DYNAMICS OF LOCALIZED ELECTRONS IN METAL-MOLTEN SALT SOLUTIONS

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The properties of electrons in molten salts are reviewed with special emphasis on the dynamics of electrons in alkali halides. Lattice polarization effects (polarons) are of great importance for the binding of electrons in F-center analogues and for the stability of hole centers. The latter may determine the recombination times for electrons studied by optical transient absorption. A simple non-activated model of transport by localized electrons is outlined.

I. INTRODUCTION

Understanding the behavior of electrons introduced into the highly coulombic structure of a molten salt presents a continuing challenge. Among the various methods of introducing excess electrons, the best known is the addition of metal to form a metal-molten salt solution. Many metals form such solutions and in some cases metal solubility is so high that homogeneous solutions can be formed over the full range of concentration up to the pure metal. Relatively low electron concentrations may be achieved without addition of metal by direct injection from a cathode or by ultraviolet irradiation.

The structure of the states occupied by low concentrations of excess electrons together with their transport characteristics are problems of central importance. After considerable and longstanding controversy it has been established during the last few years that the electrons are invariably localized rather than forming some kind of dilute metal (1). However, the forms of the localized states differ markedly among different classes of molten salt. In the alkali halides, for example, the states are closely analogous to the F-centers in which excess electrons localize in alkali halide crystals. In addition, there is evidence in these salts for spin-paired two-electron species such as $M^-$, $M_2^-$, paired or doubly occupied F-centers, etc. (2,3) In polyvalent metals, two-electron species in the form of lower valence ions frequently dominate. The formation of $\text{Bi}^+$ in the bismuth trihalides $\text{Bi-BiX}_3$ is an example of this type of localized state.

My concern in this paper is mainly with the time-dependent properties of electrons in the alkali halides. The static structure of the F-center analogues in these salts is now reasonably well established, at least at low electron concentrations. However dynamic properties of the electrons present some apparent inconsistencies which have not yet been addressed in a comprehensive manner. I will discuss the available experimental results, including nuclear
magnetic resonance and picosecond transient optical absorption, and will describe a simple picture relating the observed lifetimes of localized electronic states to electronic transport.

II. PROPERTIES OF ELECTRONS IN ALKALI HALIDES

Perhaps the most direct demonstration of the localization phenomenon is provided by measurements of the hyperfine correlation time in nuclear magnetic resonance. The rate for longitudinal relaxation of nuclear spins interacting with unpaired electrons is

\[ 1/T_1 = \omega_i^2 \tau_e \]

where \( \omega_i \) is a frequency characterizing the strength of the magnetic hyperfine coupling and \( \tau_e \) is a correlation time for the rapid local field fluctuations. For mobile electrons \( \tau_e \) is essentially the association time for a particular electron-ion pair.

The concentration dependence of the hyperfine correlation time in Cs-CsI solutions is shown in Fig. 1 for the full range of concentrations (4). From a value of about \( 10^{-15} \) s typical of electron-ion interactions in a metal, \( \tau_e \) increases dramatically with decreasing cesium content reaching a value of about \( 2 \times 10^{-12} \) s for concentrations around 1%. In this limit the electron-ion correlation time \( \tau_e \) is comparable with the ion-ion correlation time \( \tau_i \) estimated from the diffusion coefficient. Thus the electrons are localized in the vicinity of particular ions only as long as is permitted by fluctuations of the liquid structure itself.

Excess electrons localized in molten alkali halides are responsible for strong optical absorption bands in the red or near infrared. The spectrum of K-KCl shown in Fig. 2 is typical (5). The similarity of these bands to F-bands observed in the crystalline state made plausible Pitzer's suggestion (6) of the F-center model for electrons in the liquid. In this model the electron is solvated by cations and roughly fulfills the role of an anion in the strongly charge-ordered structure. The magnitudes of the magnetic hyperfine fields felt by neighboring ions are in excellent agreement with this model (2,7). Further support has come from recent path integral-molecular dynamics calculations (8) which show the electron solvated by roughly four neighboring cations. Finally, Senatore et al. (9) calculated the trend of the optical absorption energy through the family of alkali halides using a spherical approximation for the F-center potential and they obtained good agreement with experiment.

Several experiments provide information on the dynamics of the excess electrons. NMR relaxation, already mentioned, shows that electrons interact with neighboring ions for times comparable with ion-ion interaction times. The electrical conductivity, however, shows that the average mobility of the electrons greatly exceeds that of the ions. Addition of excess metal produces an electronic contribution to the conductivity on the order of \( 1 \) (\( \Omega \) cm\(^{-1} \)) percent excess
metal (1,10). This corresponds to an average electronic mobility \( \mu_e \approx 10^{-1} \text{cm}^2/\text{Vs} \). The ionic mobility \( \mu_i \) is of the order of \( 10^{-3} \text{cm}^2/\text{Vs} \). Thus the electrons move rapidly from one localized state to another, spending a small fraction of the time moving much more rapidly than the ions. Yet another time scale is introduced by recent electron spin resonance (ESR) studies. Nicoloso and Freyland (11) observed ESR signals in several solutions of excess metal in eutectic alkali halide mixtures. The ESR lines, which they attribute to F-center analogues, are very narrow (5-10 G) implying spin lifetimes \( \tau_s \geq 10^{-8} \text{s} \).

We have recently undertaken a series of picosecond transient absorption studies with the hope of gaining an additional perspective on electron dynamics in alkali halides (12). These experiments utilize a pulsed YAG laser which produces pulses of 30-50 ps width at 1064 nm. In the experiment, a fourth-harmonic pulse (266 nm) creates an initial population of electron-hole pairs by two photon absorption. The absorption due to localized electrons is probed with the 1064 nm fundamental. The excitation and probe energies are compared with the absorption spectrum of K-KCl in Fig. 2. In preliminary experiments, an excitation of roughly \( 10^{18} \) photons/cm\(^3\) yielded a 25% reduction in transmission at 1064 nm. Under the assumption that the short-time absorption spectrum near 1 eV is the same as shown in Fig. 2, we estimate that a density \( n_F \sim 10^{17} \text{cm}^{-3} \) of F-center analogues is created in the irradiated portion of the sample. Our observation that the induced absorption develops in less than 100 ps is consistent with a previous report of transient absorption at 532 nm in KCl at a single delay time of 46 ps (13). We found that the induced absorption persists with no detectable change out to at least 1 ns. Thus the recombination time exceeds by at least one order of magnitude the estimated mean time (\( \sim 100 \text{ps} \)) between electron-hole collisions at a density of \( 10^{17} \text{cm}^{-3} \).

The various time-dependent properties discussed above raise several problems concerning the electron dynamics:

(i) The optical absorption energy \( \Delta E_{\text{opt}} \sim 1 \text{eV} \) indicates that the localized electron sits in a potential well whose depth (\( > 1 \text{eV} \)) greatly exceeds \( kT \) (\( \sim 0.1 \text{eV} \)). A crude estimate of the maximum rate for thermal hopping out of such a well gives \( \nu_{\text{hop}} \leq 10^{14} \exp(-\Delta E_{\text{opt}}/kT) \sim 10^9 \text{ s}^{-1} \). For a diffusive transport process with mobility

\[
\mu = e a^2/6kTr, \quad (2)
\]

an enormous mean hopping distance \( a \geq 700\text{Å} \) is required to achieve the observed mobility \( \mu = 0.1 \text{cm}^2/\text{Vs} \) with a hopping rate \( \nu_{\text{hop}} = 1/\tau \leq 10^9 \text{s}^{-1} \).

(ii) The NMR correlation times \( \tau_e \) indicate that a given electron-ion configuration is stable for only a few ps. What is the relationship of \( \tau_e \) to the spin-lifetimes \( \tau_s \sim 10^{-8} \text{s} \) inferred from the ESR linewidths?
(iii) Why does the recombination time in the transient absorption experiments so greatly exceed the mean collision time with recombination centers?

We will discuss these points in the next section after consideration of lattice relaxation effects (polarons).

III. POLARON EFFECTS

A. Localized Electrons (F-centers)

The importance of lattice polarization around F-centers in crystals is well-known. Compared with an unoccupied vacancy, the distance from an F-center to the first neighbors is contracted by about 10% (14). Because of the looseness of the liquid structure and relative ease with which second neighbors can adapt to movement of the first neighbors, it is reasonable that polarization effects should be larger in molten salts. In fact, the recent numerical work of Parrinello and Rahman (8) yielded a 30% contraction relative to the normal anion-cation distance. This implies a self-trapping effect in which the potential well is deepened substantially by the presence of the electron.

The optical transition, in the Franck-Condon approximation, occurs in a static lattice. In the thermal release of an electron during the transport process, in contrast, ions are free to move. The energy needed to excite an electron out of the static potential well is offset by the large coulomb energy recovered as the neighboring cations expand outward. For the polarization calculated by Parrinello and Rahman, this energy is several electron volts and is comparable with the cohesive energy of the salt. Thus the energy of the final state (electron removed, structure relaxed) is much closer to that of the initial configuration (electron bound, structure polarized) than implied by the static potential well.

It is a simple fact that thermal energies are sufficient to permit diffusion of the ions even though the energy to remove an ion is very large. Since the coulomb energies involved are comparable, this suggests a diffusion-controlled mechanism for electron transport as well. The model summarized in Fig. 3 is based on this idea. A localized electron is initially bound in its cage of neighboring cations which are polarized. Now a diffusing anion penetrating this configuration will repel the electron, pushing it onto the cations. In terms of the potential well picture, the presence of an anion weakens the potential, allowing the electron wavefunction to spread (15). This further weakens the potential until the bound state is pushed up into the continuum. Delocalization by this process occurs on the diffusion time scale of a few picoseconds.

The continuum states lie at the bottom of the “conduction band” and are primarily metal s-states. We might expect the mobility in these states to approximate the Ioffe-Regel mobility $\mu_{IR}$ in which electrons scatter with a mean free path comparable with the interionic separation (16). The Ioffe-Regel mobility
lies in the range 1-5 cm$^2$/Vs (17). If the NMR correlation times $\tau_c$ are used for the lifetimes in the localized states, the magnitude of the conductivity requires that the electrons move 10-20Å before forming a new localized state. If the mobility in the continuum is $\mu_{IR}$, they can cover this distance in a time on the order of $10^{-14}$ s.

The picture we have described for dilute electron concentrations has much in common with earlier suggestions by Durham and Greenwood (18) and by Littlewood (19). The former authors proposed that a certain fraction of electrons are localized while the conductivity is due to the remainder. Littlewood discussed exchange between localized and delocalized electrons. In the present picture, all the electrons participate in conduction on the picosecond time scale, each spending some very short time in a high mobility state.

There is evidence at higher excess metal concentrations for the presence of additional two-electron states which affect the conductivity significantly (2,3). When such species ($M^-$, $M^2$, etc.) are stable for long times with respect to the diffusion-limited structural lifetime, such states effectively remove electrons from the conductivity process. This appears to be the case for systems such as Na-NaX at low temperatures (2). On the other hand, rapid equilibrium between two-electron species and F-center analogues can enhance the average electronic mobility giving a concentration-dependent mobility as is observed, for example, in Cs-CsX solutions (2).

Let us return to the question of the long spin relaxation times implied by the narrow observed ESR lines (11). If these electrons in eutectic hosts are as mobile as those in single salts, they must retain phase memory over a large number of conduction hops. If this were not so and electrons remained in one ionic configuration for $10^{-8}$ s, they would have to remain in conduction states for several hundred ps to provide the observed conductivity. The initial evidence from transient absorption studies indicates the electrons in conduction states localize more rapidly than this. Thus the observed spin relaxation times require spin-orbit coupling to be sufficiently weak that an electron hop has a low probability ($\sim 10^{-4}$) of producing a spin-flip in the eutectic hosts. Strong spin-orbit coupling in Cs-CsX melts was given as the reason for the absence of observable ESR in those single-salt solutions (11). The possibility that ESR in eutectic hosts is due to a minority of low mobility states in special ionic configurations is an alternative which has yet to be explored.

**B. Localized Holes**

In order to discuss the recombination dynamics of electrons generated by ultraviolet irradiation, it is necessary to consider the nature of the recombination centers, i.e., the holes. Our knowledge of these states is due in large part to studies of alkali halides (mainly iodides) containing excess halogen. The magnetic properties shown in Fig. 4 illustrate two important differences between the hole and
electron states in such solutions. The first point is the strong asymmetry in the magnetic susceptibility (3,20) with respect to stoichiometric CsI. While both excess Cs and excess I introduce paramagnetic contributions, the susceptibility increase per atom of excess I is substantially smaller than the increase per Cs atom. A significant fraction of the excess I therefore forms diamagnetic species. Second, on the scale shown in Fig. 4, there is no increase in the $^{133}$Cs nuclear relaxation (4) on the excess I side in contrast with the rapid rise which occurs as Cs is added. This shows that the paramagnetism associated with excess I resides on the I ions and couples only weakly to the Cs nuclei.

In alkali halide crystals, the dominant hole center at low concentrations is the $V_k$-center, an associated I-I$^-$ pair. The liquid-state counterpart of this simple polaron is the I$_2^-$ molecular ion. The data shown in Fig. 4 as well as optical and ESR studies (20) strongly indicate that this species is responsible for the paramagnetism associated with excess I. The diamagnetic species is believed to I$_3^-$. The concentration of paramagnetic species increases sharply with increasing temperature as might be expected from the equilibrium

$$I_3^- + I^- = 2I_2^-.$$  \hspace{1cm} (3)

In sum, there are two types of recombination centers ($X_3^-, X_2^-$) which must be considered. Both of them are small species in which the "polaron energy" is represented by the binding energy of the polyhalide ion.

We can now consider the possible recombination reactions in the irradiated pure halides. The two simplest are

$$e^- + X_2^- \rightarrow 2X^-$$  \hspace{1cm} (4)

$$2e^- + X_3^- \rightarrow 3X^-.$$  \hspace{1cm} (5)

Since both reactions involve dissociation of polyhalides, an activation energy will control the rate of recombination. In addition, reaction (5) is third order and requires simultaneous recombination of two electrons. Both factors act to reduce the recombination rate relative to the frequency of collision between a single electron and a single localized hole.

IV. SUMMARY

Polaron effects in the form of structural polarization around F-center analogues and bonding of polyhalide species play an important role in electron dynamics in molten alkali halides. The energies associated with these effects are many times thermal energies and they help account for the large optical absorption energies, low barrier to electron delocalization and long electron recombination times. I have outlined a qualitative model of electron transport in which electrons are temporarily delocalized by the diffusive motions of ions. Localization times on the order of a few ps alternate with rapid motion to new localization sites. The
transport process resembles in many respects a hopping process but no appreciable energy barrier is involved. Compared with the F-center analogues, the polyhalide hole states are more stable and recombination requires formation of an activated complex and dissociation of the species.

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Figure 1. Magnetic hyperfine correlation times for $^{133}\text{Cs}$ nuclei in Cs-CsI solutions (4).

Figure 2. Optical absorption spectrum of K$_{0.017}$ (KCl)$_{0.983}$ solution at 860°C (5). Arrows indicate energies of probe and excitation photons in ps transient absorption measurement (12).

Figure 3. Schematic representation of diffusion-controlled electron transport process in molten alkali halides. Electron initially localized in F-center analogue is delocalized as ionic diffusion destroys favorable configuration. After brief period in high mobility state, electron again forms F-center analogue at new location.

Figure 4. Magnetic properties of excess Cs and I in molten CsI. Open points, molar susceptibility (3,20); closed points $^{133}\text{Cs}$ nuclear spin relaxation rate (4).