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LETTER TO THE EDITOR

Direct spectroscopic observation of localized band gap states in liquid Na–NaI

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Abstract. We have studied the optical absorption of fluid $\text{Na}_x\text{NaI}_{1-x}$ solutions at high temperatures up to 1073 K and in the energy range from 0.5 eV to 3.6 eV. The metal mole fraction x has been varied *in situ* by coulometric titration in the range from 10^{-3} to 4×10^{-2} . This ensures a precise control of changes in the spectra as a function of x . Besides the well known F centre excitation and a Drude-like contribution the most striking characteristic of the spectra is a step-like intensity profile in the UV. Its main features and variation with x are consistently described by excitations from the F centre-like trap states into states of the conduction band tail above the Fermi energy.

In studying the electronic processes of non-crystalline materials in the concept of mobility gap has proven to be fundamental [1]. Its important feature is a continuous density of states where states in the respective band tails are localized by disorder having a low mobility. For a detailed description of the electronic properties of these materials a knowledge of the nature and distribution of these tail states is central. This is particularly the case if one considers larger changes in the electronic structure accompanying an electronic or metal–non-metal transition in condensed disordered phases. However, to our knowledge a direct spectroscopic probing of these states has not been reported so far.

In alkali metal–alkali halide melts a metal–non-metal transition occurs continuously as a function of composition at elevated temperatures of the order of 1000 K [2]. In fluid systems it can be followed in permanent thermal equilibrium, in a homogeneous phase. Experimental results of the magnetic and electrical properties of these metal–molten salt solutions indicate [3,4] that the onset of metallic characteristics appears at relatively high metal mole fractions x , $x \sim 0.2$, which corresponds to a number density of the order of 10^{21} cm^{-3} . This is a remarkably high doping of the non-metallic fluid. It implies that strongly localized electronic states prevail over a wide range of excess metal.

Various spectroscopic and theoretical investigations have been performed which deal with the character of these states [5–8]. They lead to the conclusion that in dilute solutions generally F centre or polaronic species—and possibly aggregates of these—are the predominant isolated strongly localized states, although for molten halides of the lighter alkali metals (Li, Na) the formation of dipolar atoms cannot be excluded [7,8]. However, in this paper we focus on conduction band tail states and therefore will not distinguish between the nature of strongly localized trap states. To simplify matters we will refer only to F centre-like states. Furthermore it is of interest that a dynamical equilibrium between

F centre ground states and electrons localized in band tails must be considered which show up by a Drude type contribution in the optical conductivity [5]. This is consistent with the quantum molecular dynamics calculations of Parrinello and coworkers and with a recent theoretical estimate of the Madelung energy fluctuations in these liquids [9]. If this assignment is correct optical excitations from localized trap states into unoccupied localized states in the conduction band tail should be detectable spectroscopically in these fluid systems approaching a non-metal-metal transition.

This is the main objective of this study. We present measurements of the optical absorption of $\text{Na}_x\text{NaI}_{1-x}$ solutions at temperature between 973 to 1073 K and at various metal mole fractions x ($10^{-3} \leq x \leq 4 \times 10^{-2}$) which have been precisely controlled *in situ* by coulometric titration. Besides the F centre and Drude absorption, contribution is observed which is characterized by a step-function-like intensity profile. This mainly reflects the distribution of occupied states around the Fermi energy, E_F convoluted with the F centre distribution and is indubitably attributed to optical excitations from the F centre ground state to localized states in the mobility gap above E_F . In this way a direct insight into the density of localized gap states and their variation with doping has been obtained for the first time.

The experimental technique we have used in this study is similar to that described in [5] and may be summarized as follows. The molten salt NaI has been contained in an optical cell with sapphire windows which have been vacuum tightly sealed with thin Ta wires of different diameter. In this way the optical film thickness of the melt has been varied down to 6 μm with an absolute accuracy of μ . A vacuum tight connection of the optical cell with an EMF cell [10] allowed *in situ* doping of the molten salt with excess Na metal. A precise and reproducible variation of x over a wide range of compositions has been achieved. The optical and combined EMF cell have been mounted inside a high-temperature high-vacuum furnace and the optical absorption measurements have been performed in a Cary 17H UV-VIS spectrometer. With this combined technique the influence of background absorption (optical windows, molten salt absorption) can be controlled *in situ* and changes in the spectra as a function of x can be detected with high precision.

Figure 1 shows a selection of typical absorption spectra of $\text{Na}_x\text{NaI}_{1-x}$ at 700 °C at different metal mole fractions x . Plotted are the absorption constants K in cm^{-1} which have been determined from the measured absorbance A according to $A = K \times t$ (t = film thickness). In these spectra the absorption edge of the pure molten salt at 700 °C has been subtracted. It may be approximated by a simple Urbach behaviour [1], i.e.

$$K(\omega) = K_0 \exp(-\alpha(E_0 - \hbar\omega)/kT). \quad (1)$$

From measurements of $K(\omega)$ of pure molten NaI at various temperatures, T , as a function of the photon energy, $\hbar\omega$, we have determined the fundamental excitation energy $E_0 = 4.6$ eV (optical gap) with $\alpha = 0.61$. This value is in good agreement with a theoretical prediction of Tosi *et al* [11]. Due to the Urbach tails of the pure molten salt which in NaI become appreciable above 3.6 eV the discussion of the difference spectra in figure 1 is restricted to photon energies $0.5 \leq \hbar\omega \leq 3.6$ eV. In this energy range the following observations are of particular interest. The most prominent feature is a broad absorption band with a maximum near 1.7 eV and a half-width of roughly 1 eV. This band exhibits the typical optical characteristics of F centre absorption in M-MX melts [8]. Their line shape is well approximated by a Gaussian [5, 8]. However, the spectra in figure 1 clearly deviate from a simple Gaussian both at low and high photon energies. At low metal concentrations an enhanced absorption around 0.5 eV is evident which cannot be attributed to the F band. As demonstrated in more detail recently [5] for the example of $\text{K}_x\text{KC1}_{1-x}$ and $\text{Na}_x\text{NaBr}_{1-x}$

melts this absorption stems from Drude electrons with mobilities of the order of $0.1 \text{ cm}^2 \text{ V}^{-1}$ which contribute a continuous absorption underneath the F band. This deconvolution is unique, and F centres together with Drude electrons are sufficient to describe these systems. However, this is not the case in $\text{Na}_x\text{NaI}_{1-x}$. Here an additional absorption shows up on the high energy side of the F band which becomes pronounced at high x . In the following interpretation we focus on this part of the absorption spectra.

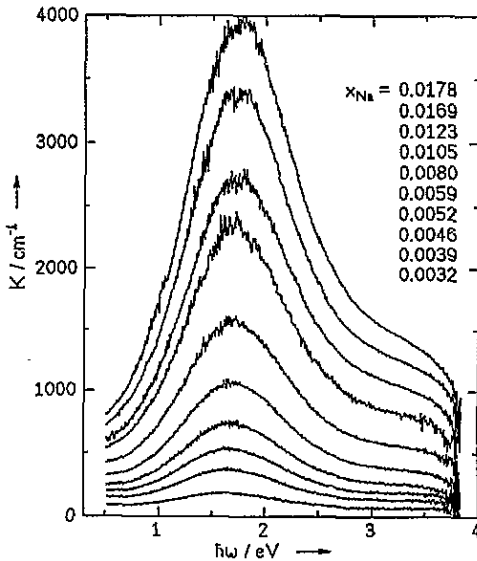


Figure 1. Optical absorption spectra of liquid $\text{Na}_x\text{NaI}_{1-x}$ for various metal mole fractions x at 700°C . Plotted is the absorption constant K against photon energy $\hbar\omega$. The contribution of the pure salt edge has been substrated.

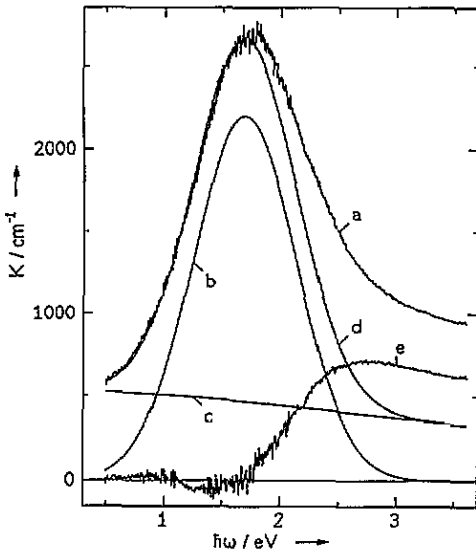


Figure 2. Typical deconvolution of an absorption spectrum: (a) original spectrum, (b) Gaussian and (c) Drude component, (d) sum of (b) and (c), (e) difference spectrum of (a) and (d) yielding step function.

For this we have deconvoluted the total absorption into the Gaussian component of the F band and the Drude component of localized electrons below E_F . The difference yields

the high energy absorption. A typical example of this deconvolution is given in figure 2. In first approximation the remaining absorption above ~ 2 eV has the shape of a step function. It definitely cannot be described by e.g. a Gaussian as is the case for isolated states like the F centre.

In order to get further insight into the change of this high energy absorption with composition we have fitted the spectra (see e.g. figure 1) by a sum of a Gaussian, a Drude component and a Fermi type function, the latter representing the step shape absorption. From the optimum fits the following results have been obtained. For $10^{-3} \leq x \leq 4 \times 10^{-2}$ the energy maximum of the F band varies from 1.65 to 1.75 eV and the half-width from 1.0 to 1.2 eV. These variations increase slightly with temperature. The DC electronic conductivity determined from the fit of the Drude parameters quantitatively agrees with independent measurements [12], both for the magnitude and the concentration dependence [13].

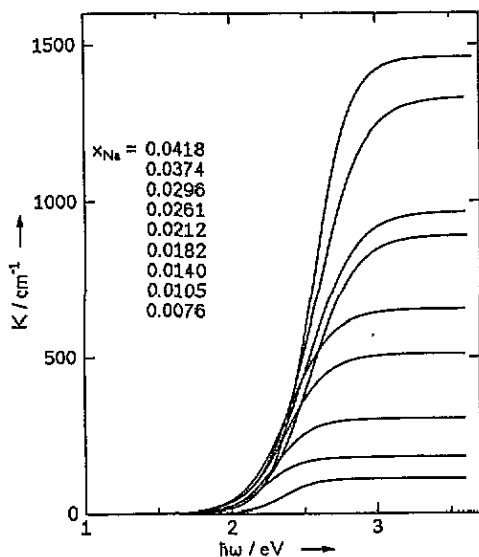


Figure 3. Absorption constant against photon energy of the fitted absorption step of $\text{Na}_x\text{NaI}_{1-x}$ metals at 750°C at different metal mole fractions x increasing from bottom to top.

Based on these observations we have extracted the remaining absorption at higher energies as a function of x as shown in figure 3. The peculiarities of this absorption are: its shape is well approximated by a step function, the step is smeared out over roughly 1 eV, the inflection point of the curved step shifts from 2.3 eV (low x) to 2.5 eV (high x) and, most interestingly, the height the step correlates linearly with the integrated F band intensity over the whole concentration range studied (see figure 4). As described below, these results give strong evidence that this absorption is due to excitations from strongly localized trap states into localized gap states above E_F . For this we consider the Kubo–Greenwood equation for $K(\omega)$ with a constant matrix element [1]:

$$K(\omega) \propto \omega^{-1} \int n_F(\epsilon) n_C(\epsilon + \hbar\omega) (f(\epsilon) - f(\epsilon + \hbar\omega)) d\epsilon \quad (2)$$

where $n_F(\epsilon)$ denotes the density of states F centre ground states, n_C that of the conduction band tail, and $f(\epsilon)$ is the Fermi–Dirac distribution function. In discussing the results on the basis of (2) we first have to consider the possible location of the Fermi energy inside the mobility gap. If one compares the observed inflection point energy of 2.3 eV at low x with

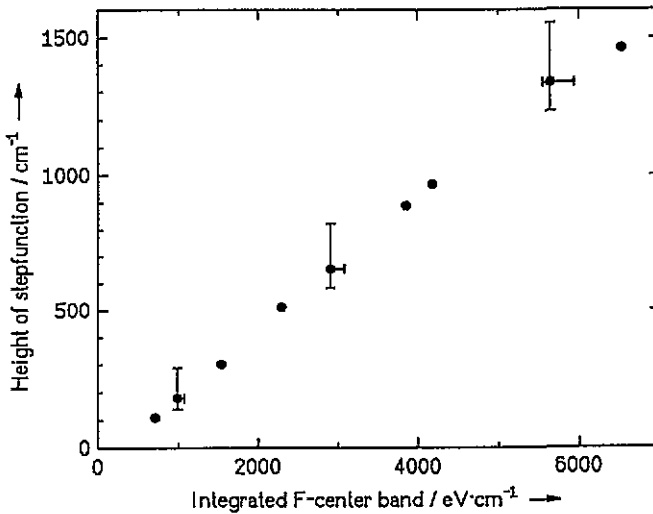


Figure 4. Strong and linear correlation of the height of the step function with the integral of the F centre band. The error bars show the variation of the fits if the Drude parameters (electronic conductivity and mobility) are changed within reasonable limits.

the optical gap energy of 4.6 eV for NaI in first approximation one might expect that E_F lies near mid gap. However, taking into account the broad tailing of the Urbach absorption of the pure molten salt— $K \sim 10^3 \text{ cm}^{-1}$ for $\hbar\omega > 3.6 \text{ eV}$ —and making the reasonable assumption that the F centre ground state energies do not lie inside the valence band, we have to conclude the E_F is shifted towards the conduction band even at low x . Therefore a positive slope of $n_C(\epsilon)$ at E_F has to be considered.

In the light of the theoretical calculations of Logan and Siringo [9], $n_F(\epsilon)$ for the energy range of interest may be approximated by a Gaussian with a half-width of the order of 1 eV. With these assumptions (2) yields the following interpretation of the high energy part of the spectra. The step-like absorption is determined by the Fermi functions; the rounding of the step of $\sim 1 \text{ eV}$ mainly reflects the half-width of $n_F(\epsilon)$ and finally, the height of the step should be proportional to the F centre concentration. If $n_C(\epsilon) = \text{constant}$, then according to (2) the apparent plateau of the step should decrease as ω^{-1} . As the examples of figure 3 demonstrate this is not the case (but see also figure 2). So we may conclude that $n_C(E_F)$ has a positive slope which is consistent with E_F being shifted towards the conduction band. An important consequence of these assignments is that the turning point of the smeared step-like absorption reflects the energy separation of the F centre ground state and the Fermi level. It shifts only slightly from 2.3 to 2.5 eV varying x over more than one order of magnitude. These energies together with the spread of the step rounding of $\sim 1 \text{ eV}$ imply that the F centre is located near the valence band edge. Finally, we would like to stress that the observed high energy step-like absorption in $\text{Na}_x\text{NaI}_{1-x}$ cannot be explained by K or L bands as are observed in some crystalline additively doped alkali halides. If this were the case these bands should also be visible in liquid $\text{K}_x\text{KCl}_{1-x}$ or $\text{Na}_x\text{NaBr}_{1-x}$, which does not occur [5]. On the other hand, the step-like absorption in these salts is expected in the UV region due to the larger optical gaps of KCl and NaBr by more than 1 eV in comparison to NaI [11] and thus has not yet been observed.

In summary, optical excitations from F centre states into localized band gap states in disordered systems are accessible by simple absorption spectroscopy. This has been shown here for the first time for the example of fluid $\text{Na}_x\text{NaI}_{1-x}$ solutions. The high optical sensitivity necessary for deconvoluting the spectra is only achieved via the technique of

in situ doping. The separate components of the spectra together with their concentration dependence give a coherent picture of electron localization in these melts. Over a wide composition range of the non-metallic solution, strongly localized states like F centres prevail whose ground state energies are located deep in the gap, near the valence band edge. This implies that trap states and band states coexist at the same energy and, for instance, that the excited F centre state may lie below the Fermi energy. These trap states may pin the Fermi energy in dilute solutions. This is displayed by the distinct step absorption whose inflection point shifts only slightly with x from 2.3 to 2.5 eV. For the problem of metal–non-metal transition in these fluids the following scenario opens up: if with increasing x the electronic screening changes, more and more states in the conduction band tail will be occupied and E_F crosses the mobility edge; this is the signature of a Mott–Anderson transition. Further ellipsometric measurement may elucidate this.

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