ELECTRON LOCALIZATION AND METAL-NONMETAL TRANSITION
IN ALKALI-METAL/ALKALI-HALIDE SOLUTIONS

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Dedicated to Professor Dr. E. U. Franck
on the occasion of his sixty-fifth birthday

ABSTRACT

This paper reviews recent results from spectroscopic experiments which give strong evidence that electron localization by F-center or polaronic states occurs in non-metallic alkali-metal/alkali-halide melts. Spectroscopic and thermodynamic measurements indicate that, with increasing metal concentrations, aggregation of localized states occurs and leads to the formation of stable diamagnetic F-center dimers or bipolarons. This is discussed for the example of Na\(_x\)(NaBr)\(_{1-x}\) solutions. The experimental characterization of the metal-nonmetal transition region is critically analyzed. It is shown that the electronic transition occurs at lower metal concentrations than the critical point of some alkali-metal/alkali-halide solutions. The correlation between electron localization and thermodynamic phase separation is qualitatively discussed.

I. INTRODUCTION

In recent years metal-molten salt solutions have attracted renewed attention, motivated by the interest in metal-nonmetal (M-NM) transitions in various disordered systems - for recent reviews see (1) and (2). Alkali-metal/alkali-halide (M-MX) solutions are relatively simple systems. They exhibit complete ionization in condensed phase and form true solutions, as has been shown by the work of Bredig and coworkers (3). At elevated temperatures they exhibit a continuous transformation from an ionic to a metallic liquid. A characteristic of the phase behavior of some M-MX solutions (3) is the occurrence of a critical point of liquid-liquid immiscibility with consolute temperatures in the range of 634°C (Rb-RbI) to 1180°C (Na-NaF). In experimental investigations, the high chemical reactivities at these temperatures together with increased vapor pressures of the metal require new high-temperature techniques.

In the discussion of the M-NM transition in M-MX solutions a central question concerns the nature of the metal valence electrons in salt-rich solutions. Different types of localized electronic states
have been discussed in the literature (1) (2). We shall confine ourselves here to a brief description of recent results from spectroscopic experiments, which clearly show that liquid F-center or polaronic states form in the nonmetallic solutions. With increasing metal concentrations, interaction between localized states and aggregation of F-centers become important, probably in the form of dimers (the $F'$- or $F_2$-center analogue) or bipolarons. Approaching the M-NM transition region, the possibility of small metal clusters has been conjectured (4). On the basis of new information from spectroscopic and thermodynamic measurements, the dimer-F-center equilibrium will be discussed in some detail for the example of $Na_x(NaBr)_{1-x}$. In the second section of the paper we will focus on the question: where in the phase region can we identify the transition? Changes in the electronic structure in relation with the phase behavior will briefly be discussed.

II. ELECTRON LOCALIZATION IN M-MX SOLUTIONS

A. EVIDENCE FOR LIQUID F-CENTERS

In an analysis of the phase diagrams of liquid M-MX solutions Pitzer (5) first suggested that electron solvation similar to crystalline F-centers might occur, i.e. an electron might occupy the site of an anion vacancy. Clear experimental confirmation of this type of electron localization in concentrated solutions up to several mole percent metal has recently been obtained from NMR (6), ESR (4) and optical absorption measurements (7) in various M-MX systems.

The main optical evidence for liquid F-centers is summarized in Fig.1, where the energy $E_m$ of the maximum of the optical absorption band (F-band) in various M-MX systems is plotted versus the sum of ionic radii at a constant reduced temperature. The dependence of the optical excitation on the salt matrix is obvious. In the crystalline case this relation presents the optical characteristic of F-centers, known as the Mollwo-Ivey relation. It also holds in the liquid state and a best fit of the data in Fig.1 yields (7)

$$E_m = 13(r_+ + r_-)^{-2.0},$$

where $E_m$ is in eV and $(r_+ + r_-)$ is in Å-units. In comparison to the crystalline F-center, the liquid $E_m$-values are shifted to lower energies; this shift is due to changes in the local structure and thus the Madelung energy on melting (see also (8), (9)).

The ESR-spectra observed in different solutions of excess metal in eutectic salt mixtures give additional evidence for the liquid F-center model. First, the spectra do not change if different metals are dissolved in the same salt. This demonstrates that the metal valence electron is solvated according to

$$Na_x + e^- \rightarrow Na_x^+ + e^-$$
i.e. the metal does not go in solution in atomic-like states $M_g$. A second characteristic of the ESR-spectra is the systematic shift of the resonance position with varying salt matrix measured by the g-factor shift $\Delta g = g_e - g$, where $g_e$ is the free electron g-factor. In general, $\Delta g$ is determined by the spin-orbit coupling constant $\xi$ and a characteristic excitation energy $\Delta E$, i.e.

$$\Delta g \approx \frac{\xi}{\Delta E}.$$ 

As $\xi$ scales with the atomic number $N$, one expects an increased shift with increasing $N$ of the salt cation or anion. This trend is demonstrated by the results given in Table 1, which also show the strong similarity with the g-factor of crystalline F-centers. In a first approximation the g-factor for F-centers in mixed crystals should lie between the corresponding values of the pure crystals.

### Table 1: g-factors of F-center resonances observed in liquid alkali-metal/eutectic alkali-halide mixtures compared with corresponding crystalline data from the literature (25)

| liquid MX-M soln | g-factor | crystal | g-factor |
|------------------|----------|---------|----------|
| (Na,K)Cl-Rb or Na | 1.995±0.002 | NaCl | 1.9978±0.0003 |
| $x = 0.04$       |          | KCl | 1.9958±0.0001 |
| (Na,Rb)Cl-Na     | 1.988±0.002 | NaCl | 1.9978±0.0003 |
| $x = 0.04$       |          | RbCl | 1.9804±0.0006 |
| (Na,Rb)I-Na      | 1.948±0.002 | NaI | 1.9494±0.0006 |
| $x = 0.025$      |          | RbI |         |

The NMR gives information on the structure and dynamics of excess electrons in M-MX solutions. Assuming Curie-type paramagnetism for the electrons, the hyperfine field can be determined from the measured chemical shift. From the magnitude of the fields Warren et al. (5) conclude that it is too low to be explained by atomic or multi-site localized states, but is consistent with F-center analogue states. A valuable insight into the dynamics is obtained from measurements of the nuclear spin relaxation rate. From this localization, times of the electron of the order of $10^{-12}$ sec have been deduced, which is comparable to the lifetime of ionic configurations in the liquid. For further details of this aspect, see the article by Warren in these proceedings.

A theoretical description of electron solvation in molten KCl has recently been reported by Parrinello and Rahman (9). Employing the methods of constant pressure molecular dynamics and treating the electron by the Feynman path integral method, they found that the electron is self-
trapped in a cation shell with an average coordination number of 4-metal ions; the electron density is spatially well localized (less smeared out than in the case of the solid); the binding energy is about 4 eV and is comparable to the potential energy per ion in the bulk salt. The authors add at the end of their paper that for two electrons, they may localize in the same cation solvation shell, i.e., the coulomb repulsion may be compensated by the strong lattice relaxation energy.

B F-CENTER-DIMER EQUILIBRIUM

With increasing metal concentrations and reducing average separation between F-centers, strong interactions between localized states become important. The concentration dependence of the static magnetic susceptibilities (4) in various M-MX solutions indicates that diamagnetic spin paired centers are formed so that an equilibrium between F-centers and aggregated centers must be considered. This is also indicated by the concentration and temperature dependence of the optical spectra. Fig. 2 shows the optical absorption of Na$_x$(NaBr)$_{1-x}$ in the range 0.005 ≤ x ≤ 0.042 at constant temperature (10); the total absorption has been deconvoluted into two bands, an F-band at 1.42 eV and a dimer band at 2 eV. At low concentrations these two bands are clearly separated in the original extinction curves (10). With increasing temperature at constant x, the intensity of the dimer band decreases in proportion to the increase of the F-band, indicating a dissociation equilibrium dimer ↔ F-center. From the optical energy of 2 eV of the dimer band, it is not likely that this excitation can be assigned to such diamagnetic species as M$^-$ or M$_2$; for the former, typical absorption energies of 1.5 to 1.8 eV have been found in different polar solvents (11).

A quantitative analysis of this equilibrium in Na$_x$(NaBr)$_{1-x}$ was recently obtained on the basis of exact sodium activity measurements (12) using the EMF technique of Egan (13). For the interpretation of these results the following thermodynamic model has been applied. At low sodium activities anion vacancies and electrons are assumed to be the major defects; with increasing metal concentrations, F-centers and F-center dimers or dielectrons—two F-centers attached or two electrons in the same anion vacancy—take over. From the corresponding chemical equilibrium equations together with the ionization and dissociation equilibria for F-centers and dimers, a relation between the metal mole fraction and the metal activity is derived—for details see the original paper (12). The important point of this model is that it yields the separate equilibrium constants from a fit of the activity relation to the measured activities. In this way a link is made between the concentration and temperature dependencies of the thermodynamic and the electronic properties. The model allows a prediction of the concentration of F-centers and aggregated localized species like dimers and explains spectroscopic and transport measurements quantitatively. An example is given in Fig. 3, where the ratio of the number of F-centers and dimers...
calculated from the thermodynamic model is compared with the corresponding result determined from the F-band and dimer band intensities of Fig. 2. The agreement between these independent results is good.

Little is known yet about the thermal stabilities, the binding energies of aggregated localized states. The temperature dependence of the ESR in (Na,Rb)Cl melts yields a dissociation enthalpy of about 0.5 eV (4). The optical absorption measurements of $K_x(KCl)_{1-x}$ give values around 0.3 eV, changing with composition (14). New measurements of the temperature coefficient of the electrical conductivity in the $K_x(KCl)_{1-x}$ (15) are consistent with these values, which is indicated by the maximum in the apparent activation energy $\Delta E_g$ as plotted in Fig. 4. Both the thermodynamic calculations (12) and the detailed analysis of the NMR results (6) show that the electronic conductivity is dominated by a diffusive transport of F-centers. From the NMR correlation times it is inferred that the activation energy of the electronic mobility is that of the diffusion of ions. Therefore the maximum in $\Delta E_g$ should be related with the dissociation energy of aggregated centers like dimers. It is interesting to note that, in Na$_x$(NaBr)$_{1-x}$, $\Delta E_g$ seems to approach a maximum of about 0.5 eV (15), whereas in the Cs$_x$(CsX)$_{1-x}$ systems no maximum of $\Delta E_g$ is observed (16).

III. EXPERIMENTAL CHARACTERIZATION OF THE M-NM TRANSITION REGION

In the fluid phase changes in the electronic structure are smeared out by the high thermal energy $kT$. Thus, many electronic properties show a smooth change as a function of composition and do not allow a simple division into metallic and nonmetallic ranges. As a first clue the behavior of the electrical conductivity is often used. For monovalent metals the nearly free electron theory of Ziman (17) predicts a negative temperature coefficient of the electrical conductivity, $\partial \ln \sigma / \partial T < 0$, in agreement with experiment. In Fig. 4 we present new measurements of $\sigma(x,T)$ for liquid $K_x(KCl)_{1-x}$ (15). A change of sign of $\partial \ln \sigma / \partial T$ occurs near $x = 0.25$. Within the nearly free electron picture this marks the lower limit of the metallic weak scattering transport regime. From this criterion the onset of electron localization in $K_x(KCl)_{1-x}$ should take place for $x < 0.25$. At this point the calculations of Morgan et al. (18) are of special interest. Using the theory of $2K_F$ scattering, they predict that localization in liquid $K_x(KX)_{1-x}$ should occur for $x = 0.15$.

Consistent with the conclusions drawn from the transport properties is the behavior of the static magnetic susceptibilities of various M-NX systems which are presented in Fig. 5. Here the ratio of the mole susceptibility of dissolved metal, $\chi_M(M)$, and of bulk metal at the same temperature is plotted versus metal mole fraction $x$ (19). In the evaluation of $\chi_M(M)$ from the total measured susceptibilities of the solutions, the assumption is made that the ionic susceptibilities of the core electrons do not change on mixing. From the data of Fig. 5 it is clear that the metallic bulk susceptibility of $K_x(KCl)_{1-x}$ is approached near $x \approx 0.2$. 

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From the nonmetallic side the transition is characterized by a strong enhancement of the dielectric susceptibility (20). First measurements of the refractive index in the infrared spectral region indicate the beginning of a polarization catastrophe approaching the transition. The existing data on $K_x(KCl)_{1-x}$ for temperatures around 850°C yield for the dielectric anomaly a concentration of $x = 0.15 \pm 0.05$. For a more precise determination of this limit, further measurements nearer to the transition are necessary which are in preparation using an ellipsometric technique.

On the basis of the present experimental information, we may conclude, at least for the $K_x(KCl)_{1-x}$ system, that the composition of the M-NM transition lies in the range $x = 0.1$ to 0.2 for temperatures above the critical temperature of $T_c = 790^\circ$C (K-KCl). As the consolute composition of $K_x(KCl)_{1-x}$ is $x_c = 0.4$ (3), a direct correlation between the thermodynamic critical point and the M-NM transition does not appear. Chieux et al. (21) have studied in detail the critical behavior of the concentration fluctuations by small angle neutron scattering in K-KBr. They find that the critical fluctuations are well described by a three-dimensional Ising model. As they state this is coherent with the fact that the miscibility gap occurs almost entirely within the metallic concentration regime. This is in contrast to the observations made in metal-ammonia solutions where the critical indices are of mean field type and the electronic transition seems to be connected with the thermodynamic phase transition.

For the general problem of M-NM transitions in disordered systems, different mechanisms have been invoked to describe the change in the electronic structure — for a detailed discussion see Mott (22). In the case of M-MX solutions, the self-trapping of electrons (polaronic states) and the effect of electron-electron correlation leading possibly to doubly occupied states are manifested in some of the electronic properties. It is not clear yet if higher aggregated localized states form. The concept of a percolation transition may apply. A first indication of aggregation in the form of small metal clusters was reported in the ESR experiments (4). Further information on this question may be obtained, possibly, from a more detailed investigation of the structural and dielectric properties.

Another unsolved problem concerns the correlation between the transformation in the electronic structure approaching the M-NM transition from the nonmetallic side and the macroscopic thermodynamic behavior. It seems that the occurrence of a miscibility gap is connected with the formation of stable aggregated localized states. A first indication for this is given in Fig. 6. Here the ratio of the number of F-centers and excess metal atoms is plotted for $Na_x(\text{NaBr})_{1-x}$ in comparison with $Cs_x(\text{CsCl})_{1-x}$ as determined from the optical spectra. As the absolute concentration of F-centers cannot be determined unambiguously from the optical data, the ratio has been normalized to 1 at the lowest metal concentration. However, this comparison shows that, in the Cs-system, F-cen-
ters prevail at low metal concentrations, whereas in the Na-system dimers are important from the beginning. The latter solutions have a wide miscibility gap; the former show no liquid-liquid phase separation. Possibly the existence and magnitude of the miscibility gap are related to the formation and thermal stability of aggregated localized states. This suggestion would explain the phase separation in the nonmetallic solutions and the trend in the phase diagrams going from the Na- to the Cs-systems. A similar proposal was recently given by Warren et al. (6) based on the dynamics of localized states as derived from NMR.

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Fig. 1. Energy of F-band maximum vs. the sum of ionic radii in dilute (x, ref. (23)) and concentrated (o, ref. (7)) nonmetallic M-MX solutions; the $E_m$ values are for the same reduced temperature of $T/T_m = 1.08$ (7).

Fig. 2. Optical absorption constant $K$ vs. photon energy in liquid $\text{Na}_x(\text{NaBr})_{1-x}$; drawn are the deconvoluted spectra of F-band and dimer-band for different compositions in mole % (10).

Fig. 3. Ratio of F-center/dimer concentrations in liquid $\text{Na}_x(\text{NaBr})_{1-x}$; (+) optical results, (—) thermodynamic model (12).
Fig. 4. Electrical conductivity, $\sigma$, and temperature coefficient, $\partial \ln \sigma / \partial T$, vs. mole fraction, $x$, in liquid $K_x(KCl)_{1-x}$; (o) points in the $\sigma(x_M)$ plot are from ref. (24), the full points and the $\partial \ln \sigma / \partial T$-data are from ref. (15).
Fig. 5. Ratio of molar magnetic susceptibility of dissolved metal, $\chi_m(M)$, and of bulk metal, $\chi_m$ (bulk M), versus metal mole fraction in various M-MX solutions at 1100°C. The upper scale gives a rough indication of the different conductivity ranges.

Fig. 6. Relative change of F-center concentration, $n_F/n_M$, vs. metal mole fraction in Cs-CsCl and Na-NaBr; $n_M$ is the number density of excess metal.