Pressure-induced orientation phase transition in solids [*]

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Abstract

The pressure-induced orientation phase transitions in both molecular and magnetic crystals are considered. On the base of elastic and inelastic neutron scattering data at high pressure up to 10 GPa, variations of structure and dynamics of ammonium halides NH_4X (X=F, Cl, Br, I) are described.

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1 Introduction

The pressure-induced orientation phase transitions in such different systems as molecular and magnetic crystals are considered. Ammonium halides NH_4X (X=Cl, Br, I) experience a series of phase transitions following changes in temperature and pressure. The order-disorder transition from the disordered CsCl-type phase to the structure with ordered hydrogen atoms occurs at the decrease in temperature and increase in pressure [1 - 4]. High-pressure studies of ammonium halides are of interest for elucidation of the interplay

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between structural and dynamical changes and of the phase transitions occurring upon volume decrease. The influence of high pressure on the libration mode of ammonium ions and the phase-transition-induced changes in its behavior are among the most intriguing aspects of the dynamics of ammonium halides. In this work, variations in structure and dynamics of ammonium halides NH_4X (X=F, Cl, Br, I) under high pressure up to 10 GPa are discussed using elastic and inelastic neutron scattering data [5 - 9].

2 Experimental

The most experiments were performed with the multi-detector powder diffractometer DISK [10] (IRT-M, Kurchatov Institute, Russia) and with the time-of-flight high-pressure neutron spectrometer DN-12 (IBR-2, JINR, Russia) [11] using sapphire anvils high pressure cells [12]. The sample volume was 3 mm^3. The pressure was determined by the ruby fluorescence technique withing an accuracy of 0.5 kbar. Low temperature of the sample was maintained by a special cryostate on the base of closed cycle helium refrigerator. The typical exposition time was 15 - 20 h. Several experiments were performed with the POLARIS diffractometer [13] (ISIS, RAL, UK) using the Paris-Edinburgh High Pressure Facility [14]. In these experiments the sample volume was 100 mm^3.

3 Results

The equations of state and the pressure dependence of interatomic distances were determined in ammonium halides. It was established that under compression the distance between the ammonium cation ND_4^+ and the anion X^- (X= Cl, Br, I) largely decreases. In doing so the covalent bond length l_{N-D} of the ammonium ion does almost not change with pressure remaining equal to 1.02(2) Å at any halide anion radii. It was found that the phase transition between the disordered CsCl-type cubic phase II and the ordered phase IV, V in ammonium halides could be ascribed to a critical value for the deuterium positional parameter u_{cr} ($u = \frac{l_{N-D}}{a\sqrt{3}}$, where l_{N-D} and a are the N-D bond length and the lattice parameter, respectively), as it is shown in Fig. 1. For a pressure range where the condition $u < u_{cr}$ is satisfied, ammonium halides exist in the phase II and for $u > u_{cr}$ we have the parallel ordered (Cl, Br) phase IV or antiparallel ordered (I) phase V.

The influence of high pressure on a rotational potential barrier in ammonium halide phases was investigated. It was found that the phase transitions
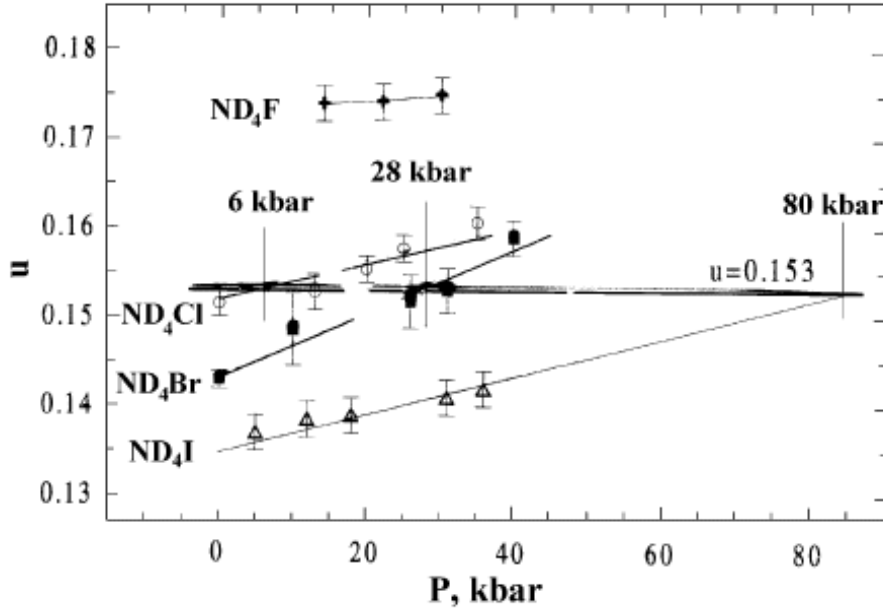
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Figure 1: Pressure dependence of the deuterium position parameter in ammonium halides. It is shown that the II-IV phase transition in ND_4Cl and ND_4Br occurs at the equal critical values u_{cr}=0.153. For ND_4I, the position parameter reaches this critical value in the phase V. For ND_4F, initial value of u is higher than u_{cr} and only the ordered CsCl - type cubic structure ND_4F(III) exists at high pressure.

from the disordered cubic phase to the phases with different ammonium ion ordering result in increasing of a rotational potential barrier value (Fig. 2). This matches a distortion of the model symmetric two-wells potential, which is shaped into an asymmetric form by increasing of the depth of one potential well. The potential change is a result of ammonium ion ordering.

The vibrational spectra of ammonium halide NH_4I were studied under pressure up to 10 GPa by incoherent inelastic neutron scattering. The behavior of the L and TO frequencies justifies the appearance of interaction between them, i.e., libron- phonon hybridization. This effect (Fig. 3) results in the successive attraction and repulsion of the vibrational branches and, respectively, in sizable changes of the Grüneisen parameters. The nature of this phenomenon is, likely, similar to the hybridization of other types of
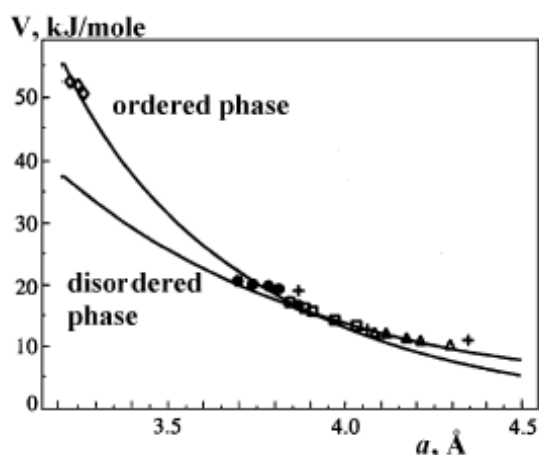
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Figure 2: Rotation potential barrier as a function of the lattice parameter a for ordered and disordered phases in ammonium halides: $\triangle$ - NH_4I, $\square$ - NH_4Br, $\bigcirc$ - NH_4Cl, $\diamondsuit$ - NH_4F. Solid lines are the theoretical curves for $V_o = B/a^c$, c=5 for disordered phases, c=7 for ordered phases.

excitations, in particular, magnons and phonons in magnetic crystals. Every ammonium ion there can be attributed with an orientation vector directed from the center of NH_4^+ tetrahedron to one of its vertices. The librations are caused by the oscillations of the orientation vectors about their equilibrium positions, such as the atomic magnetic moments oscillate in magnons. However, there is no spatial correlations between the librations of neighboring NH_4^+ ions, so that this branch is virtually dispersionless.

Thus the simple models of interatomic potential change at pressure - induced phase transitions are used to describe the observed structural changes and give possibilities to predict structural behavior of these systems for a higher pressure.

Besides the molecular systems, we have performed investigations of phase transitions in different types of magnets under pressure [15 - 19]. In particular, it was established that in the uniaxial high-temperature weak ferromagnets with similar structure (Fe_2O_3, $FeBO_3$) there is a spin-reorientation transition from the "easy-plane" anisotropy to the "easy-axis" anisotropy at relatively low pressure (15-30 kbar). At the same time in the low-temperature weak ferromagnet manganese carbonate the "easy-plane" condition persists without noticeable changes at 10-15K up to the pressure 60 kbar.
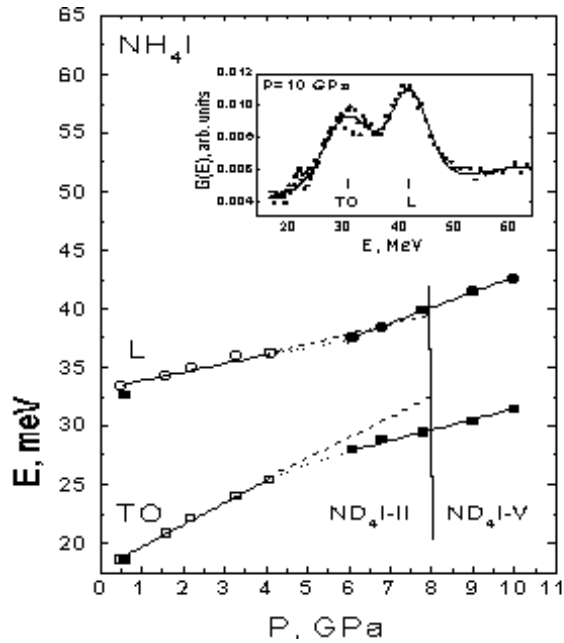
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Figure 3: Pressure dependence of the L and TO modes of NH_4I. Solid lines are the linear interpolations of experimental data in the ranges 0-4 and 6-10 GPa, respectively; dotted lines are the interpolation in the range 4-6 GPa; and dashed lines are the linear interpolation to the II-IV phase-transition point in ND_4I.

One can connect the difference in the behavior of low- and high-temperature ferromagnets under pressure with the distinction in the behavior of a magnetic-elastic gap in the excitation spectra. For the case of high-temperature weak ferromagnets like the hematite or the iron borate, $T_c > \theta_D$ and the value of magnetic-elastic gap decreases with pressure because θ_D increases and T_c decreases. As a result, the gap "collapses" and this effect brings about the phase transition in the spin system. In the case of low-temperature weak ferromagnets ($MnCO_3$, etc.) the situation is opposite ($T_c < \theta_D$) and the increasing of θ_D and decreasing of T_c under pressure must extend the gap. As a result, the reorientation phase transition is absent.

Atomic and magnetic MnAs structure was investigated under pressure up to 38 kbar in the temperature range 15-30K by the neutron diffraction

method. It was established that during temperature decreasing under high pressure, there is the spin-reorientation transition in MnAs from the ferromagnetic orthorhombic phase to the new phase having both ferromagnetic and antiferromagnetic components of magnetic moments. The transition brings about the magnetic moment deviation in the (011) plane by $\sim 50^0$ and ferromagnetic moment decreasing. In doing so, Mn and As atomic structural parameters remain constant with temperature decreasing except for the x-parameter of a Mn atom which increases slightly. It can be essential because increase in the x-parameter must change the magnetic interaction in the first and second coordination shells and can initiate the magnetic phase transition.

Finally, comparison of data obtained at hydrostatic and quasi hydrostatic condition shows that the spin-reorientation magnetic transition may be divided into two classes (pressure-induced and stress-induced). Thus on the base of the described experiments one has a possibility to predict the behavior of the wide class of weak-ferromagnetic systems depending on the relationship of elastic and magnetic performances and their changes at volume decreasing.

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