$(KI)_{1-x}(NH_4I)_x$: A Dipolar Glass

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Solid solutions of $(KI)_{1-x}(NH_4I)_x$ with concentrations $x = 0.14$, 0.43, and 1 were investigated using dielectric spectroscopy. The high-temperature rocksalt structure of these compounds exhibits a dipole moment of 1.4 D. For $x = 0.14$ and 0.43 the NaCl structure is stable down to the lowest temperatures and the reorienting dipoles undergo a cooperative freezing transition devoid of long-range orientational order.

An orientational-glass (OG) state occurs when reorienting moments of mixed crystals freeze into random configurations. In these systems the interplay of site disorder and frustrated interactions is thought to be responsible for the freezing transition. The moments can be assigned to orientations of aspherical molecules carrying dipolar, quadrupolar, or octupolar moments, or to off-center displacements of atoms. According to the leading interaction OG's are specified as dipolar,[1-4] quadrupolar,[5,6] or octupolar glasses.[7] The freezing transition bears similarities with the spin-glass transition in dilute magnetic systems.[8] In addition, the low-temperature heat capacity and thermal conductivity in OG's exhibit a behavior reminiscent of canonical glasses.[9] Thus OG's might be conceptual links between spin glasses and canonical glasses.

As a function of temperature and pressure the ammonium halides undergo a number of structural phase transformations.[10] In the high-temperature α and β phases, the ammonium ions are dynamically disordered. The γ and δ modifications reveal orientational order. At room temperature and ambient pressure NH_4I exhibits the α modification, which is a NaCl-type structure where the NH_4 ions undergo fast reorientations. At $T_{\alpha\beta} = 255.8$ K, ammonium iodide transforms into a CsCl structure where the NH_4 tetrahedra are randomly distributed between two energetically equivalent orientations. Finally, below $T_{\beta\gamma} = 231.8$ K octupolar order is established in a slightly distorted CsCl structure of tetragonal symmetry.[10]

It has been known for a long time that KI and NH_4I are completely miscible.[11] Early heat-capacity measurements by Stephenson, Landers, and Cole[12] revealed that NH_4I can easily be supercooled and that a sufficient amount of potassium iodide in ammonium iodide stabilizes the high-temperature fcc structure. The excess heat

capacity observed in $(KI)_{0.54}(NH_4I)_{0.46}$ has been interpreted in terms of residual orientational disorder.[12]

Recent neutron-scattering studies in $(KI)_{1-x}(NH_4I)_x$ by Bostoen, Coddens, and Wegener[13,14] supported this view and stressed some similarities with the octupolar glass $(Kr)_{1-x}(CH_4)_x$.[7] Using inelastic incoherent neutron scattering, the molecular excitations have been studied for mixed crystals with NH_4 concentrations $x < 0.45$. The results revealed that NH_4-NH_4 interactions contribute significantly to the crystal field.[14]

Gold-plated crystals with NH_4 concentrations $x = 0.14$, 0.43, and 1 have been investigated. All crystals were grown from aqueous solution. The measurements of the complex dielectric constant $\epsilon = \epsilon' + \epsilon''$ at audio frequencies were performed using an HP4274 *LCR* meter for temperatures 1.4 K $< T < 300$ K. Preliminary high-frequency data[15] were recorded utilizing an HP4191 impedance analyzer. Figure 1 shows the dielectric constant ϵ' versus temperature for NH_4 concentrations $x = 0.14$, 0.43, and 1. For pure NH_4I, $\epsilon'(T)$ reveals two successive anomalies at $T_{\alpha\beta} = 242$ K and $T_{\beta\gamma} = 208$ K. These anomalies in the dielectric constant indicate the phase transitions from the high-temperature rocksalt structure into an intermediate CsCl structure and into a low-temperature tetragonal structure. The upper transition is of the martensitic type and characterized by a large hysteresis. The data as shown in Fig. 1 were recorded on cooling. Both transition temperatures are well below those given in Ref. 10. At the martensitic transition the NH_4I single crystals broken up into macroscopic domains. This destructive process affects the accurate determination of the dielectric constants in the β and γ phases. In the high-temperature phase, a significant increase of ϵ' can be observed. It is interpreted as Curie-Weiss behavior arising from interacting dipoles which rotate with rates faster than the measuring frequency.
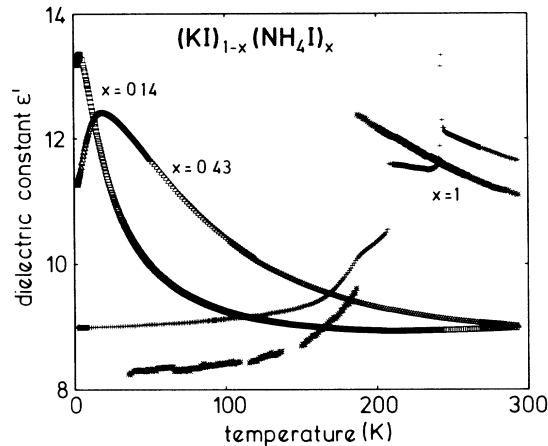
FIG. 1. Temperature dependence of the dielectric constant ϵ' in $(KI)_{1-x}(NH_4I)_x$ for concentrations $x = 0.14, 0.43$, and 1 measured at 100 kHz. Curie-Weiss behavior appears in the high-temperature modification of NH_4I and is clearly seen in the mixed crystals. $\epsilon'(T)$ is also shown for a supercooled sample of NH_4I where the NaCl structure is stable down to 190 K. Here the probing frequency was 331 MHz. The difference in the absolute values of ϵ' gives an estimate of the geometrical uncertainties of the capacitors.

In subsequent experiments we supercooled the α phase of NH_4I and observed Curie-Weiss behavior for $T > 190$ K (Fig. 1). The existence of a quenched NaCl modification down to these temperatures is in agreement with the specific-heat results.[12]

We are aware of only two dielectric investigations of NH_4I. Both report measurements on powdered samples and find dielectric constants of $\epsilon' \approx 3$ (Ref. 16) and $\epsilon' = 9.8$ (Ref. 17) at ambient temperature and pressure. These values are well below those from the present investigation. It is suggestive that the filling of the capacitors with the NH_4I powder was not ideal in the previous experiments.

No indications of phase transitions can be seen for mixed crystals with $x \leq 0.43$ (Fig. 1). Here, apparently the high-temperature NaCl structure is stable down to the lowest temperatures. The Curie-Weiss behavior of $\epsilon'(T)$ indicates that in the octahedral environment the NH_4 ions exhibit a dipole moment which reorients faster than the probing field. At low temperatures, the real part of the dielectric constant starts to decrease. Obviously, the ammonium reorientations slow down on the time scale of the dielectric measurements. At a given measuring frequency the cusp in $\epsilon'(T)$ is shifted with concentration. It appears at 18 K for $x = 0.43$ and is shifted to 4.5 K for $x = 0.14$ ($v = 100$ kHz). It has been pointed out by Brout[1] that pure dipolar systems reveal freezing temperatures which scale linearly with concentration. Limitations to this ideal behavior come from (i) contributions from the lattice anisotropy, (ii) a concentration dependence of the attempt frequencies, and (iii)

quenched random strain fields which are introduced by the impurity atoms and which contribute to the lattice anisotropy. In $(KI)_{1-x}(NH_4I)_x$ the scaling is stronger than linear (the x ratio is 3.1, while the T ratio of the cusp maxima is 4). Certainly, at the high-doping levels investigated, limitations (i), (ii), and (iii) yield deviations from linear scaling. Taking this into account the agreement with the theoretical predictions for a pure dipolar system is reasonably good.

Neutron-scattering results[14] on the tunneling excitations in $(KI)_{1-x}(NH_4I)_x$ revealed that the octupole-octupole interactions are far too weak to explain the experimentally observed increase of the effective hindering barriers. From a detailed analysis the authors of Ref. 14 concluded that dipolar interactions may play an important role.

The frequency dependence of the dielectric loss for mixed crystals with concentrations $x = 0.43$ and 0.14 is shown in Fig. 2. Here $\epsilon''(v)$ is plotted versus temperature for different measuring frequencies v. In the 43% sample the maxima of the loss peaks appear at 10 K, while they are shifted below 2 K for $x = 0.14$. For $(KI)_{0.57}(NH_4I)_{0.43}$ the temperature dependence of the dielectric loss maxima is given in the lower inset of Fig. 2.

We parametrized the experimental results with an Arrhenius law using an attempt frequency of $v_0 = 10^{26}$ Hz and a hindering barrier of 460 K (solid line in the lower inset of Fig. 2). This barrier is low compared to experimentally observed barriers against reorientation in pure NH_4I ($E/k_B = 1400$ K).[18] It is, however, significantly larger than the lattice anisotropy which is experienced from NH_4 defects in KI ($E/k_B = 285$ K).[14] An unphysically high prefactor v_0 is often observed in the relaxation dynamics of complex materials. It can be explained by taking, in addition to the true energy of activation, an entropy term into account: For example, one possible explanation is a linear temperature dependence of the hindering barriers. But the unphysical prefactor might also signal the breakdown of a single-ion model in the description of a highly cooperative freezing transition.

A further important result is the observation that the low-temperature relaxation rates decrease slower than expected even from a pure thermally activated behavior. The freezing dynamics in glasses is characterized by a faster decrease of the mean relaxation rates which can be parametrized in terms of the well-known Vogel-Fulcher law. We interpret these deviations as owing to a transition from thermally activated behavior to a tunneling phenomenon. This speculation if further substantiated by the highly anomalous low-temperature tail of the dielectric loss which points towards the existence of additional excitations below 9 K. We are aware that spin-conversion processes have to be taken into account at low temperatures. However, spin-conversion delay should be important only well below 4 K.[19,20]

The frequency dependence of the dielectric loss for

$x = 0.43$ is depicted in the upper inset in Fig. 2. Here ϵ'' is plotted versus $\log_{10}(\nu)$ for different temperatures. It shows that the dipolar absorption spectra of this sample are extremely broad. The width further increases with decreasing temperatures. The temperature, frequency, and concentration dependence of the complex dielectric constant exhibit the fingerprint of a transition into a glassy low-temperature state which is driven by dipolar interaction forces. The concentration dependence of the freezing-in shows that it is not a single-ion phenomenon of isolated dipoles in their anisotropic environment. The strong frequency dependence and the broad distribution of relaxation times reveals that it is not a transition into a long-range-ordered polar state.

From the results given in Fig. 1 we calculated the dipole moment of the NH_4 ion in its octahedral environment of the NaCl structure. To this end, the lattice polarization contributions $\epsilon_\infty = 4.68 + T/700$ of pure KI (Ref. 21) were subtracted from the data given in Fig. 1. In Fig. 3 the difference is plotted as inverse static susceptibility $\chi_s^{-1} = 4\pi/(\epsilon' - \epsilon_\infty)$ versus temperature. The straight lines were computed using Curie-Weiss laws $\chi_s = C/(T - \Theta)$, where $\Theta < 0$ is a measure of the antiferroelectric dipolar correlations. The Curie constants and the absolute values of the Weiss temperatures Θ decrease
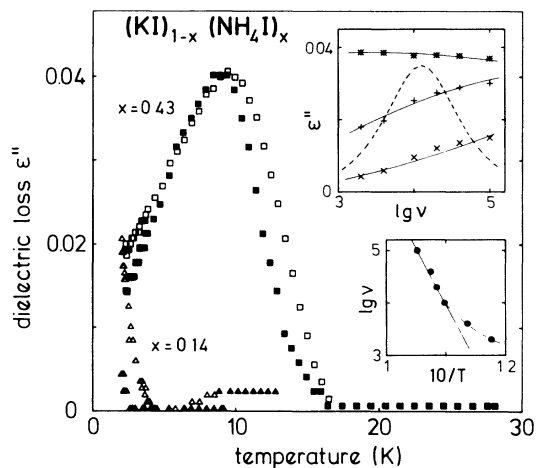
with decreasing concentration: for $x = 1$, $C = 331$ K, $\Theta = -345$ K; for $x = 0.43$, $C = 117$ K, $\Theta = -163$ K; and for $x = 0.14$, $C = 38$ K, $\Theta = -50$ K. From the Curie constants $C = n\mu^2/3k_B$ and the number densities n, the dipole moments μ were calculated. After Lorentz local-field corrections the following dipole moments were estimated for the data in Fig. 3: $x = 0.14$, $\mu = 1.4$ D; $x = 0.43$, $\mu = 1.4$ D; and $x = 1$, $\mu = 1.6$ D. The analysis of the measurements of the supercooled NH_4I sample yielded $\mu = 1.4$ D with a Curie-Weiss temperature of $\Theta = -235$ K.

We calculated the dipole moment under the assumption that locally the cubic symmetry is not broken and that the dipole moment can reorient almost free. From this analysis we cannot specify between bare or dressed moments. Under these assumptions the permanent dipole moment of the NH_4I ion in the rocksalt modifications of NH_4I and $(KI)_{1-x}(NH_4I)_x$ is given by $\mu = 1.4$ D. Taking into account the model assumptions, the unknown temperature dependence of the polarizability of the ammonium ion, and the uncertainties in the determination of the geometrical capacitances, it seems fair to estimate an error of 0.3 D.

The existence of this dipole moment was the first rather unexpected result of the present dielectric experiments. We note, however, that it naturally explains the reported failure of the Lyddane-Sachs-Teller relation[22] in NH_4I which was calculated assuming only ionic contributions to the dielectric constant. There are several mechanisms that could result in a dipole moment: From an analysis of neutron-scattering studies, Ozaki[23] concluded that C_{3v} is the most appropriate symmetry of the ammonium ion in an octahedral field. In this C_{3v} orien-
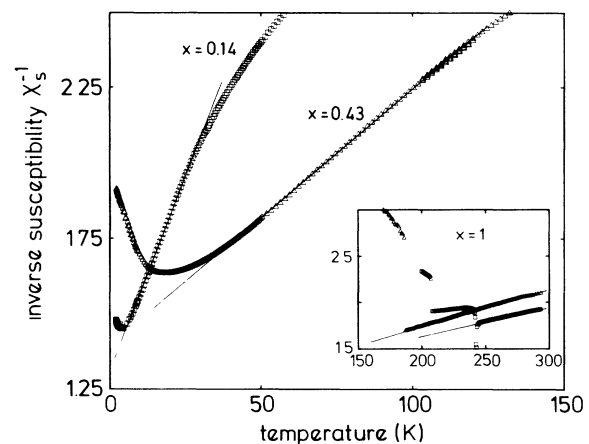

FIG. 2. Temperature dependence of the dielectric loss ϵ'' in solid solutions with $x = 0.14$ (triangles) and 0.43 (squares), measured at different frequencies: 100 kHz (open symbols) and 4 kHz (solid symbols). The data of the 43% crystal reveal the existence of additional excitations at low T. Upper inset: The frequency dependence of the dielectric loss $\epsilon''(\log_{10}[\nu/(1\ Hz)])$ for $x = 0.43$ as observed for various temperatures ($*$, 8.4 K; +, 11.9 K; ×, 14.0 K). The solid lines are drawn to guide the eye. For comparison the dashed line is calculated using the Debye relaxator model, i.e., assuming a single relaxation time. Lower inset: The temperature dependence of the frequency at which the dielectric loss maxima occur for $x = 0.43$ plotted as $\log_{10}(\nu/(1\ Hz))$ vs inverse temperature. The straight line is the result of a fit with an Arrhenius law. Deviations occur below $T \leq 9$ K.

FIG. 3. Inverse static susceptibility of $(KI)_{1-x}(NH_4I)_x$ for $x = 0.14$, 0.43, and 1 as a function of temperature. For ammonium iodide the audio-frequency data (100 kHz) and the high-frequency (331 MHz) results in a supercooled sample are shown. The lattice polarization was assumed to be identical to the one observed in pure KI (Ref. 22). The solid lines were calculated using Curie-Weiss laws as described in the text.

tation three of the hydrogen ligands exhibit a strong affinity to the neighboring iodide ions, while the fourth hydrogen points along the body diagonal. Because of the large polarizability of the iodide ions, this could result in a net dipole moment. On the other hand, it seems plausible that the mismatch of the ammonium ion in an octahedral environment results in an off-center position of the center of mass of the NH_4 ion. With the dipole moment as given above this off-center shift would be of the order of 0.03 nm, if this mechanism were acting alone. From an analysis of single-crystal neutron-diffraction experiments,[24] it has been speculated that the NH_4 ion exhibits displacements of about 0.01 nm from the face-centered positions.

The appearance of a frustrated ground state in $(KI)_{1-x}(NH_4I)_x$ through the interplay of site disorder and the anisotropic dipole-dipole interactions is the second appealing results of these investigations. Specifically, we want to emphasize that $(KI)_{1-x}(NH_4I)_x$ is dominated by dipolar interactions and that the dipolar glass state can be studied in a wide concentration range without complications due to quadrupolar interactions.

Dipolar glasses have a number of advantages: Dielectric spectroscopy can be performed in a huge frequency range and thus the evolution of the mean relaxation time with decreasing temperatures and the distribution of relaxation times can be studied in full detail. Field-cooled and zero-field-cooled experiments can be performed and one is able to receive the same quality of information as in spin glasses. From a theoretical point of view, the experimental findings in this dipolar glass can directly be used to test the model predictions from Fischer and Klein.[2]

Finally, we draw attention to theories by Sethna and Chow[25] who have directly connected the secondary relaxation in certain orientational glasses with the appearance of a linear term in the specific heat. In a dipolar glass only primary relaxation modes are expected and it would be worthwhile to check the low-temperature thermodynamic properties in a system with no secondary relaxation. Preliminary calorimetric experiments for concentrations $x = 0.07$ and 0.14 revealed Schottky-type anomalies near 0.5 K and no glasslike anomalies at low T.[20] It is also pointed out that the solid solutions of NH_4I and KI are dominated by quantum effects at temperatures $T \leq 10$ K. Therefore this dipolar glass appears ideal to test the influence of quantum fluctuations on the glass transition.[26]

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