# Optical Study of Electron Localization Approaching a Polarization Catastrophe in Liquid $K_x$-$KCl_{1-x}$

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The absorption constant $K(\nu)$ and refractive index $n(\nu)$ have been measured at photon energies of $0.5 \leq h\nu \leq 5.5$ eV in liquid $K_x$-$KCl_{1-x}$ solutions for $0.001 \leq x \leq 0.05$ and temperatures up to 900 °C, approaching the metal-nonmetal transition. The absorption spectra give clear evidence for $F$-center states existing at all $x$ in equilibrium with aggregated centers, probably small metal clusters. The dielectric susceptibility increases with $x$ by almost 2 orders of magnitude. A fit of the dielectric enhancement by a critical form yields a critical exponent, $\zeta = 1.4 \pm 0.2$.

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In the current discussion of nonmetal-metal (NM-M) transitions in fluid one-electron systems such as expanded supercritical alkali metals or various alkali-metal solutions,[1] the nature of localized electron states is a problem of primary interest (see also Mott[2]). At high dilution, atomic or solvated electron states may exist depending on the dielectric properties of the fluid. Increasing the metal concentration towards the NM-M transition region, spin pairing becomes important which may lead to various kinds of aggregated centers.[1] Little is known, however, about the nature of these aggregated electron states and, especially, about their influence on the physical properties of homogeneous fluid one-electron systems approaching the NM-M transition region.

A particular example are solutions of alkali metals in their molten halides which exhibit complete miscibility at elevated temperatures.[3] In extremely dilute solutions, electron states very similar to that of solid $F$ centers may exist. This has been concluded from several experimental[4] and theoretical[5] investigations of the optical excitation spectrum. Recent studies of the magnetic properties[6, 7] suggest that at higher metal concentrations $F$-center-like states persist in equilibrium with spin-paired species or higher aggregated centers, possibly small metal clusters.[7] The NM-M transition in alkali-metal–alkali-halide solutions may be expected for a metal mole fraction of about $x = 0.1$; here, the electrical conductivity[3] reaches a value of about $10^2\ \Omega^{-1}\ \mathrm{cm}^{-1}$ which is comparable in magnitude with Mott's minimum metallic conductivity.

In this Letter, we report the first measurements of the concentration dependence of the optical properties (absorption constant and refractive index) of concentrated liquid $K_x$-$KCl_{1-x}$ solutions approaching the NM-M transition region ($0.001 \leq x \leq 0.05$, $T \leq 900\,^{\circ}\mathrm{C}$). We observe optical characteristics which may be attributed to liquid $F$ centers. From the intensity of the $F$ band, we estimate an approximately constant concentration of the order of $10^{19}\ \mathrm{cm}^{-3}$. In addition, we find features in the optical spectra similar to colloid absorption in the corresponding solid systems. The most striking observation is a strong enhancement of the dielectric susceptibility with increasing $x$ deduced from the refractive index. It follows a critical form with an exponent $\zeta = 1.4 \pm 0.2$. This type of dielectric divergence which suggests the beginning of a polarization catastrophe near the NM-M transition is reported here for the first time for a homogeneous liquid. We find similar behavior in other concentrated alkali-metal–alkali-halide solutions.[8]

The absorption constant, $K(\nu)$, and the refractive index, $n(\nu)$, have been measured simultaneously in a conventional transmission experiment at vertical incidence of the light. With the high absorption of the concentrated solutions studied, extremely thin liquid films with thicknesses ranging from 40 $\mu$m for $x = 0.001$ down to 4 $\mu$m for $x = 0.05$ had to be prepared. Because of the thin films, clearly defined interference patterns (channeled spectra) have been observed for transmissions higher than about 5% (see the inset in Fig. 2). The refractive index has been determined from the first-order interferences. The maximum absolute error for $x = 0.05$ is estimated to be less than 15% for $n(\nu)$ and 30% for $K(\nu)$; it is smaller for lower concentrations where thicker optical films could be used and the reflection corrections for $K(\nu)$ were smaller.

Figure 1 shows the results of the absorption constant for different metal concentrations, $0.001 \leq x \leq 0.05$, at a constant temperature of 860 °C. The solid lines refer to the experimental curves

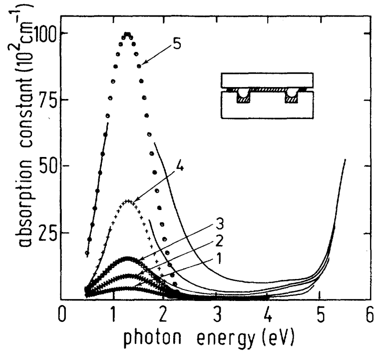

FIG. 1. Absorption constant vs photon energy in liquid $K_x$-$KCl_{1-x}$ solutions at 860 °C for different metal mole fractions $x = 0.001$ (curve 1), 0.007 (curve 2), 0.017 (curve 3), 0.023 (curve 4), and 0.05 (curve 5). The solid curves show the experimental results; the symbols represent Gaussian fits of the absorption band at 1.31 eV (see text).

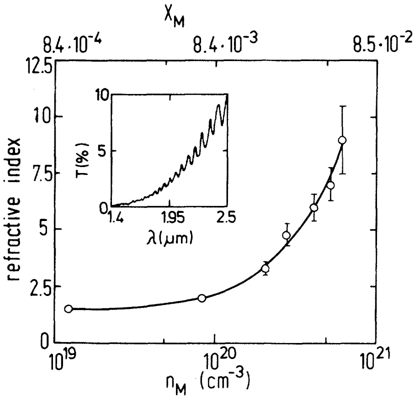

FIG. 2. Refractive index vs metal concentration in liquid $K_x$-$KCl_{1-x}$ solutions at 860 °C and a wavelength of 2.4 μm. Inset: a typical interference pattern measured in transmission vs wavelength for a liquid sample with $x = 0.05$ and a film thickness of 4 μm.

after smoothing of the interference pattern. We observe a strong absorption band with a peak at $\epsilon_m = 1.31$ eV. Its intensity increases with temperature, whereas $\epsilon_m$ has a negative temperature dependence. A weak absorption near 4.5 eV precedes the fundamental absorption edge of the pure molten salt. Its intensity decreases markedly as a function of $x$ relative to the band at 1.31 eV and has a negative temperature dependence. Because of the relatively large experimental errors in $K(\nu)$, a detailed quantitative analysis of the line shape of the main absorption band is not possible. However, for low $x (\leq 0.007)$ we could fit the band $(0.5 \leq h\nu \leq 2.5$ eV) by a single Gaussian with a standard deviation of $\delta \leq 1\%$. This was not possible for higher $x$ ($> 0.007$) as is shown in Fig. 1. Here the Gaussian fits of the low-energy part ($h\nu \leq 1.3$ eV) deviate strongly from the experimental curves above about 2 eV. We think that this is indicative of a distinct optical excitation.

From the present results and our measurements[8] on liquid $Cs_x$-$CsCl_{1-x}$, $Cs_x$-$CsI_{1-x}$, and $Na_x$-$NaBr_{1-x}$ solutions, the following relation is derived:

$$\epsilon_m = 13.0 a^{-2.03}, \tag{1}$$

where $a$ is the interionic distance in angstroms and $\epsilon_m$ is in electronvolts. As $\epsilon_m$ decreases with increasing temperature, the coefficients have been evaluated for a constant reduced temperature of $T/T_m = 1.08$, where $T_m$ is the melting point of the salt. It is interesting to note that the absorption peaks observed in various liquid alkali-metal–alkali-halide solutions in the dilute limit[9] obey relation (1) with a standard deviation of $\delta \leq 0.03$ eV. The existence of such a simple empirical relation very similar to that in the crystalline state—the so-called Mollwo-Ivey relation[10]—gives strong optical evidence that liquid $F$ centers exist in concentrated alkali-metal–alkali-halide solutions. An exponent of $-2.03$ in Eq. (1) is consistent with an approximation of the $F$-center model by a simple spherical square-well potential. In comparison with the crystalline case, the prefactor in Eq. (1) is smaller by about 30%, i.e., the ground-state energy of the $F$-center electron is reduced in the liquid. This can be related to changes in the local structure of the salt on melting (see also Ref. 5).

With the assumption that within experimental errors, the $F$ band may be approximated by a Gaussian line shape, we have subtracted the Gaussian curves shown in Fig. 1 from the experimental spectra. For these difference spectra we obtain a separate peak at 2.3 eV ($x = 0.023$) and 2.2 eV ($x = 0.05$). This observation and the weak absorption in the uv region described above are very similar to the optical features of colloids in solid K-KCl.[11] These optical indications are consistent with our previous conjecture based on ESR[7] spectra that small metal clusters may form in concentrated metal–molten-salt solutions.

The concentration dependence of the refractive index shown in Fig. 2 yields further support for this suggestion. These data have been determined for wavelengths above 1.5 μm where no dispersion of $n(\nu)$ was detectable. The observed strong increase of $n(\nu)$ with $x$ by almost an order of

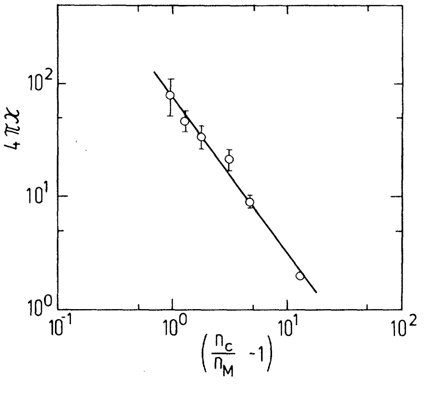

FIG. 3. Log-log plot of the dielectric susceptibility vs reduced metal concentration. A least-squares fit of the experimental points with Eq. (2) yields a critical exponent $\zeta = 1.4 \pm 0.2$ with $n_c = 1.2 \times 10^{21}$ cm$^{-3}$.

magnitude implies a drastic enhancement of the polarizability approaching the NM-M transition.

In order to compare these results with disordered solid systems like doped Si:P,[12,13] or Ag:KCl,[14] where a dielectric divergence has been observed approaching the NM-M transition, we have determined the dielectric susceptibility $\chi$ as a function of $x$ from the refractive indices according to $4\pi\chi = n(x)^2 - n(x=0)^2$. In highly doped Si:P, it has been shown that, within experimental errors, the low- and high-frequency dielectric susceptibility obeys the same critical form[13]:

$$4\pi\chi = \mathrm{const}\,(n_c/n_M - 1)^{-\zeta}, \tag{2}$$

where $n_M$ is the number density of doped metal and $n_c$ that at the NM-M transition, respectively. A fit of the data in liquid $K_x$-$KCl_{1-x}$ according to Eq. (2) is plotted in Fig. 3. With $n_c = 1.2 \times 10^{21}$ cm$^{-3}$ corresponding to $x_c = 0.1$ we obtain a critical exponent of $\zeta = 1.4 \pm 0.2$. The error in $\zeta$ contains an uncertainty in $x_c$ of $\pm 0.03$. We find that the dielectric susceptibility obeys a scaling law with a critical exponent comparable to that in Si:P where clustering of the dopant approaching the NM-M transition has been discussed.[13] On the other hand, a critical exponent of 1.4 is larger by a factor of 2 than that in solid mixed Ag:KCl where classical percolation behavior prevails.[14]

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