A Theoretical Interpretation of the Electronic Properties of Metal–Molten Salt Mixtures

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Abstract: This paper suggests a theoretical interpretation of the electronic properties of metal-molten salt mixtures using as a basis recent developments in the theory of the electronic structure of disordered systems. It is argued that there can be both localized and extended states in metal-molten salt systems. The localized states arise because of the existence of fluctuations of the potential and are not necessarily related to particular structural features in the liquid. The qualitative implications of this proposal are examined with respect to the conductivity, the magnetic susceptibility, and the absorption spectra of various metal-molten salt systems. It is found possible to interpret the striking difference between the concentration and temperature dependencies of the conductivities of dilute Na–NaX and K–KX melts and the insensitivity of their spectra to the anion species. The interpretation put forward also permits prediction of the qualitative behavior of Li–LiX and Cs–CsX melt properties. Tests of this set of predictions can provide the information necessary for the confirmation or the rejection of the model proposed.

Some years ago it was discovered that there is a component of the dc conductivity of an alkali metal–molten alkali halide mixture that can be attributed to electronic motion.[1,2] In the almost pure salt region the behavior of the conductivity, and of the magnetic susceptibility, suggests the existence of localized states, while in the high metal concentration region (greater than about 50 mol % metal), the data available are consistent with a model in which nearly free electrons are scattered by the anions in the mixture. Experimental studies of other metal-molten salt systems have established the existence of similar phenomena. These observations imply that alkali metal-molten alkali halide mixtures exhibit the nonmetal → metal transition. Given that, in these mixtures, all the ions are spherically symmetric, and the lowest unoccupied orbital of the alkali ion has s symmetry, they are probably the simplest systems to undergo this transition.

Theories of the electronic states of disordered systems have been put forth by Mott,[3] Cohen,[4] and others.[5] These predict that disorder increases the widths of the one-electron bands relative to those in the corresponding perfect crystals, and also broadens the sharp band edges into "tails." The states in these tails are localized and electrons which occupy them have a small, thermally activated, mobility. In contrast, in the center of the band the states are best represented by impurity scattered extended waves. Electrons which occupy these states have a large mobility which decreases as the temperature increases.

It is important to emphasize that the localized states to which we refer are not (necessarily) the same as those commonly spoken of by chemists. In particular, they are not (necessarily) associated with specific structures in the liquid. The point is, rather, that fluctuations in potential associated with irregularity in the positions of the ion cores lead to localization. This can occur without the creation of specific structures such as vacancies.

It is the purpose of this paper to apply the ideas of the theory of the electronic structure of disordered systems to the interpretation of the properties of metal–molten salt mixtures. In the absence of detailed knowledge of the ionic distribution functions, and of the effective electron–ion interaction potentials, we cannot compute the properties of these mixtures. Consequently our analysis will be of a qualitative nature, employing only general arguments which have sound physical basis. In addition, we make some predictions which can be used to test the consistency of our interpretation.

Some Experimental Data

In this section we cite the observations which any interpretation of the electronic properties of metal–molten salt mixtures must explain in an internally consistent fashion. The reader is referred to the original literature for the data from which the following statements are derived.

A. Conductivity. Bronstein and Bredig[2] studied the conductivities of Na–NaX and K–KX melts, varying both temperature and the metal concentration. They demonstrated that there is a striking difference between the concentration and temperature dependences of the conductivities of K and Na systems. The salient features of these data are the following. (i) In the zero (excess metal) concentration limit the mobility of the electrons in Na systems is about twice that in the equivalent K systems. (ii) In the zero (excess metal) concentration limit the temperature dependence of the mobility is very much smaller in the Na–NaX than in the K–KX melts. (iii) As the concentration of the metal increases the average electron mobility in Na–NaX melts decreases, while in K–KX melts it rises rapidly. (iv) The temperature dependence of the average electron mobility in Na–NaX melts increases from (near) zero to a positive value as the Na concentration increases. (v) The reported studies of Na–NaX systems cover only the low metal concentration range. The available data do suggest, in the case of Na–NaBr, that, following the initial decrease with increasing concentration, the average electron mobility starts to increase when the metal concentration reaches 10 mol %.

B. Magnetic Susceptibility. Studies of the magnetic susceptibility of Na–NaCl melts have been reported by Arendt and Nachtrieb.[6] These show that the molar susceptibility of the added metal decreases with increasing metal concentration even more rapidly than one would expect from a simple free electron gas model.

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[1] M. A. Bredig, *Molten Salt Chem.*, 367 (1964).

[2] H. R. Bronstein and M. A. Bredig, *J. Amer. Chem. Soc.*, 80, 2077 (1958).

[3] N. F. Mott, *Advan. Phys.*, 16, 49 (1967).

[4] M. H. Cohen, *J. Non-Cryst. Solids*, 2, 432 (1970); 4, 391 (1970).

[5] E. N. Economu and Morrel H. Cohen, *Mater. Res. Bull.*, 5, 577 (1970).

[6] R. H. Arendt, Ph.D. Thesis, University of Chicago, 1968.

C. Absorption Spectra. Gruen, Krumpelt, and Johnson[7] have reported studies of the electronic absorption spectra of M–MX systems just above their melting points. Their spectra show insensitivity to the species of halide ion and depend, almost exclusively, upon the species of metal (Na or K) present. In both Na–NaX and K–KX melts the reported spectra are single peaked broad absorption bands. The spectra of the K–KX melts seem to have a low energy cutoff, but in the Na–NaX systems there is still strong absorption at the lowest energy for which data are reported.

Some Theoretical Notions

We consider first the essential features of the electronic structure of a disordered material.[3–5] For the present we are not concerned with the source of the disorder; we shall return later to a discussion of the special features of the M–MX melt.

Suppose a perfect crystal is disordered continuously through some process. In the perfect crystal the band edge is sharp, the band gap is well defined, and the density of one electron states (in the free electron approximation) is of the form

$$D(E) \propto E^{1/2} \tag{1}$$

where E is the energy above the bottom of the band. As the crystal is disordered the band edge first ceases to be sharp and then further broadens as the disorder increases. The electron wave functions change accompanying the change in form of the density of states. It is assumed (and verified by model calculations) that there exists some critical energy, E_c, such that for $E < E_c$ all states are localized and for $E > E_c$ all states are extended. A wave function corresponds to an extended state if there are paths extending to the boundaries of the system lying entirely in regions where the wave function is not negligibly small in amplitude. Put another way, if one were to insert into the band an electron at time $t = 0$, and place that electron on, *e.g.*, an ion, the probability of finding the electron on that same ion in the limit as $t \rightarrow \infty$ is ($a(t)$ is the probability amplitude function at time t)

$$\lim_{t \rightarrow \infty} \langle a(0) | a(t) \rangle = 0 \tag{2}$$

for an extended state[8] and

$$\lim_{t \rightarrow \infty} \langle a(0) | a(t) \rangle \neq 0 \tag{3}$$

for a localized state. The limit (3) has been asserted to be equivalent to the vanishing of the conductivity at $T = 0°$K and conversely the limit (2) to be equivalent to the existence of a nonzero conductivity at $T = 0°$K.

The energy E_c dividing the regions of localized and extended states varies with the extent of disorder but is precisely defined for any given amount of disorder, for localized and extended states cannot belong to the same energy except accidentally, since any infinitesmally small perturbation would mix the two states and thereby generate two extended states.

We must expect that in the general case there are, in fact, two characteristic energies, E_c and $E_{c'}$, separating localized and extended states near the bottom and top of the band, respectively. As s a disorder increases more and more localized statethere created and E_c and $E_{c'}$ move deeper into the band. When E_c and $E_{c'}$ merge, at some critical level of disorder, all the states in the band are localized. For our purposes we need consider only the states near the bottom of the band. A schematic representation of the properties of states near the bottom of the band is displayed in Figure 1.

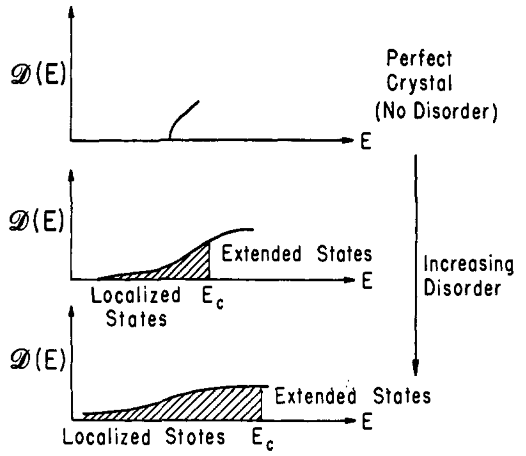

Figure 1. A schematic representation of the change in the density of states with increasing disorder.

Associated with the change from localized to extended states is a dramatic change in conductivity. There is, therefore, a "mobility edge" at or very near to E_c.

The conductivity, σ, at finite temperature for a partially filled band is given by

$$\sigma = e\int D(E)\mu(E)\mathrm{f}(E)\mathrm{d}E \tag{4}$$

where e is the electronic charge, $\mu(E)$ the mobility at energy E, and $\mathrm{f}(E)$ the Fermi distribution function. The density of states, $D(E)$, $\mathrm{f}(E)$, and the number of electrons in the band N are related by the conservation condition

$$N = \int_{-\infty}^{\infty} D(E)\mathrm{f}(E)\mathrm{d}E \tag{5}$$

which also determines the Fermi energy E_F.

The mobility of electrons in localized states is given, approximately, by the relation[3]

$$\mu_{\mathrm{loc}} \approx \left\langle \frac{e\nu_{\mathrm{loc}}R^2}{k_BT} e^{-W/kT} \right\rangle \tag{6}$$

with ν_{loc} a "phonon" frequency, R the separation of localized state centers, and W the energy of activation. For large T, W is independent of T. Equation 6 is a good representation only when the electron energy lies well below E_c.

In the case that the electron energy exceeds E_c the conductivity is no longer thermally activated. However, in a disordered system even low-lying extended states do not have relative phase coherence (from site to site) in the electron wave function. Because of the randomness of phase, and because of resonant scattering, the mobility of electrons in extended states just above E_c is considerably smaller than in the corresponding "almost free electron" band of a crystal. Mott[3] and Cohen[4] have independently suggested that

$$\mu_{\mathrm{ext}} \approx \left\langle \frac{e\nu_{\mathrm{ext}}R^2}{k_BT} \right\rangle \tag{7}$$

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(7) D. M. Gruen, M. Krumpelt, and I. Johnson in "Molten Salts," Marcel Dekker, New York, N. Y., 1969, p 169.

(8) P. W. Anderson, *Phys. Rev.*, **109**, 1432 (1958).

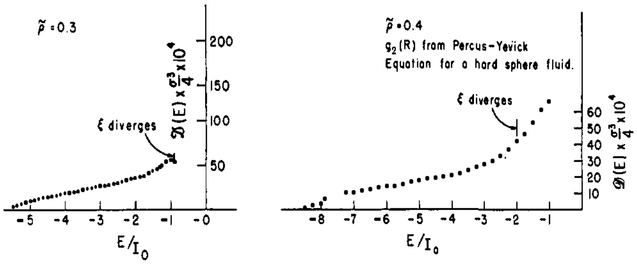

Figure 2. Results of the calculation of the density of states of a fluid from the Katz–Rice theory. The energy is measured in units of the ionization potential of the localized state and the reduced density is defined by $\tilde{\rho} \equiv 8N/\alpha^3\Omega$, where there are N centers in the volume Ω and the localized wave function is of the form $\psi \propto \exp(-\alpha r)$. The quantity ξ is related to the thermal average of the two-site one-electron Green's function. The integral equation is so defined that the divergence of ξ means that there can be no localized states in the system. Hence these figures show only the structure of the tail of localized states in the fluid.

where ν_{ext} is an exchange frequency resulting from electronic interactions. It is visualized that the electronic motion near the mobility edge is of the diffusive type whether the states are localized or extended, because in each case phase randomness limits the coherence length of the electron wave function to about one internuclear separation. However, in the localized states below E_c thermal activation is required, whereas in the extended states just above E_c the overlap of wave functions corresponding to neighboring sites permits motion of the electron without thermal activation. In general $\mu_{\text{ext}} > \mu_{\text{loc}}$.

Localized States in a Liquid

The properties of disordered materials described in the last section have been deduced from the common features of a number of models. Until recently, however, none of the models considered had characteristics in any way similar to those which are typical of a liquid. In a separate paper[9] we have proposed a theory of the density of states of a moderately dense fluid, including the special role played by short range ordering.

The basic mathematical technique employed is the conversion of partially summed, infinite order, perturbation theory to integral equation representation. Two integral equation approximations to the renormalized perturbation series for the one electron two-site Green's function of an off-diagonal disordered system have been developed. These treat the radial disorder in a realistic, although not exact, fashion. The integral equations themselves have a structure analogous to that of the successful Percus Yevick and hypernetted chain approximate theories of the pair distribution function of a simple liquid. Numerical calculations, which delineate the properties of the integral equations developed, show the existence of localized states below a critical energy and are consistent with the predictions from much simpler lattice models of disordered systems. In particular, the breadth of the tail of localized states depends on the density. One such calculation is presented in Figure 2; it refers to reduced ion core densities of 0.3 and 0.4, quite close to typical cation densities in molten salts.

The ubiquity of localized states in disordered media leads us to examine the extent to which we can interpret the properties of metal–molten salt mixtures given the following general hypotheses. (1) In the melt there is a low energy tail of localized states in the density of states. (2) In the low metal concentration region only part of the low energy region of the alkali s band is occupied.

It is appropriate to again emphasize that the localized states arise in the spectrum because of fluctuations of the potential about its mean value. Our calculations (and those of others) are not based on assumed local trapping structures.

Alkali Metal–Alkali Metal Halide Melts

A. Interpretation of the Conductivity. The conductivities of K–KX, Bi–BiX and higher metal concentration (>10%) Na–NaX systems have been successfully[3] explained in terms of a thermally activated hopping model.[10,11] However, as mentioned in the experimental data, the conductivities of the low concentration sodium–sodium halide melts do not conform to this picture. In the limit of zero excess metal concentration sodium–sodium halide systems have unexpectedly high electron mobilities, as compared to their potassium analogs, and the mobilities are insensitive to temperature. As the metal concentration increases one does not find the exponential increase of mobility predicted by the hopping model; indeed, there is a sharp initial decrease in mobility accompanied by a strong, positive temperature dependence of the mobility. Then as the metal concentration exceeds approximately 10%, the mobility, which is now thermally activated, starts to rise and appears very similar to that in the other metal–molten salt mixtures.

Let us make the following assumptions. (1) When the anions are the same species, the fluctuations in the liquid medium perturb the sodium 3s wave function in the Na–NaX less than they do the potassium 4s wave function in K–KX since the sodium electron is more tightly bound (by about 1 eV) and less diffuse ($\psi_M \propto e^{-\alpha r}$; $\alpha_{Na} > \alpha_K$). (2) The fluctuations in potential in the liquid medium arise from the existence of a distribution of ion–ion separations and, when metal is added to the salt, from the existence of a distribution of possible local compositions. We expect that the ranges of the perturbations caused by fluctuations in the anion–metal and metal–metal interactions increase rapidly upon addition of metal to the pure salt. While detailed multicomponent band structure calculations using either experimental or Monte-Carlo radial distribution functions could test this assumption, they are, due to the complexity of the system, unavailable at this time. However, it is plausible that our assumption is valid since as metal atoms are added there are no longer sufficient halide ions available to completely coordinate each metal atom, thus allowing nearest-neighbor metal–metal distances to fluctuate from close packing to those of the pure salt.

On the basis of the first assumption one can predict that in a system of given spacial disorder the perturbations and consequently, according to the Cohen and Mott theories, the bandwidth and the number of

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(9) I. Katz and S. A. Rice, to be published.

(10) S. A. Rice, *Discuss. Faraday Soc.*, 32, 181 (1962).

(11) D. Raleigh, *J. Chem. Phys.*, 38, 1677 (1963).

localized states will be greater in a potassium system than in a sodium system. Therefore, with a given excess metal concentration it is possible for the Fermi level to be above the mobility edge, E_c, in the sodium case, and below it in the case of potassium.

On the basis of the second assumption one would expect the mobility edge to move up in energy with respect to the Fermi level as the metal concentration is increased.

We have already remarked that all models of the density of states of disordered systems have the common feature of a tail of localized states below an energy E_c. It is, therefore, possible to amplify our remark on the relationship between the number of localized states and the magnitude of the potential fluctuations by examining a model for which the appropriate numerical calculations exist. Consider the case of a Lorentzian alloy, where the off-diagonal matrix elements of the interaction, V_{mn}, are all equal and constant for nearest neighbors and zero otherwise, but the site energies, E_n, have a Lorentzian distribution of half width Γ, so that

$$P(E_n) \propto (E_n^2 + \Gamma^2)^{-1} \tag{8}$$

It has been shown that as the width of the distribution of site energies increases the mobility edge moves in toward the middle of the band.[5] When Γ is sufficiently large all the states are localized (this is an Anderson transition). While this complete localization would not occur in the case of off-diagonal randomness (*i.e.*, V_{mn} with random values as a function of m, n), it is certainly reasonable to expect the proportion of localized states to increase rapidly with increase in disorder.

It then follows directly that in the low excess metal region of a metal-molten salt mixture, where the band is sufficiently empty to neglect electron-electron effects such as screening, there exist two distinct possible dependencies of the average electron mobility upon the metal concentration. The first case arises when the pure molten salt one-electron bandwidth and disorder are sufficiently great that the band edge is more than k_BT below the mobility edge. Under these conditions as one adds metal to the melt almost all the electrons go into localized states, since, by assumption 2, the number of these states increases more rapidly than the number of electrons added. The electron mobility would then be exponentially dependent on the average metal-metal distance and $d\mu/dT$ would be greater than zero. Potassium-potassium chloride and bromide systems seem to belong to this case.

In the case where the initial states are within k_BT of the mobility edge, a majority of the electrons will be in the extended states and, due to their much higher mobility, these electrons will dominate the conductivity. In the zero concentration limit, then, the temperature dependence of the mobility should be small since, while an increase in temperature will promote more electrons into extended states, there is an opposing drop ($\propto \exp(T^{-1/4})$) in their mobility.[3] However, as more metal is added the rapid increase in the number of localized states will both lower the average electron mobility and allow the promotion effect to dominate the temperature dependence until the Fermi level is much more than k_BT below the mobility edge. Then the system will exhibit pure "hopping" mobility, as in the first case discussed above. We assert that sodium-sodium halide systems exhibit this behavior with the transition to totally localized states occurring at about 10% excess metal in Na-NaBr.

A simple demonstration model, showing that the gross features of the conductivity minimum in Na-NaX melts can be closely mimicked using these ideas, is presented in the Appendix.

B. Interpretation of the Magnetic Susceptibility. The localized states in the metal-molten salt mixture actually extended over many ionic sites. In this situation spin pairing is energetically feasible, and we then expect an "almost free electron" type magnetic susceptibility, as is found experimentally. Of course the quantitative details of the dependence of the susceptibility on concentration depend on the, as of now uncalculatable, exact density of states. In the lowest order of approximation the magnetic susceptibility of a metal is proportional to its density of states at the Fermi level. Models by Edwards[12] and others[5] for the low energy tail of the density of states in a liquid metal show in general that for a given occupation of the spectrum of states at zero temperature, the density of states at the Fermi level for a disordered system is less than or equal to that of the corresponding perfect lattice.

$$[D(E_F, T = 0)]_{\text{disordered}} \leq [D(E_F, T = 0)]_{\text{ordered}} \tag{9}$$

The equality holds only at the limit of zero occupation. Consequently, the model proposed herein agrees at least qualitatively with the results of Arendt and Nachtrieb. They found that in Na-NaCl melts the measured susceptibilities were less than those of an equivalent free electron gas. The interpretation offered by them is that the electrons move in the "free volume" of the melt which is less than the geometric volume. But the calculations of Coopersmith and Neustadter,[13] and of Eggarter and Cohen,[14] show that the density of states for an electron moving in a rigid sphere fluid (the Arendt-Nachtrieb model) has a low energy tail of localized states, in complete agreement with our arguments (see Figure 3). It is not possible to ignore these localized states and treat the electrons as if they were in extended (free electron) states in a reduced volume.

C. Interpretation of the Optical Spectrum. Our model also leads to expectations in general agreement with the observed optical spectra. In systems with localized states, *e.g.*, K-KX melts, our model leads us to expect a low energy cutoff in the spectrum corresponding to the difference in energy Δ between the highest energy significantly occupied state and the lowest energy extended state (see Figure 4). We are also led to expect that no such cutoff should exist for systems with extended states, *e.g.*, Na-NaX melts. These expectations follow from the observation that the energies of two nearby localized state centers are entirely uncorrelated. Thus, since the dipole matrix element that determines the absorption strength depends on the overlap of the wave functions of the

(12) S. Edwards, *Proc. Phys. Soc., London* (*Solid State Phys.*), 3, L31 (1970).

(13) H. E. Neustadter and M. H. Coopersmith, *Phys. Rev. Lett.*, 23, 585 (1969).

(14) T. P. Eggarter and M. H. Cohen, *ibid.*, 25, 807 (1970).

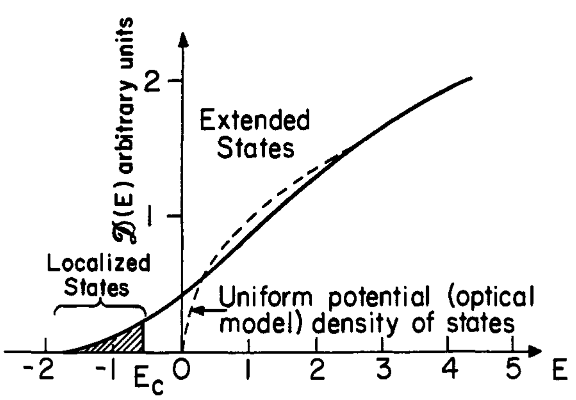

Figure 3. The density of states for an electron moving in a gas of hard spheres. The optical model refers to the energy spectrum $E(k) = V_0 + \hbar^2k^2/2m$; hence $D(E) \propto (E - V_0)^{1/2}$ for $E > V_0$ and $D(E) = 0$ for $E < V_0$, where V_0 is the optical potential $2\pi\hbar^2\rho a/m$ with ρ the density and a the zero-energy electron scattering length.

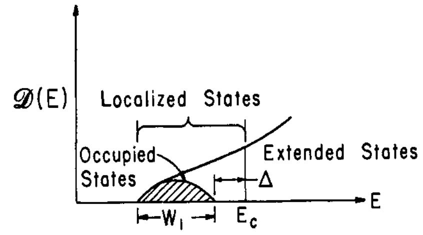

Figure 4. A schematic representation of the hypothesized density of states for K–KX melts.

initial and final states, only localized state → extended state or extended state → extended state transitions need be considered.

The absorption band shape depends on the energy spread of the initial occupied states, the increasing density of extended states as E increases, and the general E^{-s} ($s \geqslant 1/2$) decay of the oscillator strength for a discrete level, free electron band transition, as shown in Figure 5. The spectra reported by Gruen, Krumpelt, and Johns have features in agreement with the expectations cited.

Other Models

It is now necessary to examine other possible models of dilute metal–molten salt mixtures to see if they are consistent with the available data. From the spectrum of possible models of dilute metal–molten salt mixtures four may be chosen as representative of clearly different situations. 1. The electron is in a conduction state, *i.e.*, is essentially free aside from polaron-like interactions.[6,15] 2. The electron occupies an anion vacancy in the melt, much like an F-center in crystalline alkali halides.[7] 3. The electron is in an "atomic-like" bound state centered on an alkali ion.[10] 4. The electron is trapped or is strongly resonantly scattered by multisite localized states.

The free electron picture (1) fails to account for the generally nonnegative value of dμ/dT. Model 1 is grossly consistent with the magnetic susceptibility data, although a straightforward application of the theory of magnetic susceptibility of free electrons does not lead to quantitative agreement with experiment.

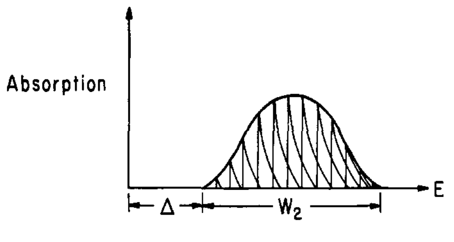

Figure 5. The absorbtion band shape corresponding to the density of states shown in Figure 2.

If model 2 were a valid representation of the metal–molten salt mixture we must expect there to be a large excess volume of mixing, as is the case for Na–NH_3 solutions where the electron is known to be localized in a cavity. This expectation is in contradiction with measurements by Bredig, which show no excess volume of mixing in Na–NaCl melts. Furthermore, if single anion cavities were the traps for electrons the coulomb repulsion between electrons would make double occupancy (and spin pairing) very unlikely. We would then expect the molar magnetic susceptibility, χ_m, for excess metal, to be constant, which it is not. The likelihood that double anion vacancies are doubly occupied by electrons appears to us to be extremely small. We do not believe such structures (double vacancies) are characteristic of the liquid, and this view is supported by the Monte-Carlo simulation studies of Singer and Woodcock[16] and Krogh-Moe, Ostvold, and Forland.[17] Finally, there appears no need to invoke specific structures, such as single or double anion vacancies, in order to have localized states. That, indeed, is the key point in our interpretation of the properties of M–MX melts.

The atomic like tight binding model 3 also leads one to expect almost constant χ_m, in disagreement with experiment. However, the qualitative behavior of the electron mobility in potassium systems agrees quite well with that expected from a tight binding thermally activated hopping model as originally proposed by Rice.[10] Localized electrons in the theory proposed here, model 4, also conduct through a thermally activated hopping process, thus resulting in the same qualitative temperature and average metal–metal separation dependences as in the Rice model. Consequently, the two models predict the same type of conductivity behavior for localized, *e.g.*, potassium, systems.

Finally, the insensitivity of the optical spectra of metal–molten salt mixtures to the species of anion is unlike the behavior of F-center electrons. Models 1 and 3 are equally incapable of explaining a simple absorption band in the optical spectrum.

We conclude that only model 4 is consistent with all the experimental data. To this negative criterion we can add some predictions with which model 4 can be tested. These are the following. (1) Li–LiX melts should exhibit mobility transitions qualitatively similar to those in Na–NaX melts. (2) In contrast, Cs–CsX melts should exhibit only a thermally activated hopping

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(15) E. G. Wilson, *Phys. Rev. Lett.*, 10, 522 (1963).

(16) L. V. Woodcock and K. Singer, *Trans. Faraday Soc.*, 67, 12 (1971).

(17) T. Forland, T. Ostvold, and J. Krogh-Moe, *Acta Chem. Scand.*, 22, 2415 (1968). J. Krogh-Moe, T. Ostvold, and T. Forland, *ibid.*, 23, 2421 (1969).

mobility in the salt rich region. (3) The excess volumes of mixing of all alkali metal–alkali halide molten mixtures should be very small. (4) At a moderate concentration of Na in NaX (say of the order of 20%) a low-energy cutoff should appear in the absorption spectrum. (5) For a given halide ion, in the limit of zero excess metal concentration in the M–MX melt, we expect that

$$\mu^e_{\mathrm{Na-NaX}} > \mu^e_{\mathrm{Li-LiX}}$$

$$\mu^e_{\mathrm{Cs-CsX}} > \mu^e_{\mathrm{K-KX}}$$

Quantitative tests of this set of predictions can provide the information necessary for the complete confirmation or the rejection of the model proposed in this paper.

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Appendix

A Simple Demonstration Model. As mentioned previously, calculations on real metal–molten salt systems are, at this time, prohibitively difficult to perform. In order to demonstrate the plausibility of the arguments advanced in the text, we have utilized the "coherent potential" model of a Lorentzian alloy to show that, given our assumptions, the qualitative behavior observed in the metal–salt systems can be reproduced.

The model considered is a simple cubic lattice with constant nearest-neighbor interactions and a Lorentzian distribution of widths for the site energies. We have set the $\Gamma = 0$ (eq 9) band width at 1 eV, $k_BT = 0.1$ eV, and assumed the dependence of Γ on concentration to be quadratic.

$$\Gamma = ax^2 + \Gamma_0 \qquad (10)$$

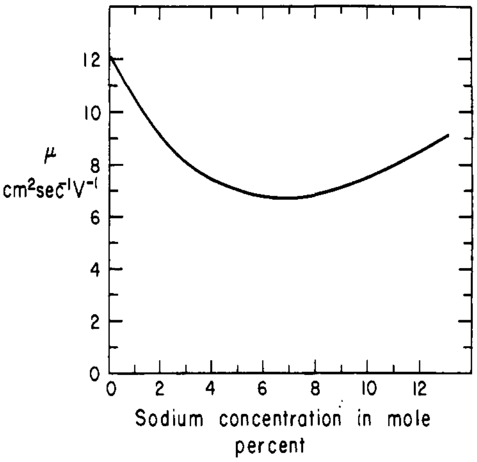

Figure 6. A demonstration model calculation of the mobility as a function of metal concentration for the model described in the Appendix.

For simplicity we assume that the extended state mobility is just the zero metal concentration limit of the electron mobility in molten sodium bromide and the hopping mobility a linear approximation to a smooth extrapolation in the greater than 10% metal region. First we set $\Gamma_0 = 0$ and choose a such that at $x = 10\%$; 10% of the states are k_BT below the mobility edge. Using the crude assumption that half the electrons less than k_BT below the edge are promoted to extended states, we obtain the results displayed in Figure 6. Note the similarity of this curve to that found by Bredig and Bronstein for Na–NaBr. In order that all states always be localized it was found that one needed an initial Lorentzian width, Γ_0, of only 0.06 eV.

It cannot be overemphasized that this calculation proves nothing; it has been presented only to demonstrate that in a calculable model of a disordered system it is possible to obtain the type of mobility behavior observed in sodium–sodium halide melts by assuming an extended to localized states transition.