Resolution of the Conductivity Dilemma in Liquid Solutions of Alkali Metals in Alkali Halides

W. W. Warren, Jr., S. Sotier,[a] and G. F. Brennert

Bell Laboratories, Murray Hill, New Jersey 07974

Nuclear magnetic resonance measurements are reported for liquid Na-NaBr, Cs-CsCl, and Cs-CsI solutions containing less than 10 mole% metal. Correlation of the resonance shifts, relaxation rates, and dc electrical conductivity shows that the electronic mobility is independent of concentration in Na-NaBr, in sharp contrast with the cesium solutions. The results provide an explanation for the apparently anomalous electronic conductivity observed in liquid-sodium–sodium-halide solutions.

Solutions of low concentrations of alkali metals in their molten halides exhibit an electronic contribution to the electrical conductivity which has been subject to speculation and controversy for a quarter century.[1-3] The electronic conductivity σ_e is determined from the measured total conductivity σ by subtracting the ionic contribution, assumed to be that of the pure molten alkali halide, i.e., $\sigma_e = \sigma - \sigma_{\text{halide}}$. Attention has been drawn, in particular, to an apparent anomaly in the concentration dependence of σ_e for Na solutions such as Na-NaCl or Na-NaBr at temperatures close to the melting point (T_m) of the pure halide. As sodium is added to these solutions σ_e increases less rapidly than linearly in the mole fraction x of added metal up to the maximum solubility determined by a liquid-liquid phase separation.[4,5] However, at temperatures closer to the critical point (T_c) for phase separation, or in solutions involving the heavier alkali metals such as K (Refs. 4 and 5) or Cs (Ref. 6) for which $T_c - T_m$ is relatively small,[7] σ_e increases more rapidly than x implying that the modiblity increases with metal concentration.[8] All the solutions exhibit continuous metal-nonmetal transitions when $T > T_c$.

In their early work, Bronstein and Bredig[4] suggested that the curious behavior of the Na solutions is due to formation of relatively stable dimers Na_2. Formation of these species would increasingly reduce the *number* of conducting electrons per added sodium atom as x increases. They argued that the effect should be less pronounced at higher temperatures or in the heavier-metal solutions because of the lower stability of the dimer under these conditions. In contrast, Katz and Rice[9] and, later, Durham and Greenwood[10] offered explanations based on decreasing electronic *mobilities* as the metal concentration is increased in Na solutions. Katz and Rice suggested that the conducting electrons might become progressively more localized by disorder[11]

at higher concentration in Na solutions but not in K solutions. Durham and Greenwood employed a nearly-free-electron model[12] with increased disorder scattering at higher concentrations in Na-NaCl solutions.

In this Letter we report and compare nuclear magnetic resonance (NMR) data for $Na_x(NaBr)_{1-x}$, $Cs_x(CsCl)_{1-x}$, and $Cs_x(CsI)_{1-x}$ solutions. The measurements resolve the controversy over the Na solutions along the lines originally suggested by Bronstein and Bredig.[4] In clear contrast with the Cs solutions, we find strong evidence that the electronic mobility in $Na_x(NaBr)_{1-x}$ is essentially independent of concentration out to the solubility limit ($x_{\text{max}} \simeq 0.055$). The "anomalous" conductivity behavior in these solutions is due to formation of nonmagnetic, nonconducting states which reduce the effective number of conducting electrons. We suggest that the stability of these spin-paired species provides a connection between the electronic transport properties, the metal-nonmetal transition, and the liquid-liquid phase separation.

There is strong evidence that the electrons introduced by low concentrations of alkali metals in their molten halides are far from being "nearly free" but are quite strongly localized. Optical absorption,[13-16] NMR,[17,18] and electron-spin resonance[19] studies show that these states are similar to F centers, as originally suggested by Pitzer.[20] Analysis of the nuclear relaxation rates for ^{133}Cs in Cs-CsI demonstrated that the average time of interaction τ of an electron and a particular nucleus becomes comparable with the lifetime of a local ionic arrangement at low metal concentrations ($\tau \simeq 2 \times 10^{-12}$ s). In this limit, where the localized electrons may be assumed to produce a Curie type magnetic susceptibility, the resonance shift relative to the pure molten halide is[21]

$$\Delta H/H_0 = (c_s/4kT)(\gamma_e/\gamma_n)\langle A \rangle, \tag{1}$$

where c_s is the mole fraction of excess, unpaired

electrons, γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, respectively, and $\langle A \rangle$ is the magnetic hyperfine interaction constant averaged over all resonant nuclear species.

The spin-lattice relaxation rate $1/T_1$ depends on both c_s and the correlation time τ characterizing fluctuations of the local hyperfine field. For the usual nuclear Larmor frequencies $\omega_0 \sim 10^8$, the so-called "extreme narrowing" condition ($\omega_0\tau \ll 1$) applies and the relaxation rate is

$$1/T_1 = (c_s/2\hbar^2)\langle A^2 \rangle \tau. \tag{2}$$

Because of the possible formation of spin-paired states, the spin concentration is unknown in general ($c_s \le x$). Thus we eliminate c_s from Eqs. (1) and (2) to obtain

$$\frac{1}{T_1} = \frac{2kT}{\hbar^2}\left(\frac{\gamma_n}{\gamma_e}\right)\frac{\langle A^2 \rangle}{\langle A \rangle}\tau\frac{\Delta H}{H_0}. \tag{3}$$

The present study is based on the application of Eq. (3). For diffusive transport, the correlation time τ is related inversely to the electronic mobility. With the reasonable assumption that $\langle A^2 \rangle/\langle A \rangle$ is independent of concentration for dilute solutions, the presence of a concentration-dependent mobility will be revealed by curvature in a plot of $1/T_1$ against $\Delta H/H_0$ measured with varying metal concentration at constant temperature.

Samples for NMR measurements were contained in cells made from refractory oxide materials (alumina and beryllia ceramic or sapphire) closed with niobium-niobium cone seals. The seal of niobium to the oxide cell had been performed on the empty cell using either oxide glazes or nickel-titanium brazing alloys. While these cells were initially vacuum tight, they eventually leaked alkali-metal vapor at the niobium-oxide seal. However, the rate of metal loss was sufficiently slow that it was possible to exploit Eq. (3) to correlate $1/T_1$ with $\Delta H/H_0$ at varying metal concentrations after initial measurements at a well-defined composition.

The NMR measurements were carried out in a high-temperature NMR furnace which provided an argon atmosphere to protect the niobium portions of the cell from oxidation. A coherent pulsed NMR spectrometer operated at 9.4 MHz for ^{133}Cs measurements and at 17.1 MHz for ^{23}Na, ^{79}Br, and ^{81}Br. Spin-lattice relaxation times were measured with standard π–$\pi/2$ pulse sequences except in the case of ^{133}Cs for which, as a result of rapid relaxation, measurement of the free-induction-decay lifetime T_2^* was more accurate. A comparison of these methods con-

firmed that $T_1 = T_2^*$, as expected for the extreme narrowing limit.

Our experimental results are summarized in Fig. 1 where the relaxation rates are plotted against $\Delta H/H_0$ for ^{23}Na and ^{133}Cs in Na-NaBr, Cs-CsCl, and Cs-CsI. This plot shows a clear difference between the Cs solutions and Na-NaBr. The former correlation is highly nonlinear, even in the range 1–2 mole% metal whereas the Na-NaBr data are linear within 10% nearly to the phase boundary. Thus, according to Eq. (3), the mobility is essentially independent of concentration in Na-NaBr but increases by roughly a factor of 2 over the same concentration range in Cs-CsCl and Cs-CsI.

The conclusion that τ and the mobility are independent of concentration in Na-NaBr may be tested further by comparison with the dc conductivity. We assume a diffusive transport mechanism with jump rate τ^{-1} so that

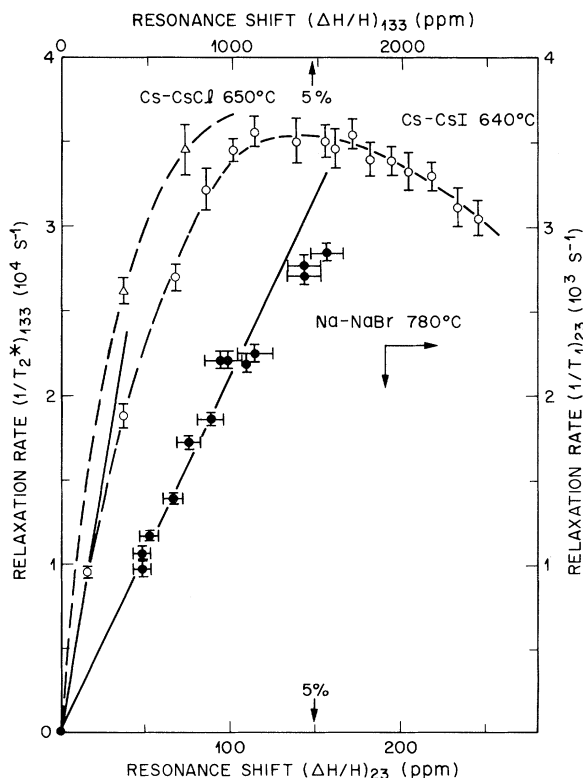$$\sigma_e = n(e^2\langle a^2 \rangle/6kT)\tau^{-1}, \tag{4}$$

FIG. 1. Nuclear relaxation rates vs resonance shift at constant temperature for ^{133}Cs in Cs-CsCl and Cs-CsI solutions (left-hand and upper scales) and ^{23}Na in Na-NaBr solutions (right-hand and lower scales). Shift values corresponding to 5 mole% metal concentrations are indicated by arrows.
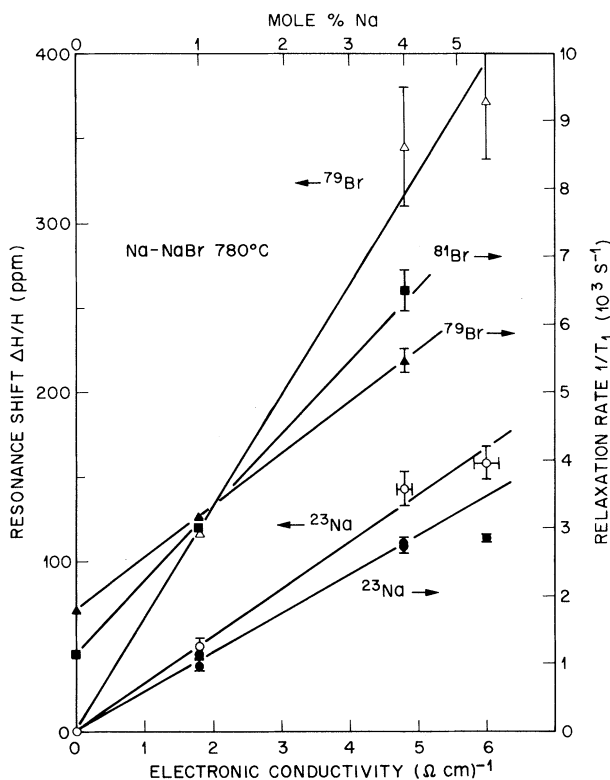
FIG. 2. Resonance shift (left-hand scale) and nuclear spin-lattice relaxation rates (right-hand scale) versus electronic conductivity for ^{23}Na, ^{79}Br, and ^{81}Br in Na-NaBr solutions. Upper scale shows Na concentration scale. Nonzero intercept for ^{79}Br and ^{81}Br is due to background electric quadrupolar relaxation process which is ineffective for ^{23}Na. Data are shown only for samples with well-defined compositions in leak-tight cells.

where n is the density of conducting electrons and $\langle a^2 \rangle^{1/2}$ is the mean jump distance. Now, if the unpaired and conducting electrons are the same, we have $n = c_s N_0 / \Omega_m$ where N_0 is Avogadro's number and Ω_m is the molar volume. The variation of Ω_m can be neglected at low concentrations so that Eqs. (1), (2), and (4) imply $\Delta H/H_0 \propto \sigma$ and $1/T_1 \propto \sigma$ provided that τ is constant. In Fig. 2, a plot of $\Delta H/H_0$ and $1/T_1$ against σ shows that this is indeed the case for ^{23}Na and ^{79,81}Br in Na$_x$(NaBr)$_{1-x}$ for $x \lesssim 0.04$. We conclude, therefore, that the anomalous behavior of Na-NaBr is due primarily to reduction of the number of conducting electrons at higher concentrations by formation of states which are both nonmagnetic and nonconducting. Formation of Na$_2$ as suggested by Bronstein and Bredig[4] satisfies this criterion but our experiments do not exclude other possible species.

Substitution of estimated values of τ in Eq. (4)

yields a value $\langle a^2 \rangle^{1/2} \simeq 20$ Å for both the Cs and Na solutions at the most dilute concentrations. We take this to be the mean separation of sites favorable for electron localization in the molten salt structure. When such a site or solvation cavity is destroyed by ionic diffusion after a typical time $\tau_i \sim 10^{-12}$ s, the electron moves to a new site. Now if the lifetime τ_s of a spin-paired species such as Na$_2$ is long compared with the structural lifetime, i.e., $\tau_s \gg \tau_i$, formation of these species simply removes electrons from the conduction process without affecting the mobility of the remainder. Eventually, of course, the concentration of such species becomes so high that a second, metallic phase is formed. This is the case for Na solutions well below T_c. Above T_c or for solutions such as Cs-CsCl we can infer that $\tau_s < \tau_i$ so that there is rapid equilibrium between solvated electrons and, for example, dimers M_2: $2M^+ + 2e^- \rightleftharpoons M_2$. For this limit, formation and dissociation of the dimer can enhance the conductivity and provide a concentration-dependent mobility since the electrons may be localized at new sites after dissociation. Eventually, this process, augmented by larger, short-lived species, would lead to a metal-nonmetal transition.[22] Thus the stability of spin-paired species relative to the underlying liquid structure may govern the metal-nonmetal transition which is discontinuous at the phase separation, where $\tau_s \gg \tau_i$, but becomes continuous for short-lived clusters.

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(a)Permanent address: Fachhochschule München, Fachbereich Physikalische Technik, and Physik Department, Technische Universität München, D-8046 Garching, West Germany.

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no liquid-liquid phase separation and are homogeneous in all proportions (see Ref. 1).

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[22]Nicoloso and Freyland recently proposed such a description of the metal-nonmetal transition based on the sequence F centers → spin-paired species → "clusters" (Ref. 19).