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X-ray evidence for a new phase in ammonium hydrogen oxalate hemihydrate under pressure

L. Bosio ⁽¹⁾, M. Oumezzine ⁽²⁾ and R. Pick ⁽³⁾⁽¹⁾ Laboratoire Physique des Liquides et Electrochimie, ESPCI, 10, rue Vauquelin, 75231 Paris Cedex 05, France⁽²⁾ Faculté des Sciences et Techniques, Monastir 5000, Tunisie⁽³⁾ Département de Recherches Physiques, Université P. & M. Curie, 4, place Jussieu, 75252 Paris Cedex 05, France

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Résumé. — Les diagrammes de diffraction obtenus à l'aide d'une cellule à enclumes de diamant ont permis d'identifier, à haute pression et basse température, les taches de surstructure caractéristiques de la phase III de $\text{NH}_4\text{HC}_2\text{O}_4, 1/2 \text{H}_2\text{O}$. A 77 K et 0,75 GPa, les taches trouvées entourent les pics de Bragg de la phase I et sont situées à $(h, k, 1 \pm \delta)$ avec $\delta \approx 0,25$.

Abstract. — Using an X-ray diamond anvil cell, we have found superlattice reflections, characteristic of the high pressure-low temperature phase III of $\text{NH}_4\text{HC}_2\text{O}_4, 1/2 \text{H}_2\text{O}$. At 77 K and 0.75 GPa, these peaks are located around each Bragg peaks of phase I at position $(h, k, 1 \pm \delta)$ with $\delta \approx 0.25$.

1. Introduction.

At room temperature and normal pressure, ammonium hydrogen oxalate $\text{NH}_4\text{HC}_2\text{O}_4, 1/2 \text{H}_2\text{O}$ crystallizes in an orthorhombic structure (phase I) with $a = 12.329$, $b = 11.228$ and $c = 6.898 \text{ \AA}$; $Z = 8$, space group Pmnb [1, 2]. The oxalate groups, located in a general position, are linked together by hydrogen bonds and form infinite chains along the b direction. The oxygen atom of the water molecule lies in the mirror plan and occupies a special position. The most striking feature of the structure is the two non-equivalent special positions of the ammonium groups: the nitrogen of one of them, lying in the mirror plan, is coordinated by seven atoms whereas the nitrogen of the second ammonium group, also in the mirror plan, is coordinated by nine oxygen atoms. This higher coordination number leads to larger bond distances so that the hydrogen atoms of this NH_4^+ ion have a larger freedom of motion, and are in fact disordered between two equivalent positions.

At normal pressure and below 145.6 K, the NH_4 groups move off the mirror planes and the compound undergoes a phase transition to monoclin-

ic space group $\text{P2}_1/\text{n}$ (phase II) with $a = 12.331$, $b = 11.2241$, $c = 6.7608 \text{ \AA}$ and $\beta = 91.64^\circ$ (at 128 K); $Z = 8$ [2]. This phase contains two independent oxalate molecules by asymmetric unit but its structure is not fundamentally different from the one in the high-temperature phase I (Fig. 1): the major structural change during the phase transition I \rightarrow II — which is a second order ferro-elastic transition —

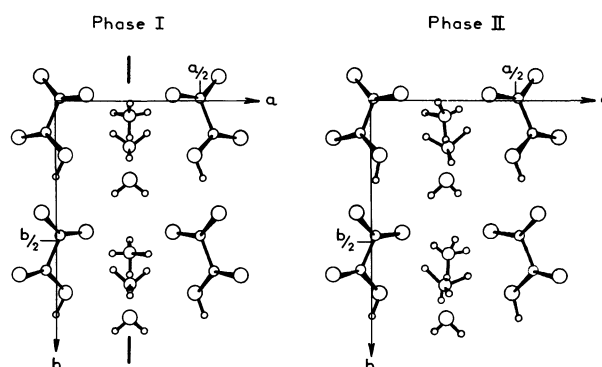


Fig. 1. — Upper half of the unit cell of phase I and II (note the disappearance of the mirror plane in the monoclinic phase II).

is a change in the hydrogen network related to the ordering of one family of NH_4^+ ions [3].

Various Raman experiments have been performed in the temperature range 80 to 300 K and under pressure up to 0.8 GPa [3, 4]. Above 0.3 GPa and at low temperature another phase (labelled phase III) was discovered (Fig. 2): in the Raman spectra, phase III is essentially characterized by peaks located at very low frequencies; the frequencies of these peaks increases with the pressure but are not temperature dependent. Several possible structures have been proposed on the basis of the Raman data for this new phase [4] among which an incommensurate phase seemed to be the most likely. But it was necessary to perform diffraction study to ascertain such a prevision. In this paper, we describe X-ray measurements under pressure which have been able to locate the superstructure peaks related to phase III.

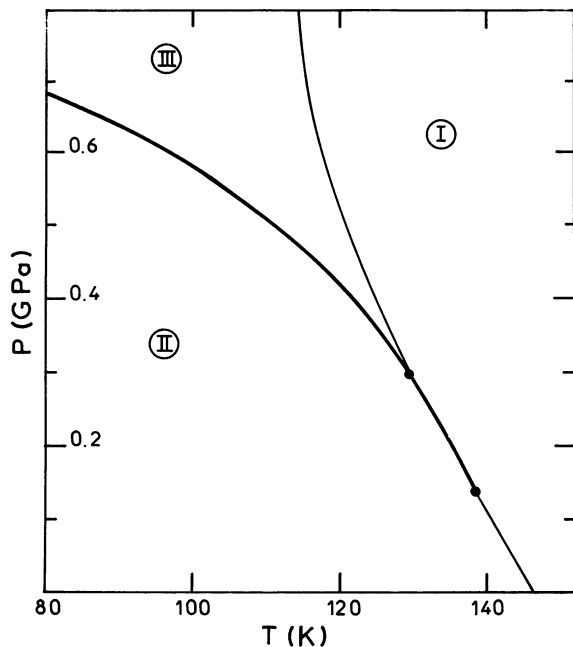


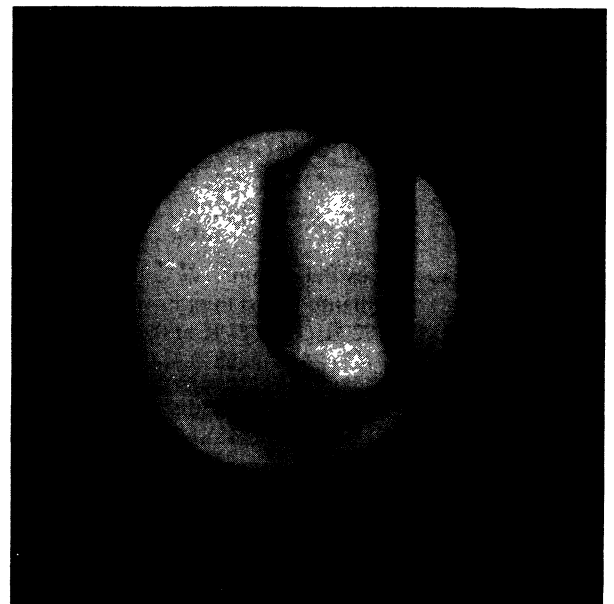
Fig. 2. — Pressure-temperature phase diagram of $\text{NH}_4\text{HC}_2\text{O}_4, 1/2 \text{H}_2\text{O}$; the darkest line is related to a first-order transition (from Ref. [3]).

2. Experimental.

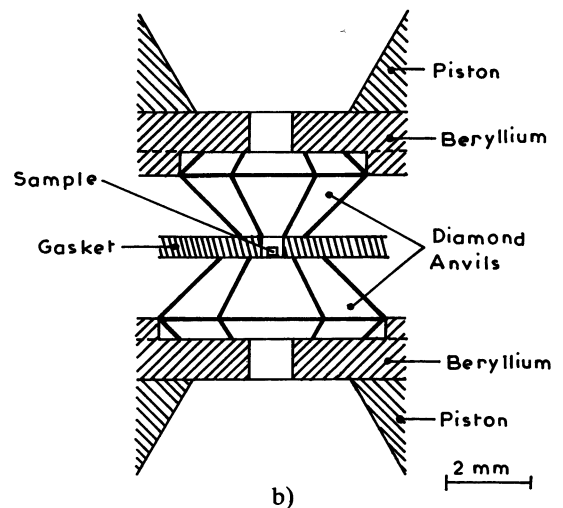
Several high pressure devices allowing X-ray study have been described; but most of them are essentially restricted to conventional diffraction measurements, that is, not suitable for satellite peaks observation in the case of a modulated structure. To our knowledge, only one apparatus has been built which allows X-ray diffuse scattering experiments [5]. Nevertheless, this device seemed to be not quite convenient for our purpose because it allows experiments up to only 0.5 GPa and also because we had to

explore a large region of the reciprocal space as we did not know anything about the structure of the high-pressure phase III.

Actually, we used a slightly modified version of a diamond anvil cell previously built for X-ray diffraction measurements [6]: in our device, the working surface area of the anvil faces was increased up to approximately 1.5 mm^2 ; with this arrangement, holes of 0.5-0.6 mm diameter could be drilled in the stainless gasket (0.5 mm thick) so that relatively large samples could be introduced between the anvil faces together with a tiny fragment of ruby for pressure calibration (Fig. 3). With the increase of



a)



b)

Fig. 3. — a) A single crystal of ammonium oxalate in the diamond cell, oriented with the c axis in the plan of the photograph. The smallest object is a crystal of ruby that acts as the pressure sensor. b) Schematic representation of the sample arrangement in the gasketed anvil cell. The hole (0.5 mm in diameter and in depth) serves as pressure chamber; the pressure transmitting fluid is silicone oil.

the diamond faces, the thickness of the anvils was reduced to minimize the X-ray beam absorption ; nevertheless, pressure up to about 1.5 GPa may be easily obtained in this configuration.

Single crystal specimens were prepared at room temperature from a supersaturated solution of an aqueous solution containing 1.2 mole of oxalic acid and 1 mole of ammonium oxalate. We selected single crystals grown with the convenient geometry and with well-shaped faces to orientate them in the pressure cell (Fig. 3). the pressure transmitting fluid was silicone oil, chosen for its inactivity with respect to the sample.

Owing to its compression system by means of six pressing screws [6], the pressure cell was small enough to be mounted at the bottom of an evacuated cryostat whose temperature could be regulated within 0.1 K in the temperature range 77-300 K. The X-ray beam entered and exited through two mylar windows. We used the $\text{Mo}_{K\alpha}$ radiation of a fine-focus tube operating at 1.2 kW ; for these experiments, it was readily established that the use of a Zr-filtered radiation was unadapted because, in this case, the background due to the diamond anvils, the beryllium seats, the gasket and the silicone oil was too high to detect any satellite peaks. The radiation was therefore monochromated by a flat pyrolytic graphite monochromator mounted between the X-ray tube and the sample. The cryostat was settled on a two-circle diffractometer the scintillation counter of which could be manually positionned out of the equatorial plane, thus allowing the measurement of any reflection located in a scattering angle 2θ of about 60° . In the configuration allowing for oscillating-crystal photographs, the counter arm was replaced by a flat camera loaded with high-sensitivity film material, the crystal-to-film distance being fixed at 80 mm. The combination of the two detecting systems allowed for a rapid determination of the crystal orientation (the orientation of the crystal could be adjusted with respect to the oscillation axis by rotating the high-pressure cell in its support about the axis perpendicular to the gasket plane).

To change the pressure, we had to open the pre-warmed cryostat, move the pressing screws and recalibrate the pressure by measuring, at room temperature, the photoluminescence spectra from the ruby chip. To evaluate the pressure variation of the sample when the cell was cooled (typically 0.05 GPa when the temperature was lowered down to 77 K) we used the phase diagram (Fig. 2), measuring the temperature at which appeared phase II : actually, as shown by Keller *et al.* [2], the monoclinic phase turns out to be twinned ; by rotating the crystal in order to observe a strong reflection (e.g. (202)) it was very easy to detect at which temperature, for a given pressure, the rocking curve of such a reflection splitted up. This measure of the low temperature

pressure is, nevertheless, somewhat imprecise because the phase II-III transition has been measured, in [4], only with a 0.02 GPa accuracy.

3. Results.

A large number of oscillating-crystal photographs was taken with various orientations of the sample. The first evident and well-established result is that the average structure remains unchanged during the I \rightarrow III transition : within the experimental accuracy, no variation of the cell parameters or of the point group symmetry of the parent orthorhombic phase could be detected either in the position or in the intensity of the Bragg reflections. An illustration of this feature can be seen in figure 4 where the

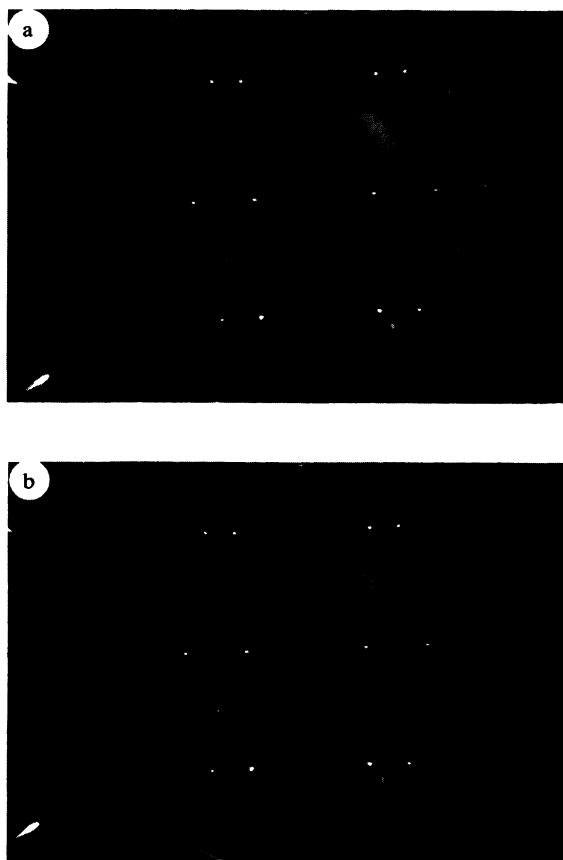


Fig. 4. — Oscillating-crystal photographs (oscillation $\pm 15^\circ$ around the c axis ; time exposure 18 h), registered from a sample kepted at 0.75 GPa. Plate a : modification I ($T = 300$ K). Plate b : modification III ($T = 77$ K).

photographs of the oscillating crystal related to the two modifications I and III are reproduced. Such a result excludes the assumption of a monoclinic average structure to explain the Raman spectra [4].

It was only when the films were totally overexposed that some satellite reflections could be observed around the strong Bragg peaks and along



Fig. 5. — Oscillating-crystal photograph registered at 77 K and 0.75 GPa (oscillation $\pm 15^\circ$; time exposure 72 h). Note the satellite peaks symmetrically located about the central Bragg reflections along the c^* axis.

the c^* axis (Fig. 5) which explains why the signal-to-noise ratio had to be optimized to detect such features under pressure. At 77 K and $P \approx 0.75$ GPa, these satellites appear at position $h, k, l \pm \delta$ with $\delta \approx 0.25$. Some rotating-crystal photographs were taken with the crystal oscillating within few degrees in the vicinity of the strong reflections (Fig. 6): the intensities of the satellite peaks are symmetric about the central peak, no systematic extinction was found and no satellite with $\delta \approx 0.5$ could be detected.

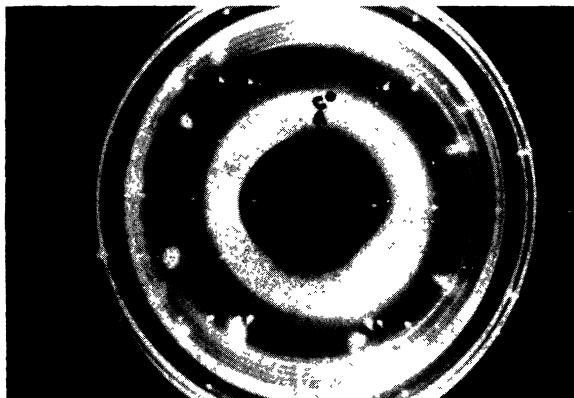


Fig. 6. — Oscillating-crystal photograph registered at 77 K and 0.75 GPa; time exposure 24 h; oscillation $\pm 3^\circ$ in the vicinity of the (400) reflection.

The position of the new peaks remained constant at 0.75 GPa, between 92 K and 77 K. Furthermore, as the thermal extension of phase III decreases with pressure and our single crystals irreversibly deteriorated if the phase III-II transition was accidentally passed, no measurement of the value of δ could be obtained below 0.75 GPa.

The present experiment thus provides the first crystallographic evidence for phase III and shows that its structure is very likely orthorhombic. It nevertheless cannot discriminate between a quadrupling of the cell along c^* , and, as suggested in [4], an incommensurate phase with a value of δ depending on the pressure but not on temperature and accidentally located, at about 0.75 GPa, in the vicinity of $\delta = 0.25$. The present measurement has, on the other hand, been the starting point for an elastic neutron scattering experiment, to be reported elsewhere [7], performed in the range 0.43 to 0.54 GPa on a fully deuterated single crystal; this last experiment has shown that δ increases with pressure and is a monotonously varying function of pressure as anticipated in [4]. Furthermore, extrapolating the neutron and Raman spectra yields $\delta \approx 0.24$ for $P = 0.8$ GPa [7], which is in good agreement with the results reported here.

4. Conclusion.

The aim of this work was to use X-ray diffraction measurements to identify the structural nature of the high pressure and low temperature phase III of ammonium hydrogen oxalate hemihydrate, previously discovered by Raman technique: by optimizing the signal-to-noise ratio, some superlattice reflections were detected along the c^* axis, and to our knowledge it is the first time that such a result can be obtained under pressure with a diamond anvil cell in despite of the very weak intensity of the satellite peaks. With this important information concerning the position of the satellites, a neutron scattering study of this phase could be planned using a triple axis spectrometer: more accurate results and further informations were obtained [7].

Let us also point out that, if X-ray measurement cannot give an explanation for the mechanism of the transition, the weakness of the satellite intensities suggests that it involves mostly the hydrogen atoms; actually, in the neutron scattering experiment these satellite intensities are much higher because deuterium atoms are strong neutron scatterers. This means that the NH_4^+ ion which plays the key role in the phase I-II transition [3], could be also responsible for the mechanism of the I-III transition.

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