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High-pressure neutron powder diffraction on the solid solution series $(ND_4)_xK_{1-x}I$

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Abstract

The system $(NH_4)_xK_{1-x}I$ is known to possess a variety of phase transitions, depending on the concentration x. For $x \leqslant 0.5$ it shows an orientational glass state below a freezing temperature $T_F \approx 10$ K. The effect of deuteration has not been studied so far. To get insight into the structural influence of an increased tunneling potential for the ammonium ions, we investigated the phase diagram of the deuterated homologues for $x = 0.5$, 0.7 and 0.8 at ambient conditions and under applied pressure of up to 13 kbar by powder neutron diffraction. At ambient conditions $(ND_4)_xK_{1-x}I$ for $x = 0.5$, 0.7 and 0.8 shows the same NaCl-type structure (α-phase) as its protonated homologues. A transition into a primitive cubic high-pressure phase has been detected. This phase transition is completely reversible. The transition pressure depends on x. We discuss a CsCl-like structure for the high-pressure phase.

1. Introduction

The concentrated systems of the completely miscible solid solution series $(NH_4)_xK_{1-x}I$ show long-range order of their orientational degrees of freedom at low temperatures. Below a critical concentration, ($x_c \approx 0.5$) such a long-range ordering of the dipolar moments of the ammonium ions is not possible anymore. Local frustration effects, due to the misfit in symmetry of the tetrahedral ammonium ions in its octahedral environment lead to a glassy state [1]. To understand the nature of the glass transition, we have started an investigation of the phase diagram of the deuterated homologues at ambient conditions and under applied pressure. The comparison with the protonated samples will provide insight into the molecular dynamics when changing the rotational mass, whereas the application of pressure is changing the tunneling potential between the different configurations of the ammonium ions.

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2. Experimental results and discussion

We have investigated polycrystalline samples of $(ND_4)_xK_{1-x}I$ by powder neutron diffraction for $x = 0.5$, 0.7 and 0.8 at room temperature and under applied pressure up to $p = 13$ kbar.

These experiments have been performed on the multidetector diffractometer E6 at the Hahn-Meitner-Institute, Berlin, employing the Kiel–Berlin pressure cell [2]. An incident neutron energy of $\lambda = 2.4$ Å has been selected by a graphite monochromator. NaCl was used as an internal pressure standard and fluorinert as pressure transmitting medium.

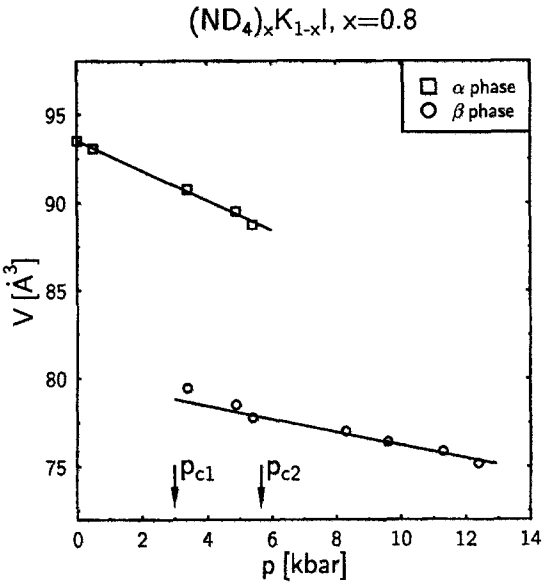

Fig. 1. Phase diagram of $(ND_4)_xK_{1-x}I$ ($x = 0.8$) under applied pressure; p_{c1} and p_{c2} denote the critical pressures, where the phase transformation begins and ends, respectively. The volume of the α-phase refer to the primitive cell of the FCC lattice.

At ambient conditions, all samples investigated showed the FCC NaCl type of structure (α-phase) [3]. It is the same high-temperature plastic phase as found in its protonated homologues [4]. With increasing pressure, additional reflections indicated the emergence of a different high-pressure phase, which could be indexed by a cubic primitive cell. As shown in Fig. 1, above a first critical pressure p_{c1} this phase coexists with the α-phase; above a second critical pressure p_{c2} the α-phase has vanished completely. The p_c's as well as linear volume bulk moduli are listed in Table. 1. Since a certain range of coexistence is observed, the transition is first order. No broadening of peaks due to pressure inhomogeneities could be observed. Cycling the pressure demonstrated perfect reversibility of the phase transition.

The ammonium halides show a variety of order–disorder phase transitions [3].

The different phases of ND_4Br had been described by [6] and a generalized p–T phase diagram has been proposed [5]. According to [5], a β-phase characterized by a CsCl-like structure should emerge under applied pressure. From Table 1 follows that the bulk moduli of the β-phase b_β are nearly twice b_α, except for $x = 0.7$. The bulk moduli b_α for $x = 0.5$ and 0.8 are in good agreement with predicted values from a linear interpolation between b_α's of the solid solution series end members. The phase transition does not change the crystal class; the corresponding space group changes from $Fm\bar{3}m$ to $Pm\bar{3}m$.

Table 1
Values of the critical pressures and corresponding linear bulk moduli for different concentrations of $(ND_4)_xK_{1-x}I$ (p_c and b are given in kbar)

x	p_{c1}	p_{c2}	b_α	b_β
0.5	3.6	$\geqslant 11$	117	192
0.7	6.0	≈ 12	149	138
0.8	3.4	5.4	110	222

High-resolution diffraction experiments in an extended q-range are needed to give detailed insight into the high-pressure structural behaviour of $(ND_4)_xK_{1-x}I$, above all to elucidate the special behaviour for $x = 0.7$.

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