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MODULATED CRYSTAL STRUCTURES  
OF VII AND V PHASES IN  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ .  
I. NEUTRON LAUE DIFFRACTION

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Мак-Интайр Г. и др. E14-2010-37  
Модулированные кристаллические структуры VII и V фаз  
в  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ . I. Нейтронная дифракция Лауэ

Проведено исследование кристаллических структур VII и V фаз в  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  с помощью нейтронной дифракции Лауэ в диапазоне температур от 5 до 300 К. Показано, что в кристаллических структурах VII и V фаз проявляется несоизмерная модуляция с разными периодами и фазовый переход из фазы VII в фазу V является переходом первого типа.

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McIntyre G. et al. E14-2010-37  
Modulated Crystal Structures of VII and V Phases  
in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ . I. Neutron Laue Diffraction

The study of crystal structures of VII and V phases of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  by means of neutron Laue diffraction is carried out at temperatures from 5 to 300 K. It is found that crystal structures of VII and V phases have incommensurate modulation with different periods, and phase transition from phase VII to phase V is transition of the first type.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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## INTRODUCTION

$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (or TAHS) undergoes the series of phase transitions [1–6]:

I  $\Rightarrow$  413 K  $\Rightarrow$  II  $\Rightarrow$  265 K  $\Rightarrow$  III  $\Rightarrow$  139 K  $\Rightarrow$  IV  $\Rightarrow$  133 K  $\Rightarrow$  V  $\Rightarrow$  63 K  $\Rightarrow$  VII.

Earlier crystal structures of different phases were studied by means of X-ray single-crystal diffraction [1–6]. It was shown, that crystal structures of different phases of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  are composed of  $(\text{SO}_4)\text{H}(\text{SO}_4)$  dimers and ammonium groups. Phase transitions in TAHS are accompanied by changes in orientational positions of ammonium and sulphate ions and positional order of hydrogen in dimers transforming from symmetric to antisymmetric hydrogen bonds in low-temperature phases.

Crystal structure of TAHS in phase I was determined at 430 K as trigonal with space group (sp. gr.)  $R\bar{3}$  [1] and at 420 K was refined as sp. gr.  $R3m$  [2]. Phase II has sp. gr.  $C2/c$  [3–6] and crystal structure is described as dynamically orientationally disordered [7, 8]. Phases III and IV are described as with sp. gr.  $P2/n$ . Phase V is as having sp. gr.  $P\bar{1}$  [6] and crystal structure of VII phase is unknown till now.

During the investigation of IV phase in TAHS at 136 K by means of X-ray single-crystal diffraction [6] the additional weak reflections with fractional indexes (0.1/2.3) and (0.1/2.5) were observed between the layers of the reciprocal lattice pointed out the modulated crystal structure. Similar weak reflections were observed also in V phase.

The investigations of phase transitions in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  were carried out earlier with the help of EPR on  $\text{VO}^{2+}$  ions substituted ammonium [9–15]. The peculiarities in  $\text{VO}^{2+}$  spectra, typical for incommensurate modulation of crystal structure, were observed at temperatures from 245 to 80 K within phases III, IV and V.

The study of crystal structures of different phases of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  by means of neutron single-crystal diffraction is of interest for more thorough understanding of the hydrogen bond of ammonium ion role in phase transitions.

There are presented new results in the investigations of crystal structures of low-temperature phases III, V and VII of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  obtained by means of neutron Laue diffraction within temperature interval from 5 to 300 K.

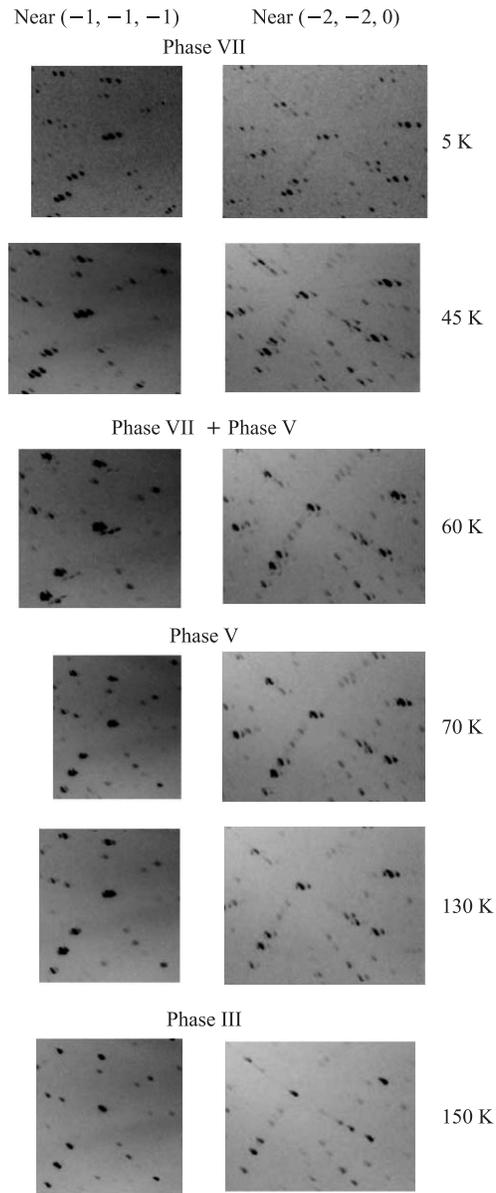
## EXPERIMENTAL RESULTS AND DISCUSSION

The growth of single crystals of  $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ , (or TRAHS) mixed crystals was accompanied by the forming of single crystals with different rubidium concentrations. Rubidium concentrations of TRAHS single crystals were determined by the method of neutron activation analysis [16]. The single crystal for neutron diffraction investigations was selected with minimal rubidium concentration equaled as  $x = 0.006$  and with the size  $1 \times 1 \times 1$  mm. The study of a phase transition subsequence in single crystal with selected Rb concentration was carried out at VIVALDI diffractometer (ILL, Grenoble, France) [17]. VIVALDI diffractometer construction permits one to carry out the measurement of Laue patterns from single crystal at fixed initial position sample at temperature change with preplanned step varied with temperature increasing from 5 to 10 K [17]. This gives the possibility to obtain the sequence of Laue reflection patterns at different temperatures in different phases. Temperature boundaries for different phases were determined using the change of Laue reflection patterns.

Initial measurement at 295 K confirmed, using known lattice parameters of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  [7, 8], that the sample appears in the phase II. Obtained patterns of Laue reflections for initial position of sample were suited to regions near Bragg reflections  $(-1, -1, -1)$  and  $(-2, -2, 0)$ . Then the sample was cooled to 5 K and starting from this temperature the measurements of Laue diffractions carried out in accordance with preplanned temperatures.

Neutron Laue diffraction patterns from TRAHS ( $x = 0.006$ ), obtained at the temperatures 5, 15, 23, 45 и 60 K are suited to the phase VII, obtained at temperatures 60, 70, 80, 90, 100, 110, 120 and 130 K are suited to the phase V, and measured at temperatures 140, 150, 160, 170, 180 and 200 K are suited to the phase III.

The Laue reflection patterns, obtained in direct space and allocated between temperature boundaries of different phases, are presented in the Figure. For fixed sample position the patterns of Laue reflections were measured in two regions near  $(-1, -1, -1)$  and  $(-2, -2, 0)$  Bragg reflections of the phase II. In all temperature regions of measurements the positions of these reflections did not change significantly. Patterns of Laue reflections for the VII phase at temperatures 5 and 45 K show that Bragg reflections are accompanied by symmetric satellite peaks. At temperatures 70 and 130 K in the V phase also Bragg reflections are accompanied by symmetric satellite peaks but with other distance from satellite peak position to Bragg reflection position. Satellite peaks accompany Bragg



Neutron Laue diffraction patterns from TRAHs ( $x = 0.006$ ) mixed crystals at different temperatures near  $(-1, -1, -1)$  and  $(-2, -2, 0)$  Bragg reflections

reflections within all temperature regions of the V phase existence. However, at the temperature 150 K in the phase III satellite peaks are absent and do not accompany Bragg reflections.

The comparison of the Laue reflection patterns which appear at temperature 60 K shows the existence of the peculiarities. There are two different patterns of Laue reflections which are related with different phases, with phases VII and V. These two different patterns of Laue reflections have small shift between the Bragg reflection positions. Also the phase transition from VII phase to V phase is accompanied by decreasing of the distance between symmetric satellite peak positions. Thus at 60 K there is observed the continue phase transition VII  $\rightarrow$  V within temperature region of the coexistence. This phase transition happens with change of lattice parameters and modulation periods and can be described by phase transition of the first type.

The phase IV in TAHS on  $x-T$  phase diagram is located within narrow temperature region, from 133 to 139 K, and was not investigated in the presented experiment. It is worth noting that small concentration of rubidium  $x = 0.006$  did not change significantly phase boundaries of TRAHS between phases V and III confirming the result of [13]. The phase transition between phases VII and V was observed as continued near 60 K, at slightly less 63 K as for TAHS in accordance with the measurements by the dielectric spectroscopy [18].

## CONCLUSION

This short report presents the first study of crystal structures of previously unknown phases VII and V of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (doped small rubidium concentration  $x = 0.006$ ) carried out by means of neutron Laue diffraction. The analysis of obtained patterns of Laue reflections for TRAHS ( $x = 0.006$ ) measured within temperature regions of phases VII, V and III showed, that modulated crystal structures arise in phases VII and V. In direct lattice of VII phase the distance between symmetric satellites more than the distance between symmetric satellites in phase V. The phase transition VII  $\rightarrow$  V happens with the volume change and it is the transition of the first type.

It is worth noting that the study of crystal structures of different phases in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  by means of X-ray and neutron diffraction conduce to two-valued results. So X-ray study of crystal structures of different phases in TAHS conduces to conclusions about commensurate modulated structures of low-temperature phases. On the other hand, the neutron diffraction study of crystal structures of phases VII and V conduces to result of the appearance of incommensurate modulation of the crystal structures in these phases. Thus crystal structures of low-temperature phases in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  have complex nature because the electron density and nuclear density take part in the formation of crystal structure with different types of modulation.

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