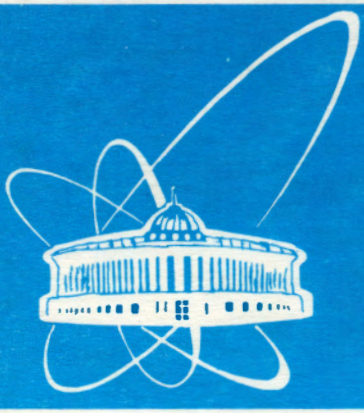

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THE NEUTRON POWDER DIFFRACTION AND ACOUSTIC INVESTIGATIONS OF THE NH_4SCN PHASE DIAGRAM

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1. INTRODUCTION

The physical and crystal structure of NH_4SCN are determined by the ability of the SCN^- and NH_4^+ ions to the orientation ordering and the enhancing of the hydrogen bonding on cooling. At normal pressures NH_4SCN undergoes an order-disorder phase transition at 391K from the high temperature paraelectric body-centered tetragonal (D_{4h}^{18}) phase I to the ordered antiferroelectric orthorhombic (D_{2h}^{11}) phase II. Furthermore, orthorhombic NH_4SCN transforms into monoclinic (C_{2h}^{5}) phase III at 360K [1—6]. The p-T phase boundary of the I-II phase transition of NH_4SCN has the positive slope [3], whereas $dT/dP < 0$ for the II-III phase transition [7].

Cooling induces an enhancement of the hydrogen bonding in NH_4SCN. Some anomalies in the temperature dependences of the Raman modes of NH_4^+ near 200K [8] are connected with the isomorphic III-IV phase transition and confirm the strengthening of the hydrogen-bond network interactions. The aim of the present work was:

a) to investigate the p-T-boundary of the II-III phase transition of the ammonium thiocyanate on cooling to 77K in order to search for a possible triple point [7];

b) to reveal possible peculiarities of the NH_4SCN p-T diagram near 200 K.

2. EXPERIMENTAL METHODS AND SAMPLE PREPARATION

Time-of-flight (TOF) neutron powder diffraction and ultrasonic pulse echo methods were used in our investigations.

The NH_4SCN samples were prepared from high purity finegrained powder-like material. The content of the main substance was not smaller than 99.9%. Because of its high hygroscopicity the powder was dried at 75°C before vacuum pressurization.

The neutron diffraction investigations of NH_4SCN were carried out over the temperature range from 10K to 430K. The measurements were performed on the NERA-PR TOF neutron spectrometer placed at the reactor IBR-2 of JINR [9].

The acoustical studies were made at pressures up to 1.6 GPa over the range of 77-323K using an ultrasonic piezometer [10] modified for low temperature investigations. The detailed description of the experimental technique will be published.

The cylinder-shaped samples had the length of 7.5—8.5 mm and a diameter of 18 mm. The volume of the samples was determined from their geometrical sizes, the density being equal to 1.29 g/cm^3 in good agreement with the X-ray data [2].

The transit time changes of the longitudinal Δt_l, and transverse Δt_t elastic waves of 5 and 3 MHz, respectively, and the sample length changes Δl were measured as functions of the pressure on the NH_4SCN polycrystalline specimens by the method described in [10—12]. The accuracy of the individual time readings was 1-2 ns. The uncertainty in the determination of the length change was 1 μm. The temperature resolution was better than 1 degree.

3. NEUTRON DIFFRACTION RESULTS

The neutron diffraction spectra of NH_4SCN were measured in the temperature interval from 10 to 430K and some of them are presented in Fig.1.

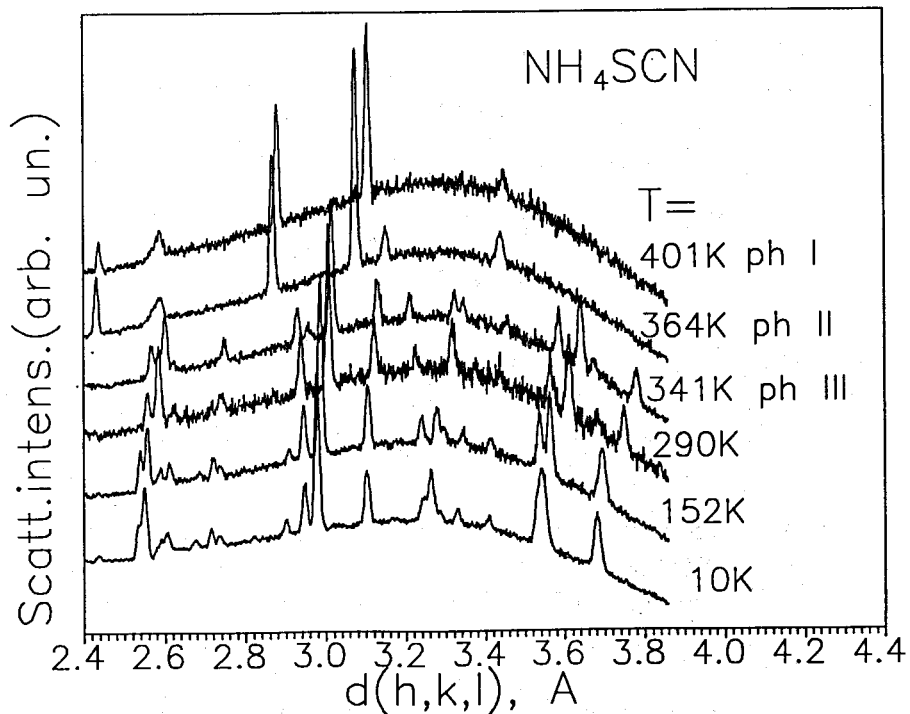

Fig.1. Measured neutron diffractograms for NH_4SCN compound in the temperature range 10—401 K

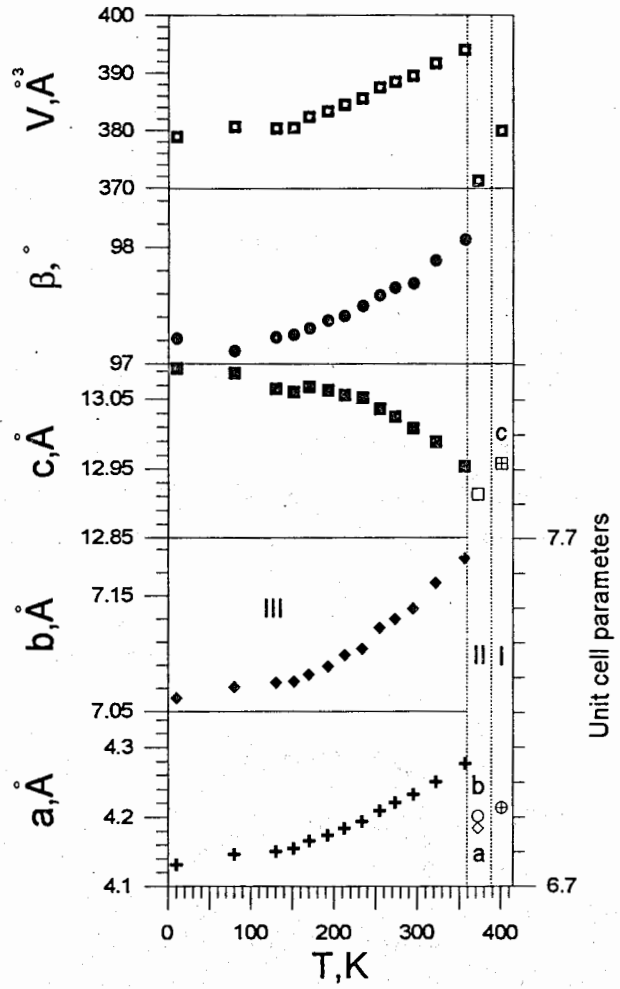

Fig.2. Temperature dependences of the unit cell parameters and volume NH_4SCN for phases I, II and III

The parameters of unit cells of the I, II and III phases were determined using the «MRIAAU»-90 program [13]. The temperature dependences of the unit cell parameters and unit cell volume of NH_4SCN are presented in Fig.2. The lattice parameters are in good agreement with the results of *X*-ray and neutron investigations [1—5]. The parameter and volume changes of NH_4SCN the unit cell at the I-II phase transition are representative for a second order phase transition; the II-III transformation is a first order type and is accompanied by

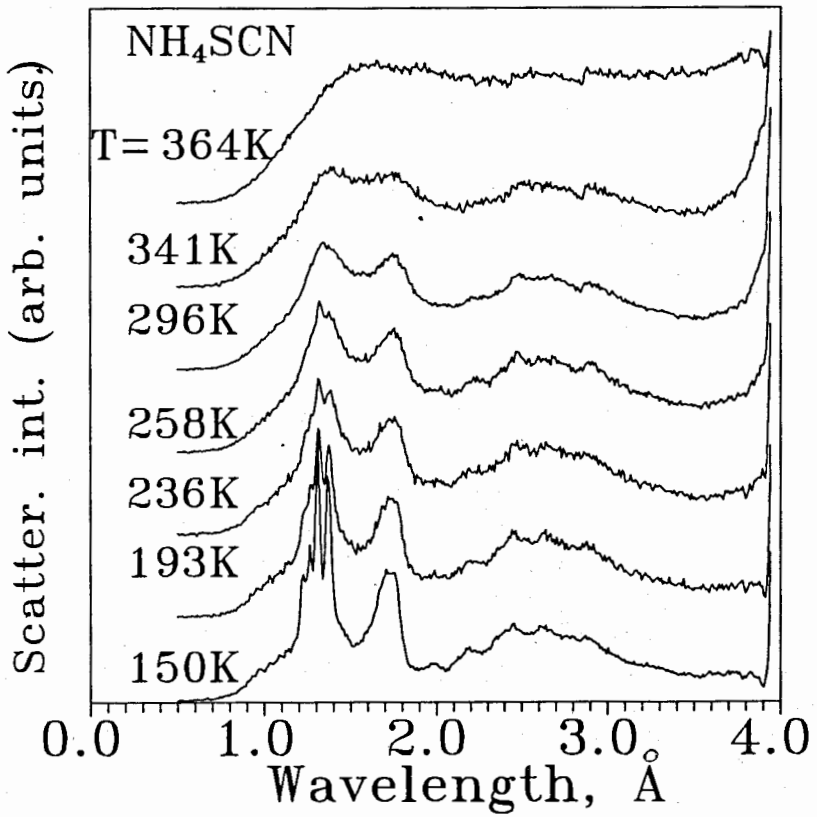

Fig.3. The temperature dependences of the TOF IINS spectra of NH_4SCN

the volume increase of phase III. The temperature dependences of the NH_4SCN monoclinic phase III unit cell parameters and volume display a change in slope near 200K.

Simultaneously measured incoherent inelastic neutron scattering (IINS) spectra of NH_4SCN at different temperatures are presented in Fig.3. These spectra show the dependence of scattering intensities on the wavelength of incoming neutrons. The energy of the scattering neutrons was determined by the pyrolitic graphite analyzer at the wavelength $\lambda_0 = 4.15$Å. In accordance with optical spectroscopy [8] the IINS spectra in the range above 1.5Å may be assigned to the lattice vibrations of NH_4SCN, and in the $1.5 > \lambda > 1$Å interval to the torsional vibrational of NH_4^+ ions. An increase in temperature noticeably

transforms the IINS spectra. The width of the torsional bands is increased, four sub-bands overlap to form one band and its centre shifts to a lower energy. At temperatures above 200K the quasielastic scattering contribution starts to build up appreciably, demonstrating the appearance of stochastic jumps by the NH_4^+ ions.

Above the temperature of the III-II phase transition (360K) the IINS spectrum of NH_4SCN is completely smeared as a result of the orientational disorder of NH_4^+ ions in the crystal lattice.

4. ACOUSTICAL INVESTIGATION OF THE *p-T* PHASE AMMONIUM THIOCYANATE DIAGRAM

The ultrasonic pulse was used to determine the *p-T* phase boundaries. The measurements of Δt_t ultrasound waves and sample length Δl changes were carried out both isothermally under pressure and isobarically during heating. The transit time change, $\Delta t_l(p)$, for longitudinal elastic waves, was measured only at room temperature. In the first series of experiments the sample was cooled to 77K, then heated to the required temperature and compressed under isothermal conditions. In the second series the high pressure cell was heated from 77K at a constant pressure.

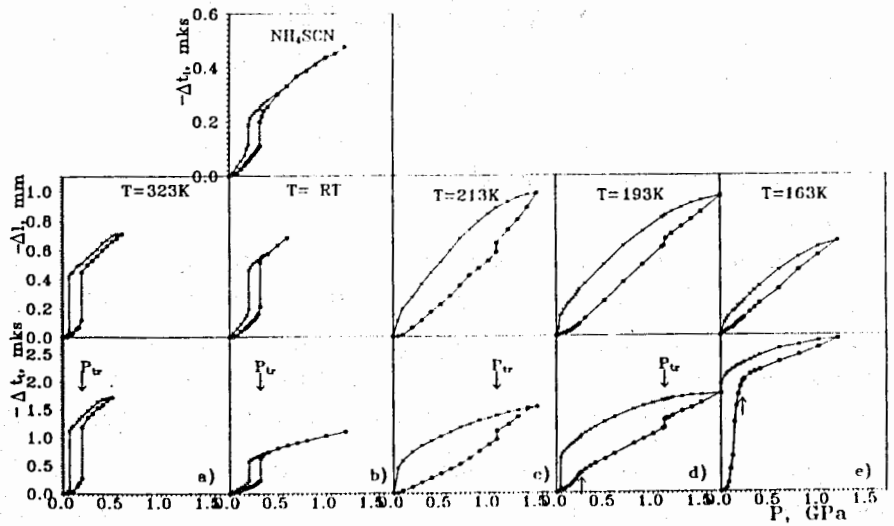

Fig.4. The isotermal pressure dependences of $\Delta l(p)$, $\Delta t_l(p)$ and $\Delta t_t(p)$ of ammonium thiocyanate

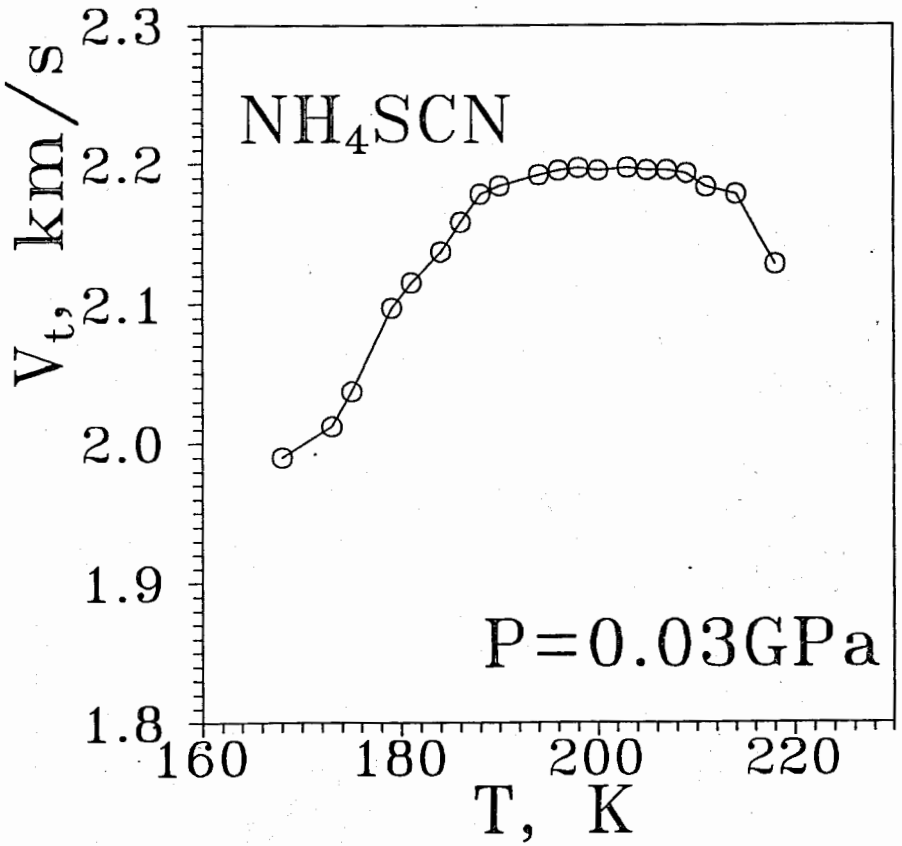

Fig.5. The temperature dependence of the shear velocity $v_t(T)$ for NH_4SCN

Figure 4 shows the pressure dependences of $\Delta l(p)$, $\Delta t_l(p)$ and $\Delta t_t(p)$ up to 1.6 GPa at isotherms in the range of 163-323K. The III-II phase transition of NH_4SCN was determined by the sharp breaks in the experimental curves at the transformation pressure P_{tr}. It should be noted that the III-II phase transition takes place at a higher pressure than the II-III one, i.e., III-II-transformation processes a hysteresis loop. As Fig.4 shows, the hysteresis loop expands and the volume jump at the III-II phase transition decreases on cooling so that this transition is not revealed below 193K and under pressures up to 1.6GPa (Fig.4e). Unfortunately, we could not load our pressure cell higher than 1.6GPa.

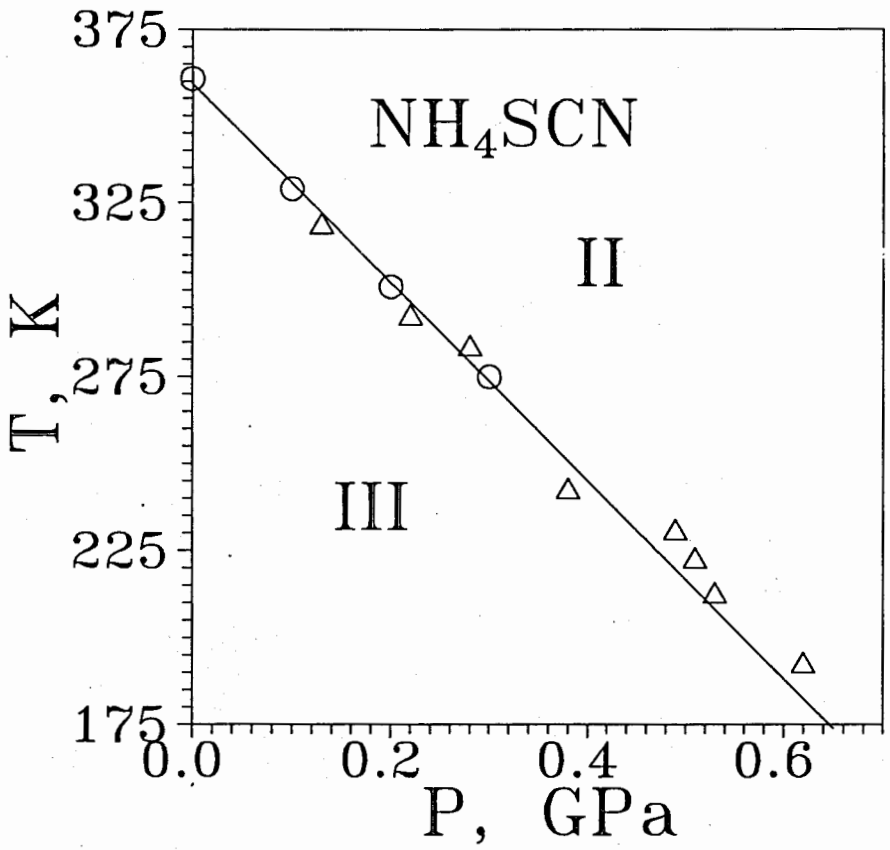

Fig.6. The p-T phase diagram for NH_4SCN

Futhermore, during isothermal compression of the NH_4SCN sample at T = 193K some additional kink was observed on the experimental curves $\Delta t_t(p)$ at sufficiently low pressures (in Fig.4d this pressure kink is shown by the arrow). The character of this anomaly differs from the effects observed at higher pressures and is not connected with the III-II first order phase transition at P_{tr}. As the pressure is reduced to sufficiently low values the kink becomes invisible because of its superposition with the effects of the transit time change accompaning the reverse II-III phase transition.

The increase of the Δt_t under pressure up to the kink (arrows in Fig.4d,e) is enhanced on cooling. The $\Delta t_t(p)$ dependences at lower temperatures (163—

77K) are qualitatively similar. As it is seen in Fig.4e, the $\Delta t_t(p)$ dependence at 163K is irreversible, whereas $\Delta l(p)$ is not.

To determine the p-T locus for these kinks the temperature dependences of the transit time $\Delta t_t(T)$ and length $\Delta l(T)$ changes were measured during the natural heating of the piezometer from 77K at a constant pressure ranging between 0.03 and 0.15 GPa. The calculated velocity of the transverse elastic waves was found to change anomalously with temperature, i.e., they increased on warming and only after reaching a maximum value at about 200K began to decrease (Fig.5). For more accurate determination of the p-T coordinates of these maxima and the nature of the revealed anomaly it is necessary to study the temperature dependences of the longitudinal elastic wave velocity $v_l(T)$ under various pressures.

Figure 6 shows the p-T phase diagram of NH_4SCN determined from our data and [7]. Bridgman's data [7] of the III-II phase boundary are shown by «o»; the boundary obtained from our $\Delta t_t(p)$ dependences are shown by «Δ». One can see that the equilibrium line extends the III-II phase boundary measured by Bridgman [7] to lower temperatures rather well. We could not reveal this phase transition below 193K because of experimental difficulties, so the expected point was not detected. One should look for this point at lower temperatures.

The measured p-T coordinates of the anomalous kinks near 200K are not shown on the phase diagram. In order to define more exactly these p-T coordinates it is necessary to measure the pressure dependences of the longitudinal elastic wave velocities at different temperatures.

5. Conclusions

The p-T boundary of the transition from the monoclinic to the orthorhombic phase of NH_4SCN was determined in the range of 193-323K and up to 1.6 GPa by the acoustic method. The volume discontinuity at the III-II phase transition decreases cooling, whereas the hysteresis loop increases. As a result, this phase transition was not detected below 193K. The temperature dependences of the unit cell parameters and volume, as well as the transversal wave velocity and the quasielastic scattering intensity, reveal some anomalies in the monoclinic NH_4SCN phase near 200K. This allows one to assume that the reorientation processes of the NH_4^+ ions freeze near 200K giving rise to anomalies in the elastic properties of NH_4SCN.

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Смирнов Л.С. и др. E14-94-266

Исследование фазовой диаграммы NH_4SCN методами порошковой дифракции нейтронов и импульсной акустики

Фазовая диаграмма NH_4SCN исследовалась с помощью методов порошковой дифракции нейтронов и импульсной акустики с целью поиска возможной тройной точки и выявления возможных особенностей вблизи 200K, наблюденных другими авторами с помощью рамановского рассеяния света. Переход из моноклинной фазы в орторомбическую был определен на *p-T* фазовой плоскости в области 193-323K и до 1.6 ГПа акустическим методом. Температурные зависимости параметров элементарной ячейки и объема и скорости поперечных волн выявили некоторые аномалии в моноклинной фазе NH_4SCN вблизи 200K. Возможно, что эти наблюдаемые аномалии обусловлены «вымораживанием» переориентационных процессов ионов NH_4^+.

Работа выполнена в Лаборатории нейтронной физики им.И.М.Франка, ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна, 1994

Smirnov L.S. et al. E14-94-266

The Neutron Powder Diffraction and Acoustic Investigations of the NH_4SCN Phase Diagram

The phase diagram of NH_4SCN was investigated by neutron powder diffraction and acoustical methods, in order to search for a possible triple point and to reveal possible peculiarities near 200K, observed by other authors, by Raman light scattering. The transition from the monoclinic to the orthorhombic phase was determined on the *p-T* phase plane in the range of 193—323K and up to 1.6 GPa by the acoustic method. The temperature dependences of the unit cell parameters and volume and of the transversal wave velocity reveal some anomalies in the monoclinic NH_4SCN phase near 200K. It is possible that these observed anomalies are due to a freezing of the reorientation processes of NH_4^+ ions.

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

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