

Spin dynamics and susceptibility approaching the NM-M transition in K_xKCl_{1-x}

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 L469

(<http://iopscience.iop.org/0953-8984/7/35/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:02

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Spin dynamics and susceptibility approaching the NM–M transition in K_xKCl_{1-x}

T Schindelbeck and W Freyland

Institute of Physical Chemistry, University of Karlsruhe, PO Box 6980, 76128 Karlsruhe, Germany

Received 12 July 1995

Abstract. We report ESR measurements of K_xKCl_{1-x} melts at 800 °C which for the first time have been studied over a wide composition range approaching the nonmetal–metal transition ($10^{-4} \leq x \leq 10^{-1}$). The concentration has been varied precisely by *in situ* Coulometric titration. The observed motional linewidth narrowing gives evidence that fast electronic exchange processes prevail in the nonmetallic melts. The spin susceptibility exhibits strong deviations from a simple Curie limit and its magnitude strongly indicates that only a small fraction of excess electrons exists in paramagnetic states. Both the spin dynamics and the spin susceptibility show clear changes near $x = 0.05$ indicative of the onset of a Mott–Anderson transition. Over the whole nonmetallic regime the ratio of spin susceptibility and electronic conductivity is found to be constant.

At elevated temperatures alkali metal–alkali halide (M–MX) melts exhibit a continuous transformation from metallic to nonmetallic states varying the composition in the homogeneous fluid phase—for a recent review see [1]. This metal–nonmetal (M–NM) transition occurs at a relatively high metal doping, at a number density of roughly 10^{21} cm^{-3} or a corresponding metal mole fraction of the order of 0.1. Without knowing the mechanism of the transition in detail it is difficult to define this number more precisely.

Our present knowledge of the electronic characteristics of salt-rich nonmetallic solutions may be sketched as follows. On metal doping of the ionic melt strongly localized states such as F centres and singlet-state bipolarons may form similar in character to the corresponding solid state electronic defects. This has been observed in several spectroscopic experiments [2–4] and is found in QMD calculations [5, 6]. A recent spectroscopic study also indicates that the ground state energy of the liquid F centre lies near the valence band edge [7]. Due to the liquid characteristics, however, a dynamical equilibrium between these strongly localized states and mobile electrons must be considered. This has been first conjectured by Warren [3] on the basis of NMR relaxation rate measurements which yield an electron–ion correlation time of $\sim 10^{-12} \text{ s}$, a typical diffusional jump time of the ions. The mobility of electrons is found to be $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, nearly constant over most of the nonmetallic regime [8]. From the magnitude of the electronic mobility, which is two orders of magnitude smaller than typical values of liquid metals, we conclude that mobile electrons reside in mobility gap states, presumably weakly localized band tail states.

In order to obtain further insight into the electronic structure and dynamics of these states we have performed ESR measurements of K_xKCl_{1-x} melts and, for the first time, have succeeded in covering a wide composition range approaching the NM–M transition ($10^{-4} \leq x \leq 10^{-1}$). Several objectives have been followed. If fast exchange processes

dominate this should be manifested in the spin dynamics by a corresponding narrowing of the ESR signals. Furthermore we focused on the variation of the spin susceptibility approaching the NM-M transition. Finally, the relation between electron and spin dynamics as a function of composition is of special interest.

For the study of these distinct aspects emphasis has been given to a precise variation of composition which has been achieved *in situ* by Coulometric titration. In principle the following experimental arrangement has been employed. The molten salt was contained in a thin sapphire capillary of 1 mm inside diameter closed at one end. At the opposite end the capillary had a vacuum-tight connection to a high-temperature EMF cell similar in construction to the one described previously for simultaneous EMF and optical absorption measurements [4]. The potassium metal produced in the EMF cell equilibrated via the vapour phase with the metal dissolved in the molten salt sample. The composition was controlled via the EMF and the titrated coulombs. The sapphire was aligned in the axis of a TE_{011} cylinder cavity. The sample was heated with a CO_2 laser focused on the lower end of the sapphire capillary. A pyrometer was used for temperature control and measurement. It was calibrated at the melting point of the salt where the cavity quality factor is reduced significantly. The ESR measurements were performed with a Bruker X band spectrometer. For further details of the experiment and data evaluation reference is made to [9].

Due to the skin effect of the samples studied all spectra exhibit an asymmetric typical Dysonian lineshape, which can be explained satisfactorily by geometrical factors [9]. In order to evaluate the ESR characteristics (g factor, halfwidth and intensity of the resonance) the spectra have been fitted with the real and imaginary parts of a Lorentzian. In all cases a single Lorentzian gave a perfect fit. For the determination of the spin susceptibility the intensities have been calibrated with a Curie-type sapphire signal which has been recorded simultaneously with the sample resonances. All spectra considered here have been taken at 800 ± 10 °C.

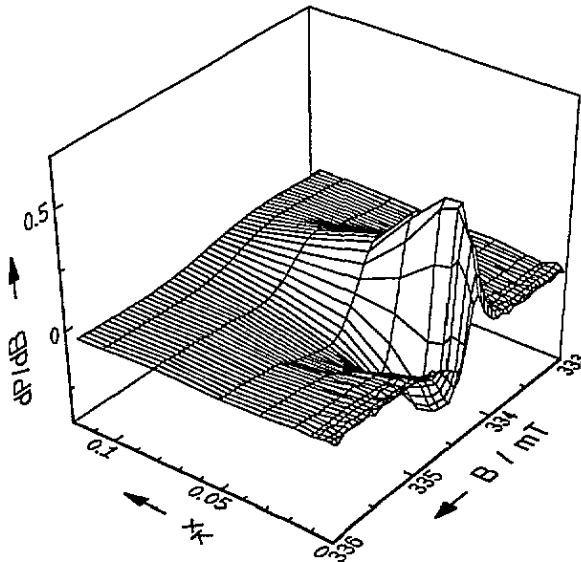


Figure 1. A selection of ESR spectra of liquid K_xKCl_{1-x} ($10^{-4} \leq x \leq 10^{-1}$) at 800 °C.

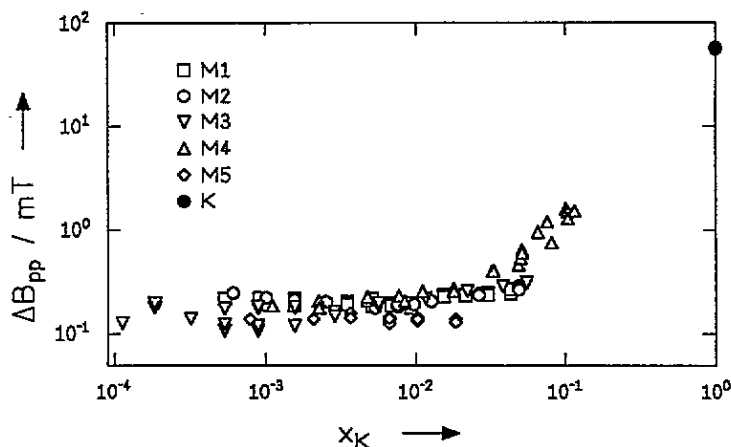


Figure 2. The peak to peak halfwidth, ΔB_{pp} , of ESR spectra plotted against metal mole fraction x ; results of different experimental runs M1–M5 are given.

Figure 1 gives a representative selection of spectra of K_xKCl_{1-x} in the concentration range studied for magnetic fields of $333 \text{ mT} \leq B \leq 336 \text{ mT}$. At low x the peak to peak intensity of the derivative signal first rises before it reaches a maximum near $x = 0.05$. The g factor is 1.994 and remains constant in the nonmetallic regime. The peak to peak halfwidth, ΔB_{pp} , stays constant up to $x = 0.05$ and then increases significantly with x . This last piece of information is presented in more detail in figure 2, which gives a plot of ΔB_{pp} versus $\log x$ determined from five different experimental runs labelled M1–M5. It is seen that $\Delta B_{pp} \sim 0.2 \text{ mT}$ is constant over almost three decades in x . A clear increase of the halfwidth occurs above $x \sim 0.05$ and it seems to extrapolate to the pure potassium value of $\sim 60 \text{ mT}$. The latter has been taken from literature data [10] extrapolated to 800°C . With regard to fast electronic exchange processes considered above, the linewidth of $\sim 0.2 \text{ mT}$ is very instructive. In the case of fast exchange or motional narrowing the ESR linewidth $\Delta\omega_0$ unaffected by exchange processes is reduced to $\Delta\omega$ according to [11]

$$\Delta\omega \simeq (\Delta\omega)_0^2 / \omega_{ex} \quad (1)$$

where ω_{ex} is the exchange frequency. With $\omega_{ex} \sim 10^{12} \text{ s}^{-1}$ the observed halfwidth of $\sim 0.2 \text{ mT}$ corresponds to a narrowing by almost a factor of 10^2 . Thus a linewidth of $\sim 5 \text{ mT}$ —representing the solid state F centre in KCl [12]—or the dipolar line broadening of statistically distributed electrons like weakly localized states may be sufficiently reduced consistent with the observed ΔB_{pp} values. An exceptional situation may arise if bipolarons form and exist only for $\sim 10^{-12} \text{ s}$. Due to the confinement of the electrons over a distance of $\sim 3 \text{ \AA}$ [6] a large dipolar line broadening may result such that $\Delta\omega$ is above the limit of detection.

From the imaginary part of the Lorentz fits to the spectra, $\chi''(\omega)$, the spin susceptibility, χ , has been determined according to [13]:

$$\chi = \frac{2}{\pi\omega_0} \int_0^\infty \chi''(\omega) d\omega \quad (2)$$

where ω_0 is the Larmor frequency. With the relatively sharp resonances observed here this evaluation is less critical. Figure 3 gives these results for separate experimental runs

(M1–M5) plotted versus $\log x$. Two features are particularly noteworthy. In the nonmetallic regime there is only a weak concentration dependence of χ and it lies well below the Curie limit for $s = \frac{1}{2}$ spins. Above $x = 0.05$ a strong change in slope of χ against $\log x$ is observed. This coincides with a strong increase of the linewidth as shown in figure 2. The clear deviation of χ from the Curie limit leads to the conclusion that in nonmetallic solutions only a small fraction of electrons are detected in the ESR experiment, the majority being either in spin-paired singlet states or in states leading to a large line broadening. This conclusion is consistent with measurements of the static magnetic susceptibility and of the concentration dependence of optical absorption and, in particular, with QMD calculations—see also [1]. The error bar indicated in figure 3 represents the maximum absolute uncertainty of the spin calibration via the sapphire signal and the concentration determination via Coulometric titration, respectively. The relative change of $\chi(x)$ has a higher accuracy.

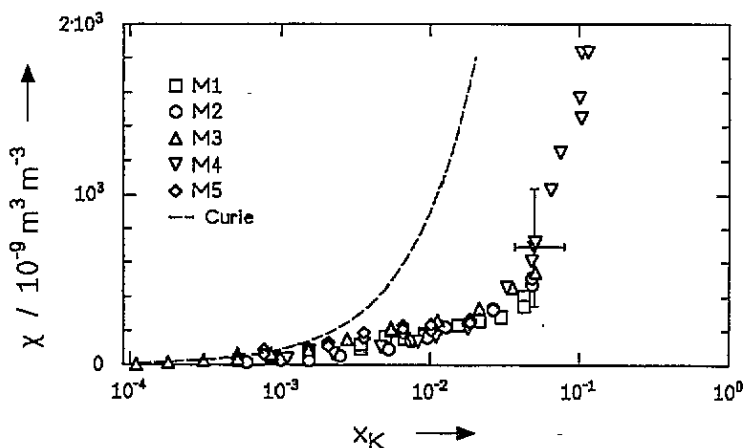


Figure 3. The ESR spin susceptibility of liquid $\text{K}_x\text{KCl}_{1-x}$ at 800°C versus x .

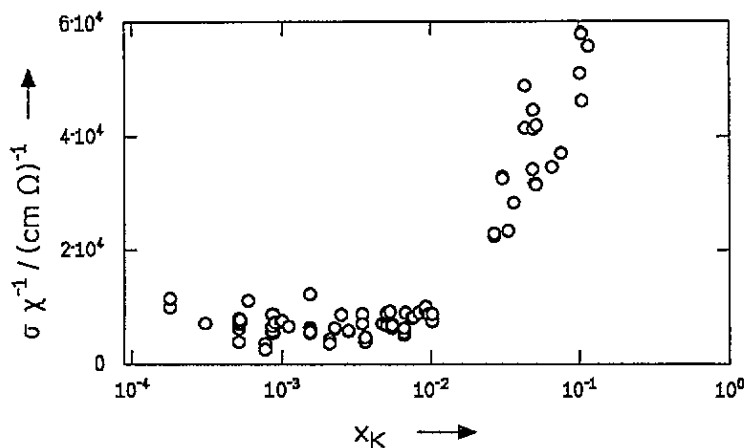


Figure 4. The ratio of electronic conductivity, σ , and spin susceptibility, χ , of liquid $\text{K}_x\text{KCl}_{1-x}$ at 800°C versus x .

In K_xKX_{1-x} melts a constant electronic mobility has been found for $x \leq 0.01$ [8]. The spin dynamics remain constant, too, in this range (see figure 2). If both experiments probe the same states then a strong correlation between the number of mobile electrons and spins may be anticipated. This is demonstrated in figure 4, where the ratio of measured electronic conductivities, σ [8, 14], and of the ESR spin susceptibilities of this work is plotted versus $\log x$. Within experimental error this ratio is constant up to $x \sim 0.01$. Above this composition there is a gap in the conductivity data available. In the range $10^{-2} \leq x \leq 10^{-1}$ the ratio σ/χ increases by more than a factor of six. In the light of figure 3 this strong enhancement gives a lower limit for the increase of the electronic mobility in qualitative agreement with independent determinations of μ —see also [1].

Summarizing we may state that the ESR spin dynamics reported here for the first time give evidence for fast exchange processes on a typical liquid time scale of 10^{-12} s between strongly and weakly localized electrons in nonmetallic K_xKCl_{1-x} melts. Both the spin dynamics and the spin susceptibility are consistent with bipolaron formation. Assuming that mobile electrons ($\mu \sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are localized in band tail states, the correlation of χ and σ may be interpreted by a Mott–Anderson transition with the onset near $x = 0.05$.

Financial support of this work by Deutsche Forschungsgemeinschaft through SFB 195 and in part by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

- [1] Freyland W 1994 *Z. Phys. Chem.* **184** 139; 1995 *The Metal–Non-Metal Transition Revisited* ed P P Edwards and C N R Rao (London: Taylor and Francis)
- [2] Nicoloso N and Freyland W 1983 *J. Phys. Chem.* **87** 1997
- [3] Warren W W Jr 1987 *Molten Salt Chemistry (NATO ASI Series 202)* ed G Mamantov and R Marassi (Dordrecht: Reidel)
- [4] Nattland D, Rauch Th and Freyland W 1993 *J. Chem. Phys.* **98** 4429
- [5] Parrinello M and Rahman A 1984 *J. Chem. Phys.* **80** 860
- [6] Fois E S, Selloni A and Parrinello M 1989 *Phys. Rev. B* **39** 4812
- [7] von Blanckenhagen B, Nattland D and Freyland W 1994 *J. Phys.: Condens. Matter* **6** L179
- [8] Haarberg G M, Osen K S and Egan J J private communication
- [9] Schindelbeck T 1995 *PhD Thesis* Universität Karlsruhe
- [10] Devine R A B and Dupree R 1970 *Phil. Mag.* **22** 657
- [11] Kittel Ch 1988 *Einführung in die Festkörperphysik* (Munich: Oldenbourg)
- [12] Seidel H and Wolf H C 1968 *Physics of Color Centers* ed W B Fowler (London: Academic)
- [13] See e.g. Slichter C P 1990 *Principles of Magnetic Resonance* (Heidelberg: Springer)
- [14] Nattland D, Heyer H and Freyland W 1986 *Z. Phys. Chem., NF* **149** 1