thus constitute anomalous exceptions to the general trend established in Table II.

Table III shows the results of our analysis for the beta-alumina family of ionic conductors. Here n_A was taken to be equal to the total number of cations

TABLE IV

FREE-ION LIKE PARAMETERS FOR THE SUPER IONIC CONDUCTORS OF THE DEFECT-STABILIZED CERAMIC OXIDE TYPE

Super ionic conductor	n (10^{21} cm^{-3})	ϵ_0 (eV)	v_0 (10^5 cm sec^{-1})	τ_0 (10^{-13} sec)	l_0 (Å)	r_0 (Å)	Reference to data
$Ca_{0.15}Zn_{0.85}O_{1.85}$	4.43	1.28	3.93	43	169	2.57	(*12*)
$Ca_{0.19}Zr_{0.81}O_{1.81}$	5.60	1.54	4.31	69	298	2.57	(*12*)
$Mg_{0.15}Zr_{0.85}O_{1.85}$	4.62	1.46	4.19	86	360	2.53	(*32*)
$Sc_{0.21}Zr_{0.79}O_{1.895}$	3.28	0.76	3.08	8	25	2.54	(*33*)
$Yb_{0.21}Zr_{0.79}O_{1.895}$	3.17	0.93	3.34	18	60	2.57	(*33*)
$Y_{0.21}Zr_{0.79}O_{1.895}$	3.13	1.02	3.50	21	75	2.58	(*33*)
$Sm_{0.21}Zr_{0.79}O_{1.895}$	3.09	0.97	3.42	10	34	2.59	(*33*)
$Y_{0.15}Hf_{0.85}O_{1.925}$	2.21	1.12	3.68	15	56	2.55	(*34*),
$Ca_{0.12}Hf_{0.88}O_{1.88}$	3.59	1.43	4.14	0.17	0.7	2.55	(*35*)
$Y_{0.18}Th_{0.82}O_{1.91}$	2.07	1.06	3.58	0.67	2.4	2.8	(*36*)

per unit area in the conducting mirror plane of the beta-alumina structure. The main feature of this tabulation is that, with the possible exception of Li^+– beta-alumina, the deduced values of τ_0 and l_0 are all considerably lower than that of a typical inverse oscillator frequency and mean interionic radius. This may indicate that the number of potential mobile ionic species in the beta-aluminas is considerably *less* than that of the total available number of conducting cation species. Such a suggestion has in fact been recently made by Whittingham and Huggins (*19*), who conjecture that the effective number of ionic carriers in the beta-aluminas are to be identified with a small fraction of cations which occupy certain interstitial sites in the conducting planes. If this suggestion is followed here, the deduced values of τ_0 and l_0 would be some 5 to 7 times greater than those shown in Table III. In this case we would have l_0 more like a mean interionic radius.

In the defect-stabilized ceramic oxides O^{2-} transport is animated by the presence of the fixed concentration of O^{2-} vacancies (*7*). In the analysis of these conductors, presented in Table IV, we have identified n with the number of vacancies per unit volume, since for small enough concentrations it is the vacancy that is the distinguishable mobile carrier. Table IV shows that the deduced values of τ_0 and l_0 are typically one or two orders of magnitude greater than those deduced for the two previous groups of super ionic conductors. The only exceptions appear to be Ca-stabilized HfO_2 and Y-stabilized ThO_2. In all cases, v_0 is of the order of several times 10^5 cm^2 sec^{-1}, i.e., a sound velocity. The present analysis would thus indicate that the translational motion of a conducting vacancy in this class of conductors persists, at sound velocities, over distances that are typically many lattice spacings. Such a conclusion would add support to the conjectures of Carter and Roth (*12*) and of Roth (*13*) that the mechanism of ionic transport in Ca-stabilized ZrO_2 involves a series of correlated ionic hops through regions of ordered arrangements of O^{2-} anions and vacancies. It should be stressed, however, that the conclusions drawn from Table IV do depend upon the assumption that the number of potentially mobile ions is to be identified with the concentration of O^{2-} vacancies. While this assumption is reasonable for small vacancy concentrations, it is not clear whether the relatively high levels of vacancy concentrations characteristic of the present materials are sufficiently small to still warrant the validity of this assumption.

In general it appears, then, that the various super ionic conductors can be classified according to whether ionic transport is associated with a mean-free path of the order of some typical interionic distance or with a mean-free path which is at least an order of magnitude greater than a typical interionic distance.

Nearly all of the super ionic conductors belonging to the first group of conductors exhibit the former magnitude of mean-free path, together with life times that are measurable in units of 10^{-13} sec. The same statement applies to the beta-alumina group if Whittingham and Huggins' interpretation of n_A is adopted. The conducting cation species present in these two groups of conductors have been often likened to a molten ionic component that is confined to the solid by the charge neutralizing crystalline framework of the nonconducting ions (*4*, *5*).* It would be of interest to compare the values of l_0 and τ_0 deduced above for these two groups of ionic conductors with those that could be deduced for the ionic component of a molten metal. The ionic density in the molten metal is, of course, quite comparable to that of the conducting species in the present solids. Now it may be shown, following a calculation similar to that given for the ionic conductivity in Section 2, that the present model of ionic transport yields for the ionic self-diffusion coefficient the result

$$D_s(T) = \tfrac{1}{3} v_0 l_0 e^{-\epsilon_0/k_B T} \qquad (k_B T \ll \epsilon_0).$$

Thus, if we assume that the present model is also applicable to the ionic component of a molten metal, appropriate values of the basic theoretical parameters may be deduced from the observed (*36*) $D_s(T)$. Values of ϵ_0, v_0, τ_0, and l_0 deduced in this way are shown in Table V for ten liquid metals. Indeed it is seen that the values of these parameters are comparable to those found above for the first two groups of super ionic conductors. The free-ion like mean-free paths deduced for the liquid metals are of the order of magnitude of the nearest-neighbor distance in the solid state.

The values of τ_0 and l_0 found for the higher temperature phase of Na_2S and for α-Ag_2HgI_4 are, however, exceptional, and these solids join most of the defect-stabilized type of conductors in exhibiting the large values of τ_0 and l_0. The question of the credibility of these large values naturally arises. Do they indicate that the particular carrier involved

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* In fact, Roth (*39*) has noted the rms vibration amplitudes of the ions in the conducting plane of beta-alumina are those expected on the basis of the Lindemann melting law for a two-dimensional liquid.

TABLE V

FREE-ION LIKE PARAMETERS FOR THE IONIC COMPONENTS OF LIQUID METALS[a]

Liquid metal	n (10^{22} cm^{-3})	ϵ_0^* (eV)	v_0 (10^5 cm sec^{-1})	τ_0 (10^{-13} sec)	l_0 (Å)	Nearest neighbor distance (Å)
Na	2.5	0.11	0.95	3.6	3.4	3.71
K	1.3	0.11	0.8	8.5	6.8	4.63
Cu	8.5	0.42	1.1	3.4	3.8	2.56
Ag	5.8	0.33	0.8	3.4	2.7	2.89
Zn	6.55	0.22	0.8	3.8	3.0	2.66
Hg	4.1	0.05	0.22	8.2	1.8	3.01
Ga	5.1	0.05	0.36	2.6	0.94	2.44
In	3.8	0.11	0.42	4.8	2.0	3.25
Sn	3.5	0.11	0.43	4.9	2.1	3.02
Pb	3.3	0.19	0.42	15.5	6.5	3.50

[a] Data of the form $D = D_0 e^{-\epsilon_0/k_BT}$ for the self-diffusion constant is taken from the tabulation of Ref. (*37*).

propagates freely over such large distances in the solid as the theoretical model would imply or, on the contrary, do they indicate that the theoretical model has broken down? There are probably more arguments to support the latter conclusion than the former. It could, for example, be argued that, in practice, the gap energy ϵ_0 should be considered a function of the absolute temperature, in which case the pre-exponential factor, σ_0, of the ionic conductivity would be enhanced by an "entropy factor" (*20*) of the form $e^{s/k}B$, where $s = -d\epsilon_0/dT$. The possibility of large mean-free paths is nevertheless an intriguing thought, and it would be interesting to have some sort of independent measurement of l_0, or equivalently, of τ_0. It is pointed out in the next section that such a measurement is afforded by the frequency-dependent ionic conductivity $\sigma(\omega)$.

Section 4. Frequency Dependent Ionic Conductivity

In this section we consider the frequency-dependent ionic conductivity and the effect of this on the phenomena of the absorption and reflection of electromagnetic radiation by an ion conducting medium.

The linear current density induced in an ionic conductor by a periodically varying external field $E = E(q,\omega)e^{-i\omega t + q\cdot r}$ is (*14*):

$$i = \sigma(q,\omega)\,E(q,\omega)\,e^{iq\cdot r - i\omega t}, \tag{4.1}$$

where $\sigma(q,\omega)$ denotes the wave-vector and frequency-dependent ionic conductivity. In the limit of a slowly varying applied field, $\sigma(q,\omega) \to \sigma(0,0) = \sigma$, which is the static conductivity considered in Sections 2 and 3. In order to calculate the q and ω dependent conductivity in terms of our present theoretical model, we need only generalize our previous static treatment of the Boltzmann equation to the case of the periodically varying field (4.1). Writing as in Section 2, $n_m = n_m{}^0 + \delta n_m$, the linearized transport equation for the increment in the thermal occupation δn_m is

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_m\cdot\frac{\partial}{\partial r} + \frac{1}{\tau_m}\right)\delta n_m = \mathbf{v}_m\cdot\mathbf{E}n_m^0\left(\frac{Ze}{k_BT}\right) \tag{4.2}$$

The solution for δn_m is of the form $\delta n_m = \delta n_m(q,\omega)e^{i\mathbf{q}\cdot\mathbf{r} - i\omega t}$, where substitution of this form into (4.2) yields

$$\delta n_m(q,\omega) = \frac{\mathbf{v}_m\cdot\mathbf{E}(q,\omega)\,\tau_m Zen_m{}^0/k_BT}{1 - i\omega\tau_m + i\mathbf{v}_m\cdot\mathbf{q}\tau_m}. \tag{4.3}$$

The resulting ionic conductivity may be calculated with the use of (2.10) and the definition (4.1), giving, in general, the q- and ω-dependent ionic conductivity tensor

$$\boldsymbol{\sigma}(q,\omega) = \frac{(Ze)^2}{k_BT}\int d\epsilon_m g(\epsilon_m) \times \int \frac{d\Omega}{4\pi}\frac{\mathbf{v}_m\mathbf{v}_m\tau_m e^{-\epsilon_m/k_BT}}{1 - i\omega\tau_m + i\mathbf{v}_m\cdot\mathbf{q}\tau_m}. \tag{4.4}$$

For wave vectors sufficiently small that $ql_m \ll 1$, or alternatively, for sufficiently large electromagnetic phase velocities, $\omega/q \ll v_m$, the third term in the denominator of (4.4) may be discarded. Within these limits $\sigma(q,\omega)$ is independent of $\mathbf{q}$ and the isotropic frequency-dependent conductivity is

$$\sigma(q,\omega) = \frac{1}{3}\frac{(Ze)^2}{k_BT}\int d\epsilon_m g(\epsilon_m)\int \frac{d\Omega}{4\pi}\frac{v_m l_m e^{-\epsilon_m/k_BT}}{(1 - i\omega\tau_m)}, \equiv \sigma(\omega). \tag{4.5}$$

With the use of our model (2.8) and the result (2.29), (4.5) reduces, for $k_B T \ll \epsilon_0$, to the expression

$$\sigma(\omega) = \frac{1}{3}\frac{(Ze)^2}{k_B T}\frac{n v_0 l_0}{(1 - i\omega\tau_0)} e^{-\epsilon_0/k_B T}.$$

In view of (2.31), we may write this result as

$$\sigma(\omega) = \sigma/(1 - i\omega\tau_0), \tag{4.6}$$

where σ denotes the static ionic conductivity. Thus, we have the simple result that the frequency dependence of the ionic conductivity is determined by the dimensionless product of the frequency ω and the life-time τ_0 of the free-ion like state at the gap energy ϵ_0. This type of dependence is well known in the electron theory of metals, in which a result of the form of (4.6) is known as a Drude formula (*14*). The result is of particular interest from the point of view of our theoretical model, for according to it *measurement of the frequency-dependent ionic conductivity would determine the characteristic free-ion like lifetime* τ_0. As pointed out in the previous section, an independent measurement of τ_0 would enable one to settle the question of the validity of the large values of l_0 and τ_0 that were empirically deduced in Section 3 for some of the super ionic conductors.

The frequency-dependent ionic conductivity may be an important factor in governing the absorption and reflection of electromagnetic radiation incident on a specimen of super ionic conductor. For the wave vector q for the propagation of electromagnetic radiation in a conducting dielectric medium is given by the solution of the well-known (*14*) dispersion relation,

$$\begin{aligned} q^2c^2/\omega^2 &= \epsilon_D(q,\omega) + (4\pi i/\omega)\,\sigma(q,\omega),\\ &= \epsilon_I(q,\omega), \end{aligned} \tag{4.7}$$

where c denotes the velocity of light *in vacuo* and $\epsilon_D(q,\omega)$ denotes the q,ω dependent dielectric constant of the medium. $\epsilon_I(q,\omega)$ defines an "apparent" dielectric constant for the medium. If over some range of frequency the dielectric constant function $\epsilon_D(q,\omega)$ is either known or unimportant compared with the second term of (4.7), electromagnetic absorption and reflection measurements will be able to provide an experimental determination of $\sigma(\omega)$, and hence of τ_0. In order to gain an idea of what one might expect to observe experimentally we present some calculations of the electromagnetic absorption and reflection coefficients based on a simple model in which $\epsilon_D(q,\omega)$ is taken to be some real constant ϵ_D. These model calculations will not, of course, be applicable to regions of frequency for which $\epsilon_D(q,\omega)$ is in reality a strongly varying function of ω, such as the frequency range covering the optical lattice vibrations (*21*). The effects arising from any such strong structure of $\epsilon_D(q,\omega)$ would have to appear as appropriate superpositions on the simpler calculations which we present here.

In terms of the constant ϵ_D model, our result (4.6) for $\sigma(\omega)$ yields the following solution of the dispersion relation (4.7):

$$q = q' + iq'',$$

where the real and imaginary parts, q' and q'', of the wave vector q for the propagation of electromagnetic radiation of frequency ω in the medium of the ionic conductor are given by

$$q' = \frac{\omega}{c}\cdot\sqrt{\epsilon_D/2}\cdot[(A^2 + B^2)^{1/2} + A]^{1/2}, \tag{4.8}$$

$$q'' = \frac{\omega}{c}\sqrt{\epsilon_D/2}\cdot[(A^2 + B^2)^{1/2} - A]^{1/2}, \tag{4.9}$$

where

$$A = 1 - [\alpha/(1 + \omega^2\tau_0^2)], \tag{4.10}$$

$$B = \frac{\omega_0/\omega}{(1 + \omega^2\tau_0^2)}, \tag{4.11}$$

on having introduced the definitions

$$\alpha = \omega_0\tau_0, \tag{4.12}$$

$$\omega_0 = 4\pi\sigma/\epsilon_D. \tag{4.13}$$

The results (4.8) and (4.9) have been written in such a way that the quantities A and B give, respectively, the real and imaginary parts of the apparent dielectric constant $\epsilon_I(\omega)$ of the conductor in units of the constant ϵ_D. Equation (4.12) defines the dimensionless parameter α as $\omega_0\tau_0$. From (4.13) we see that ω_0^{-1} is just the characteristic time of spontaneous decay of an arbitrary net charge placed in a medium of dielectric constant ϵ_D and conductivity σ. The parameter α thus specifies the magnitude of τ_0 in units of this characteristic decay time.

The electromagnetic absorption coefficient **a** is defined as the imaginary part of q and is thus given by (4.9). The reflection coefficient R, for electromagnetic radiation incident normally on a plane surface of ionic conductor, is

$$R = \frac{q''^2 + [q' - (\omega/c)]^2}{q''^2 + [q' + (\omega/c)]^2}. \tag{4.14}$$

Figure 3 shows the calculated absorption coefficient, in units of $(\omega_0/c)\sqrt{\epsilon_D/2}$, as a function of the reduced frequency $\omega\tau_0$ for various values of the parameter α. In order to calculate the reflection coefficient, it is necessary to actually specify the value of ϵ_D. We have arbitrarily taken the value $\epsilon_D = 3$ and the resulting calculated values of R are shown in Fig. 4 as a function of $\omega\tau_0$ for the same values of α as

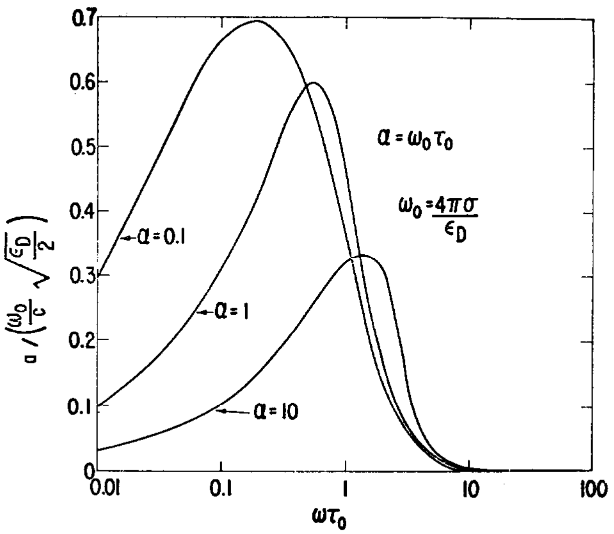

FIG. 3. The calculated electromagnetic absorption coefficient versus frequency for various values of the parameter α.

were used in Fig. 3 for **a**. Figures 3 and 4 exemplify the theoretical behavior of the Drude conductivity (4.6). The functional form of the absorption coefficient as a function of frequency is that of a broad maximum, the position of which increases with increasing values of α. The reflection coefficient falls off from its low frequency limit of unity as $\omega\tau_0$ increases from zero to values approaching 1, while for large $\omega\tau_0$ it approaches the optical limit $(\epsilon_D^{1/2} - 1)^2/(\epsilon_D^{1/2} + 1)^2$. As the value of α increases, the transition between these two regions of behavior becomes sharper, giving rise to the appearance of a "transmission edge".

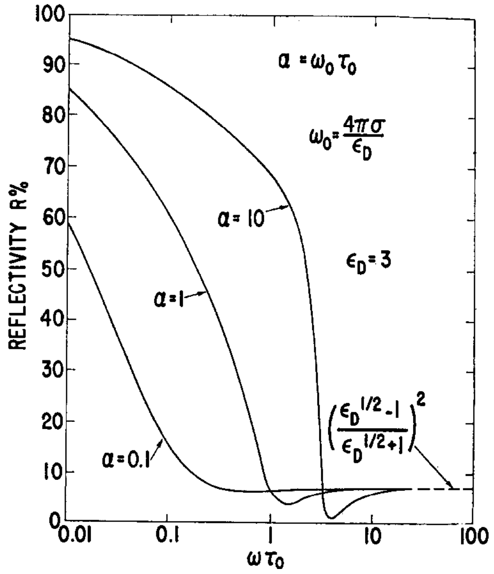

FIG. 4. The calculated electromagnetic reflection coefficient versus frequency for various values of the parameter α.

The magnitude of α is determined by the product of ω_0 and τ_0. Assuming that ϵ_D is of the order of a few times unity (4.13) gives $\omega_0 \sim 10^{13}$ sec^{-1} for σ of the order of a few Ω^{-1} cm^{-1}, corresponding to the highest levels of ionic conductivity possible for the super ionic conductors. If the free-ion like mean-free path is of the order of an interionic distance, we expect τ_0 to be of the order of a few times 10^{-13} sec. In these cases, we have the parameter α of the order of unity or so. Values of α far in excess of unity are not expected. The value of the absorption coefficient α for $\tau_0 \sim 10^{-13}$ sec, $\omega_0 \sim 10^{13}$ sec^{-1}, and $\epsilon_D \sim 3$, is of the order of 250 cm^{-1} for $\omega\tau_0 \lesssim 1$. The experimental observation of such absorptions would, of course, depend on whether or not these absorptions could be separated out from those due to other effects in the ionic crystals, particularly from those due to optical phonons (*21*).

If τ_0 is considerably larger than the typical value of 10^{-13} sec, corresponding to large free-ion like mean-free paths, it is possible to have the parameter α very much greater than unity. For example, if we accepted the large mean-free paths deduced for the ceramic oxides in Section 3 as true, then at the best levels of ionic conductivity the value of α might be as large as 10^2. For such large values of α the ionic conductor behaves as though it had an effective dielectric constant $\epsilon_I(\omega)$ given by

$$\begin{aligned}\epsilon_I(\omega) &= \epsilon_D A(\omega),\\ &= \epsilon_D\{1 - [\alpha/(1 + \omega^2\tau_0^2)]\}.\end{aligned}$$

This dielectric constant has a zero at $\omega = \omega_c$, where

$$1 + \omega_c^2 \tau_0^2 = \alpha \qquad (\alpha > 1),$$

or, for $\alpha \gg 1$,

$$\omega_c = \sqrt{a}/\tau_0.$$

For $\omega < \omega_0$, $\epsilon_l(\omega)$ is negative, and there is no propagation through the conductor, while for $\omega > \omega_0$, $\epsilon_l(\omega)$ is positive and the conductor becomes transmitting.* Thus for large α the conductor should exhibit a "transmission edge" at $\omega = \omega_c = \sqrt{\alpha}/\tau_0$. Assuming $\alpha \sim 10^2$ and $\tau_0 \sim 10^{-11}$ sec for a particular case, we have $\omega_c \sim 10^{12}$ sec^{-1}. From the experimental standpoint, a possible search for such a transmission edge in the ceramic oxides is probably made difficult by the high temperatures ($T \gtrsim 1500$°K) at which reflection measurements would have to be carried out.

Section 5. Connection with the Conventional Hopping Theory

We now conclude this paper with a brief discussion of the connection of the present theory with the conventional hopping theory.

Our result (3.1) for the ionic conductivity bears a close formal resemblance to the Arrhenius expression for the ionic conductivity of a conventional ionic conductor. Supposing, for example, that at a temperature T we have a concentration $n_i(T)$ of interstitial ions present in a conventional ionic conductor. Then the Arrhenius expression for the ionic conductivity resulting from this concentration of interstitials is, assuming cubic symmetry (*22*),

$$\sigma = \tfrac{1}{3}[(Ze)^2/k_B T]\, n_i(T)\, a_0^2 \nu_0\, e^{-E/k_B T}. \qquad (5.1)$$

Here a_0 denotes the "hopping" distance between an interstitial ion and a neighboring (vacant) interstitial site, ν_0 the vibrational frequency of the localized interstitial ion and E the "migration energy" required to effect the ionic hop. The charge on the interstitial is Ze. If we now compare (5.1) and (3.1) and identify $n_i(T)$ with n and E with ϵ_0, then the two expressions differ only in that the factor $v_0 l_0$ appears in (3.1) in place of the product $a_0^2 \nu_0$ that appears in (5.1).

The question arises as to whether or not these two results are equivalent. We argue that they are, in fact, equivalent.

If (5.1) and (3.1) are equivalent, then we must have

$$v_0 l_0 \equiv a_0^2 \nu_0,$$

or, on eliminating v_0,

$$l_0^2/\tau_0 \equiv a_0^2 \nu_0.$$

But for the interstitial hopping mechanism the free-ion like mean-free path l_0 may be identified with the hopping length a_0, so that

$$1/\tau_0 \equiv \nu_0, \qquad (5.2)$$

if (5.1) and (3.1) are to be equivalent. We now recall that *what is really meant by the ionic oscillator frequency ν_0 in the conventional hopping theory is in fact precisely the inverse of the life-time τ_0 of the excited ionic state.* Thus, for the interstitial mechanism (3.1) and (5.1) are equivalent results.

In order to demonstrate the validity of (5.2), we first note the statistical mechanical argument (*22*) that the exponential factor $e^{-E/k_B T}$ represents the fraction of time spent by a localized ion in energy states greater than E. Then if we define $P(E)$ to be the number of transitions per unit time made by a localized ion to energy states greater than E, we have by definition,* $\tau_0/P(E)^{-1} = e^{-E/k_B T}$, or

$$P(E) = \frac{1}{\tau_0} e^{-E/k_B T}. \qquad (5.3)$$

The expression used for this "hopping rate" in the Arrhenius theory (*22*) is, of course, just

$$P(E) = \nu_0\, e^{-E/k_B T}, \qquad (5.4)$$

where ν_0 is conventionally interpreted as the frequency, or some mean frequency, of oscillation of the localized ion. Clearly, however, in view of (5.3), ν_0 is to be properly interpreted as the inverse of the life-time τ_0 of the thermally excited state.

The conventional hopping theory is thus characterized by two basic phenomenological parameters, the activation energy E and the life-time τ_0 of the activated state. Applied to the conventional hopping mechanism, the free-ion like model of the present paper presents an alternative, although equivalent, formulism for constructing a transport theory in terms of these two key phenomenological parameters.

There remains, of course, one feature of the free-ion like model that has no counterpart in the conventional hopping theory, namely the postulate of the free-ion like relation $\epsilon_m = \tfrac{1}{2} M v_m^2$. We may use

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* That is, partially transmitting, since the fraction $(\epsilon_D^{1/2} - 1)^2/(\epsilon_D^{1/2} + 1)^2$ of the incident radiation is reflected by the surface.

* $P(E)^{-1}$ is the mean time which has to elapse before a transition is made to energy states $\geq E$.

TABLE VI

THE INVERSE LIFE-TIMES CALCULATED ACCORDING TO FORMULA (5.6) OF THE TEXT FOR ATOMIC SELF-DIFFUSION IN METALS

Metal	Migration[a] energy (eV)	ν_0 (10^{12} sec^{-1})	Debye frequency[b] (10^{12} sec^{-1})
Cu	1.08	7.1	7.1
Ag	0.83	4.2	4.7
Au	0.82	3.1	3.4
Al	0.62	7.4	8.8
Ni	1.5	19.6	8.9
Pb	0.56	2.1	2.1
W	2.85	6.3	6.5
Ge	1.0	6.6	7.6
Pt	1.38	4.2	4.7

[a] Data taken from the review article by N. L. Peterson (*23*). As data on germanium was also available this element has been included in the above table.

[b] Calculated according to $\nu_D = k_B \theta_D / h$, where values of the Debye temperature θ_D were taken from the tabulations given by C. Kittel (*24*).

this relation to express the free-ion like mean-free path l_0 as $l_0 = \tau_0\sqrt{2\epsilon_0/M}$. Now for the particular case of the hopping mechanism in a conventional ionic conductor we may identify l_0 with the jump length a_0, in which case it follows that

$$\tau_0 = a_0\sqrt{M/2E}. \tag{5.5}$$

Alternatively, in view of the identification (5.2), we have the result

$$\nu_0 = \frac{1}{a_0}\sqrt{2E/M}. \tag{5.6}$$

Thus, applied to the conventional hopping mechanism, the free-ion like model predicts that the atomic oscillator "frequency" ν_0 that appears in the Arrhenius hopping rate formula is related to the hopping distance a_0, the migration energy E and the ionic mass M by the explicit formula (5.6). In Table VI, we have applied formula (5.6) to the particular case of atomic self-diffusion in metals in which it is thought that the dominant mechanism of mass transport is via the vacancy mechanism. The second column shows the experimentally determined (*23*) migration energies E and the third column the values of ν_0 that are calculated from the theoretical formula (5.6). The jump distance a_0 is known from the crystal structure of a particular metal. The fourth column lists the respective Debye frequencies ν_D of the metals as obtained from specific heat data (*24*). With the exception of Ni we see that there is a remarkable agreement between the calculated values of ν_0 and the observed Debye frequencies. We consider this agreement to constitute fairly satisfactory evidence for the basic validity of the postulate of the free-ion like relation between ϵ_m and v_m. Lattice dynamical calculations of the Arrhenius frequency ν_0, based on the reaction coordinate method (*25*), give values of ν_0 somewhat smaller than, although of the same order of magnitude of, ν_D.

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