PHASE AND GLASS TRANSITIONS IN $(KI)_{1-x}(NH_4I)_x$

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Abstract : Phase transition temperatures and freezing temperatures have been determined in $(KI)_{1-x}(NH_4I)_x$ for concentrations $0 \leq x_{sol} \leq 1$ using dielectric spectroscopy. From these results a schematic x,T-phase diagram has been deduced. In addition some preliminary results on deuterated samples are presented.

INTRODUCTION

It is known since a long time that KI and NH_4I show complete solid state miscibility.[1] Only recently however the potential of this compound to form an orientational glass state [2] has been recognized by Bostoen *et al.*[3] Based on incoherent inelastic neutron scattering experiments these authors argued that the low temperature excitation spectra of $(KI)_{1-x}(NH_4I)_x$ mixed crystals are governed by long ranged interaction forces, i. e. not only by the octupole-octupole exchange between the tetrahedrally shaped ammonium ions. Indeed, subsequent dielectric[4], hypersonic[5] and Raman scattering[6] experiments confirmed this conjecture. In particular the elastic shear constant c_{44} showed a softening at low temperatures and the dielectric constant of these crystals exhibited a Curie-Weiss behavior. The latter indicated the existence of a large dipole moment ($\mu = 1.4D$) of the NH_4^+ ion when embedded in a lattice with rocksalt symmetry. No dipole moment is detectable in the low temperature CsCl-type phase of NH_4I and is presumably also absent in samples where the ammonium concentration is still high enough to drive the martensitic NaCl $\longrightarrow$ CsCl transformation. However the phase diagram of this binary system is not

known. Therefore we have investigated five mixed crystals covering the entire concentration range $0 < x < 1$ using dielectric methods. This allowed the determination of important features of the phase diagram of $(KI)_{1-x}(NH_4I)_x$ as well as of the critical concentration x_c up to which the mixed crystals maintain their rocksalt structure down to lowest temperatures. In this concentration regime the strong and anisotropic dipolar interactions together with the random distribution of the NH_4^+ dipoles on the lattice sites favor the establishment of a dipolar glass state[4].

We will briefly discuss the effect of deuteration on the freezing process, which is of interest also in other dipolar systems like the RADP-type proton glasses[2] or in the octupolarly disordered methane-krypton solid solutions[7].

EXPERIMENTAL

Small crystals of $(KI)_{1-x}(NH_4I)_x$ with $x_{sol} = 0.7$, 0.8, 0.9 were grown from aqueous solution. Here x_{sol} characterizes the NH_4I concentration in the solution. In order to perform dielectric measurements on these relatively small ingots they were powdered and filled into a capacitor for which the geometrical capacity was 5 pF. The filling factor of the configuration was estimated to be about 25 %. Measurements on gold plated single crystals were performed for concentrations $x_{sol} = 0.5$ (actual ammonium fraction $x = 0.43$) and 1 [4], as well as for a deuterated sample $(KI)_{1-x}(ND_4I)_x$ with $x_{sol} = 0.5$. The complex dielectric constant $\epsilon = \epsilon_1 - i\epsilon_2$ was measured in the frequency range 10^{-2} Hz to 10^7 Hz using two and four wire impedance techniques as described previously[8].

RESULTS AND DISCUSSION

In pure NH_4I the real part of the dielectric constant ϵ_1 increases with decreasing temperature until at 242 K the martensitic phase transition causes a sudden drop in ϵ_1 [4]. Lowering the concentrations to $x_{sol} = 0.9$ respectively 0.8, the general behavior is the same as in the pure compound (see fig.1): the drop in ϵ_1

smeares out and is shifted to lower temperatures. The step in ϵ_1 broadens with decreasing concentration of the ammonium ions. This indicates that the increasing distortion of the lattice by replacing K^+ for NH_4^+ ions drives the lowering of the phase transition temperature. The lack of relaxation in the dielectric loss ϵ_2 of the samples with $x_{sol} > 0.8$ indicates that the step in ϵ_1 is induced by a phase transition. In the sample $x_{sol} = 0.8$ the imaginary part ϵ_2 shows a slight and also smeared out maximum without dispersion, which indicates the onset of a glass like behavior as observed more distinctly for the samples with lower concentrations[4]. In addition in temperature cycling experiments a hysteresis of about 60 K was observed which is quite large and may be compared to that observed for example in NaCN by X-ray diffraction[9]. This hysteresis can be interpreted in terms of the still existing martensitic phase transition. These observations suggest that $x_{sol} = 0.8$ is near the critical concentration of this binary system.

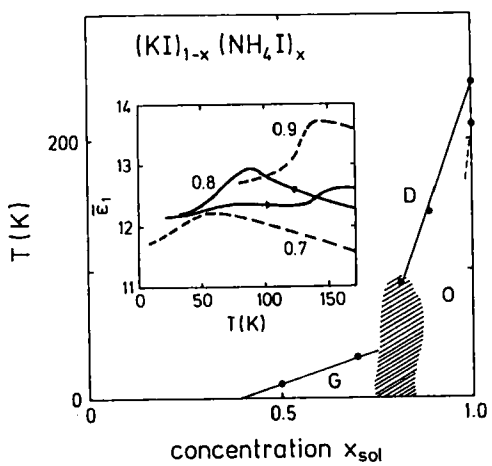

FIGURE 1 Schematic phase diagram of the binary system $(KI)_{1-x}(NH_4I)_x$. ϵ_1 versus temperature is given as an insert for several concentrations x_{sol}. The transition temperatures for $x_{sol} = 0.9$ and 0.8 are determined by the corresponding cusps in ϵ_1.

The real parts of the dielectric constants ϵ_1 for samples with the concentrations $x_{sol} = 0.7$ and 0.5 (the actual concentration in this crystal is x = 0.43) are given in the insert of fig. 1, respectively in fig. 2. For these crystals a Curie-Weiss behavior $\chi = C/(T - \Theta)$ of the static susceptibility $\chi = (\epsilon_1 - \epsilon_\infty)/4\pi$ was observed at high temperature. By taking into account the lattice polarization contributions $\epsilon_\infty = 4.68 + T/700$ of pure KI[10] we calculated the Curie constant C = 117 K and the Weiss temperature Θ = -163 K. The negative value of Θ is a measure of the antiferroelectric dipolar correlations.

At low temperatures the real part of the dielectric constant ϵ_1 drops to lower values and is indicative for glassy freezing as studied previously in more detail for a $(KI)_{1-x}(NH_4I)_x$ sample with $x_{sol} = 0.5$. The imaginary part ϵ_2 shows maxima. From the temperature shift of the loss maxima the hindering barrier E and the attempt frequency ν_0 were estimated by parameterizing the experimental results with an Arrhenius law.

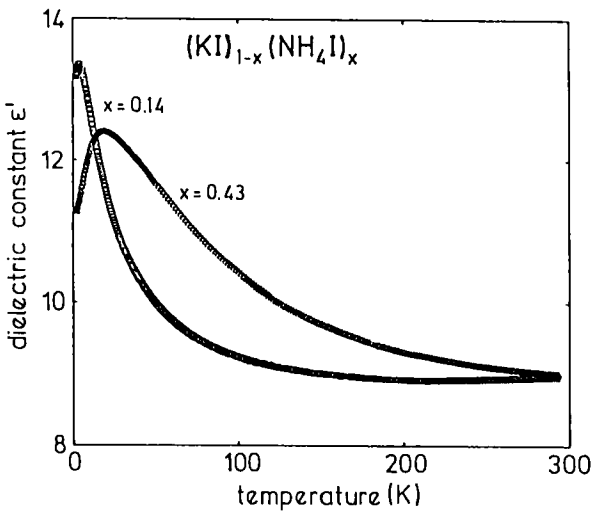

FIGURE 2 Dielectric constant ϵ_1 versus temperature T for $(KI)_{1-x}(NH_4I)_x$. The concentrations are $x_{sol} = 0.2$ and 0.5 The corresponding concentrstions in the crystals are x = 0.14 and 0.43. The measuring frequency was 100 kHz.

In order to find out how deuteration effects the freezing we investigated a deuterated sample with $x_{sol} = 0.5$. We find that the general behavior of the dielectric constant of the deuterated (D) sample was similar to that observed in the protonated (H) sample. In the D-compound also a Curie-Weiss behavior was seen with a Curie constant of C = 125 K and a Weiss temperature of $\Theta = -131K$. Within the experimental error this leads to the same dipole moment μ as in the protonated sample. A difference was observed in the temperatures where the cusps in ϵ_1 and the loss maxima appeared. The temperatures are shifted to lower values which is the opposite of what is usually observed upon deuteration[7]. The temperature shift of the loss maxima is different from that observed in the H-sample and gives a significantly lower hindering barrier. A full account of our results will be given elsewhere.

SUMMARY

In conclusion we have presented preliminary results on protonated and deuterated crystals of $(KI)_{1-x}(NH_4I)_x$. For the protonated compounds a schematic x,T-phase diagram is presented. the critical concentration x_c is close to 0.8. In the rocksalt structure the deuterated compounds reveal a similar magnitude of the dipole moment ($\mu \approx 1.4$ D). The freezing temperatures in the deuterated samples are shifted to lower values.

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