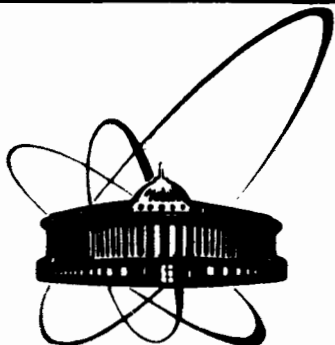


85-811



ОБЪЕДИНЕННЫЙ  
ИНСТИТУТ  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ  
ДУБНА

E14-85-811

A.V.Belushkin, I.Natkaniec, N.M.Plakida,  
L.A.Shuvalov,\* J.Wasicki

NEUTRON SCATTERING STUDIES  
OF VIBRATIONAL SPECTRA  
AND STRUCTURAL TRANSFORMATIONS  
IN SUPERIONIC CONDUCTORS  
 $\text{CsHSO}_4$  AND  $\text{CsHSeO}_4$

\*Institute of Crystallography, 117333, Moscow, USSR

1985

## 1. Introduction

In recent experiments<sup>/1-3/</sup> a new class has been revealed of solid electrolytes, protonic superionic conductors with close phase-transition temperatures:  $T_c=414\text{K}$  ( $\text{CsHSO}_4$ ),  $401\text{K}$  ( $\text{CsHSeO}_4$ ),  $417\text{K}$  ( $\text{NH}_4\text{HSeO}_4$ ),  $446\text{K}$  ( $\text{RbHSeO}_4$ ). The first-order superionic transition in them is accompanied by sharp increase in the conductivity by 3-4 orders of magnitude up to  $10^{-2}\text{Ohm}^{-1}\text{cm}^{-1}$  at the activation energy  $0.3 + 0.4\text{ eV}$  for  $T > T_c$ . By the NMR method in  $\text{NH}_4\text{HSeO}_4$ ,  $\text{RbHSeO}_4$ <sup>/3/</sup> and in  $\text{CsHSO}_4$  (CHS),  $\text{CsHSeO}_4$  (CHSe)<sup>/4/</sup> it has been directly shown that the high conductivity stems from the proton diffusion with the diffusion coefficient  $D \approx 10^{-7}\text{cm}^2\text{s}^{-1}$  in CHS and CHSe.

The phase transition in CHS at  $T_c$  accompanied with large entropy change,  $\Delta S=1,32R$ , was first discovered in measuring the dielectric constant and specific heat.<sup>/5/</sup> Plastic deformation of the CHS crystal while the twin formation in the b-plate crystal in a monoclinic phase (space group  $P2_1/m$  at a room temperature<sup>/6/</sup>) was observed<sup>/7/</sup>. Optical studies of the deuterated crystal  $\text{CsD}_{0.7}\text{H}_{0.3}\text{SO}_4$  (CDS)<sup>/8/</sup> have shown that the superionic phase transition in it at  $T_c=412\text{K}$  is accompanied by ferroelastic transition from the monoclinic phase  $2/m$  into a phase of a more high, possibly tetragonal, symmetry  $4/mmm$ .

The phase transition in CHSe crystal at  $T_c=410\text{K}$  accompanied also with large entropy change,  $\Delta S=1.93R$ , has been discovered in<sup>/9/</sup> in dielectric and thermal studies. Further X-ray and optical studies<sup>/10/</sup> have led the author to the conclusion that the observed first-order phase transition is ferroelastic with the change of symmetry  $2/m \rightarrow 4/mmm$  with a large spontaneous shear strain ( $\sim 10^{-2}$  in the monoclinic phase  $P2_1/c$  at a room temperature). In<sup>/10/</sup> author was unable to determine the space group of the tetragonal phase at  $T > T_c$  because of the plastic properties of the crystal.

The neutron-scattering method is a most convenient direct method for studying the structural phase transitions and phonons in

crystals, and it has certain advantages in studying the crystals with hydrogen bonds. Taking into account the correlation between structural and superionic transitions in the above-mentioned crystals, we have carried out first experiments on the neutron diffraction (ND) and inelastic neutron scattering (INS) on the powder samples of CHS, CDS and CHSe.

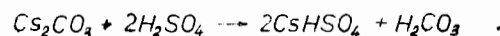
In this paper we report basic results of the performed studies in part published earlier <sup>/11-13/</sup>. The results of diffraction studies on monocrystals are presented in papers <sup>/14,15/</sup>.

In the next section results are expounded of experimental studies of the neutron diffraction and inelastic scattering. In section 3 we discuss the vibrational spectrum and quasielastic scattering. A theoretical interpretation of the ferroelastic superionic phase transition <sup>/16/</sup> is given in sect. 4. Basic results are collected in sect. 5.

## 2. Experimental Results

### 2.1. Conditions of experiment

Polycrystal samples were obtained by synthesis according to the scheme:



For deuterated CDS samples the deuterated sulphuric acid was used, and a single recrystallization in D<sub>2</sub>O was performed. The powder obtained was dried at T ≈ 350K for several hours and was put into a flat aluminium holder with sizes 15 x 15 cm<sup>2</sup>. The neutron transmission was about 95%. The holder was put into a cryostat that allowed us to vary the temperature from 80K to 500K. The stability of sustaining and control of the temperature was ±0.2K.

The ND and INS spectra measurements were performed simultaneously at the pulsed reactor IBR-2 with the time-of-flight spectrometer KDSOG-M <sup>/17/</sup>. For monochromatization of the scattered neutrons we used a berillium filter cooled by liquid nitrogen and the following after it analyser composed of pyrographite plates. The width on a half-height of the elastic line was 0.6 meV at the mean energy of elastic peak 4.9 meV. Simultaneously we measured the INS spectra for four scattering angles and ND spectra for four scattering angles in the case of CHS and CDS and for one angle in the case of CHSe. The spectra have been measured while heating the samples above the superionic transition temperature and their subsequent cooling.

## 2.2. Neutron diffraction

### 2.2.1. Phase transitions in CHS

According to the x-ray data <sup>/6/</sup>, the CHS crystal at a room temperature is monoclinic with the unit-cell parameters  $a = 7.304\text{\AA}$ ,  $b = 5.810\text{\AA}$ ,  $c = 5.491\text{\AA}$ ,  $\beta = 101.51^\circ$ ,  $Z = 2$  the space group  $P2_1/m$ . Recent measurements of ND spectra of the initial single crystal of CHS <sup>/15/</sup> reveal that the monoclinic unit-cell proposed is twice as large along the c-axis and therefore should be described by the following parameters:  $a = 8.223\text{\AA}$ ,  $b = 5.814\text{\AA}$ ,  $c = 10.99\text{\AA}$ ,  $\beta = 119.4^\circ$ ,  $Z = 4$  and the space group  $P2_1/c$ . This structure at room temperature will be referred to in what follows as phase III.

When the sample was heated up to 333K, there occurred the phase transition that ended at about 370K (keeping the sample at temperature 350K for 10 hours did not provide the complete disappearance of phase III), and the sample went over into a new phase II that is also monoclinic and is described by the unit-cell parameters:  $a = 7.75\text{\AA}$ ,  $b = 8.17\text{\AA}$ ,  $c = 7.64\text{\AA}$ ,  $\beta = 110.5^\circ$ ,  $Z = 4$  the space group  $P2_1/c$  <sup>/18/</sup>. In heating to 410K there starts one more structural transition into the superionic phase I <sup>/1/</sup>. This transition controlled by the change of the ND spectrum ends at 413 K. The unit-cell parameters of the phase I that is possibly tetragonal could not be determined because of insufficient number of the observed reflections.

Characteristic ND spectra being corrected with respect to the incident-neutron spectrum, upon subtracting the incoherent background, are drawn in Fig. 1.

In lowering the temperature the inverse transition from phase I to II occurred by 2° lower than the transition while heating. A further cooling of the sample down to 123K and its subsequent keeping in vacuum at a room temperature for 10 days did not result in the transition into the initial phase III. To control the properties of the sample, it was heated again up to the transition into phase I (at 414K) and slow cooling from 415K. Like in the first experiment, there was observed the transition into phase II (in the temperature range from 410 to 395 K), but phase III did not occur.

### 2.2.2. Influence of the moisture of the CHS sample on phase transitions

To study a possible influence of the moisture of the sample, on phase transitions in the CHS powder, the sample after the above measurements, being in phase II, was put into the atmosphere of water-

-saturated vapours where it was kept at a room temperature for 10 hours. The measurement of ND spectrum of this water-saturated sample at 290K has shown that it is in phase III. This phase retained till 123K, and ND spectra were measured. In a subsequent heating the transition from phase III into phase II starts at 340K, i.e. by 30° lower than in the initial sample.

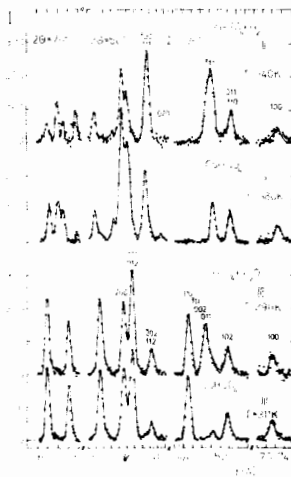
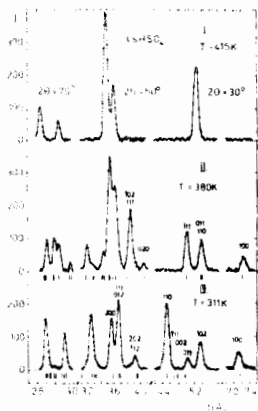


Fig. 1. Characteristic ND spectra in three phases of CHS. Fig. 2. ND spectra for "dry" and "wet" samples of CHS.

In Fig. 2 we show ND spectra for a "dry" and a "wet" sample, that are in phases II and III; as it is seen, the moisture considerably increases the reflection intensity at  $d_{hk\ell} \approx 5\text{\AA}$  both in phase II and III. Thus, the moisture of a polycrystal CHS sample essentially influences the stability of the metastable phase II and the transition from phase II into III. Single crystal CHS samples are influenced by moisture more weakly<sup>/14/</sup>.

#### 2.2.3. Deuterated crystals

For studying the dynamics of protons in the CHS crystal and their influence on the structural phase transitions the ND and INS spectra were measured on partly deuterated CDS samples ( $\text{CsH}_{0.3}\text{D}_{0.7}\text{SO}_4$ ).

Measurement of the ND spectrum on the CDS powder at a room temperature has shown that its structure corresponds to phase II of CHS. (The unit-cell parameters of phase II of CDS are given in sect. 2.2.1).

While heating the sample, no change was observed in the diffraction pattern up to 403K. Near 410K the transition starts into phase I (a superionic state)<sup>/8/</sup>, and at 413K the sample is completely in phase I. The position of reflections in ND spectra in phase I is the same for protonated and deuterated samples which proves the identity of their crystalline structures in this phase. In Fig. 3 plotted are the characteristic ND spectra of the CDS powder. We note a considerable lower intensity of the reflection at  $d=5\text{\AA}$  in phase II of CDS as compared to that of CHS (see Fig. 1). Cooling of the sample down to 123 K did not lead to phase III observed in CHS. Earlier<sup>/8/</sup> only one transition in CDS at 412K was also observed.

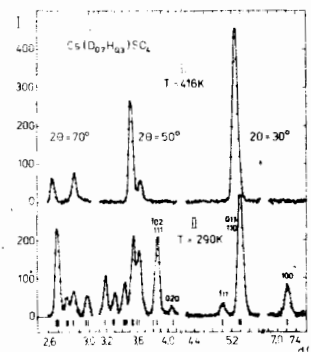
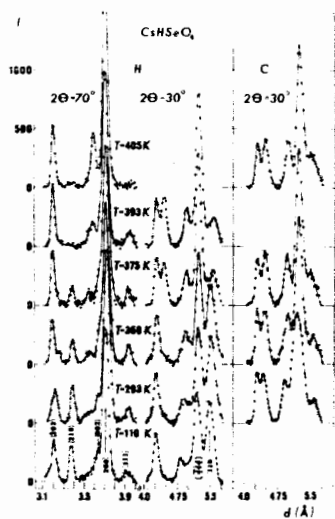


Fig. 3. Characteristic ND spectra on the CDS powder.

#### 2.2.4. Phase transitions in CHSe

In a low-temperature phase the diffraction spectrum of the CHSe powder is well described by the monoclinic unit cell parameters:  $a=7.972\text{\AA}$ ,  $b=8.427\text{\AA}$ ,  $c=7.811\text{\AA}$ ,  $\beta=111.2^\circ$ ,  $Z=4$  the space group  $P2_1/c$ <sup>/10/</sup>. Not described reflections at 4.25Å and 4.8Å correspond to the diffraction on the sample holder (Fig. 4). Recent ND measurements on a single crystal of CHSe<sup>/15/</sup> prove this monoclinic unit cell parameters but the observed space group is  $P2_1/c$ ,  $Z=4$ .

When the temperature increases, the CHSe diffraction spectra start to change as early as 360 K. Note that each of the spectra drawn in Fig. 4 was measured for about 10 hours. A complete rearrangement of the spectrum takes place only above 400 K, and a further heating up to 425 K does not change the ND spectra; this picture allows us to assume that the structural phase transition in the CHSe powder starts as early as about 360 K and it is very extended in temperature; in the range from 360 to 400 K there is a two-phase system.



In a high-temperature phase the diffraction peaks are not described by tetragonal unit cell parameters given in /10/.

As it is seen from Fig. 4c, cooling of the sample from 425 K down to 293 K with temperatures 405, 375 and 360 K kept stabilized for several hours did not result in the initial ND spectrum. Upon being kept at a room temperature for four weeks the sample was still in a two-phase state.

Fig. 4. ND spectra of CHSe: H stands for heating, C for cooling of the sample.

### 2.3. Inelastic scattering

The INS spectra measured on polycrystals in a wide temperature range allows us to draw certain conclusions on the nature of motion of protons in different phases. In Fig. 5 shown are the INS spectra of the CHS powder obtained in heating and cooling the sample.

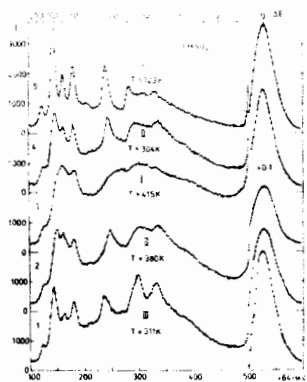


Fig. 5. INS spectra for different phases of CHS.

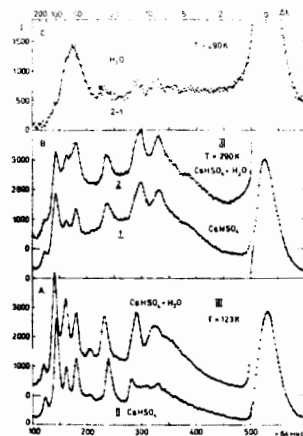


Fig. 6. INS spectra for "dry" and "wet" samples of CHS (see 2.2.2)

The results are normalized to the same monitor count, the background is subtracted, and summation is performed over four scattering angles ( $80^\circ$ ,  $100^\circ$ ,  $120^\circ$ ,  $140^\circ$ ). It is seen that in the course of heating the sample, besides a usual softening and broadening of spectral bands, there occurs its characteristic change in transitions from phase III into phase I. While cooling, the shape of spectrum of phase II conserves down to 123 K, which is in agreement with the behaviour of ND spectra.

The influence of water on the INS spectra in CHS is shown in Fig. 6. The difference spectrum of "wet" and "dry" samples has the form typical of water, with a broad maximum in the energy interval about 60 meV corresponding to molecular rotations of  $H_2O$  and a broad quasielastic peak originated from the diffusion of  $H_2O$  /19/.

In Fig. 7 the temperature dependence is shown for the INS spectra of the CHSe sample. The inelastic part is a sum of eight spectra for scattering angles:  $30^\circ$ ,  $50^\circ$ ,  $70^\circ$ ,  $80^\circ$ ,  $90^\circ$ ,  $100^\circ$ ,  $120^\circ$  and  $140^\circ$  upon normalization to the monitor count and subtraction of the cryostat background. The elastic line corresponds to the scattering angle  $30^\circ$ , and for convenience its intensity is twice increased. As is seen from the Figure, basic changes in the INS spectrum, like in the ND spectra, occur as early as 360K. In the region from 50 to 100 meV one of the bands disappears; and the intensity of the elastic lines strongly decreases. A further increase in the temperature produces small influence on the INS spectra. In the course of cooling of the sample, the INS spectrum, like the ND spectrum, does not return into the spectrum of the initial phase at least, upon being kept at 293 K for four weeks.

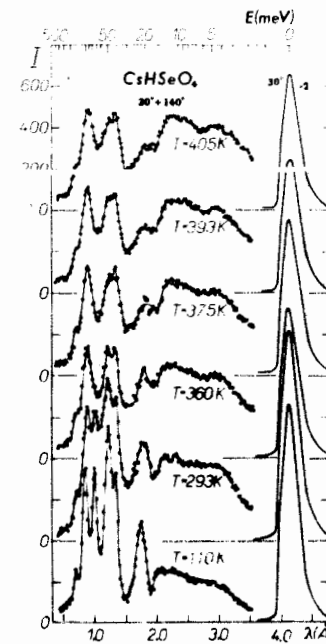


Fig. 7. INS spectra for CHSe.

### 3. Discussion

#### 3.1. Vibrational Spectrum

For discussing the vibrational spectrum and its change in phase transitions it is convenient to introduce the spectral density calculated from the INS spectrum by the formula <sup>/20/</sup>:

$$G(\omega) \propto I(t) \frac{k_i}{k_f} \frac{2M\omega}{1+n(\omega)} \frac{1}{\hbar k_i^2 n(E_i)} \quad (1)$$

where  $\vec{Q} = \vec{k}_i - \vec{k}_f$  is the neutron scattering vector,  $\hbar\omega$  - the energy transfer,  $n(\omega)$  - the Bose distribution,  $I(t)$  the time-of-flight neutron spectrum,  $n(E_i)$  the energy distribution of incident neutrons. In the case of a pure one-phonon incoherent scattering the function (1) defines the weighted density of phonon states.

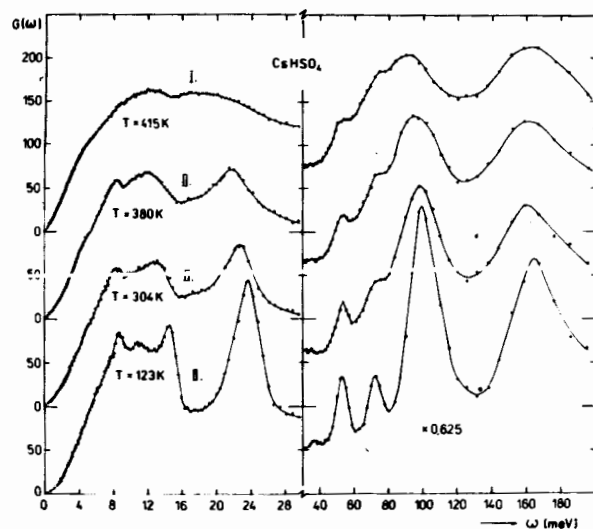


Fig. 8. The function  $G(\omega)$  for phases I and II of CHS.

In Fig. 8 the functions  $G(\omega)$  are compared for phases II and I of CHS, and in Fig. 9  $G(\omega)$  is shown for CHSe at several temperatures. The shape of  $G(\omega)$  for CHS is very close to that one for CHSe in the corresponding phases (see <sup>/11/</sup>).

The comparison of  $G(\omega)$  for the crystals reveals their considerable resemblance. In the energy region below 16 meV which corresponds to the lattice vibrations of the crystal there is observed only a usual temperature softening and broadening of the spectral lines.

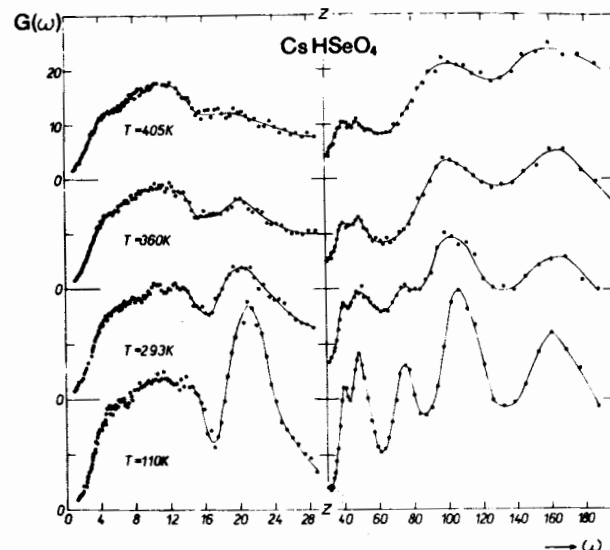


Fig. 9. The function  $G(\omega)$  for CHSe.

Essential changes with increasing temperature are observed for bands at 23 meV (CHS) and at 21 meV (CHSe). Calculating the inertia moments of the tetrahedrons  $SO_4$  and  $SeO_4$  by their known sizes <sup>/6,21/</sup>, we find that the frequencies in CHS and CHSe are connected by the simple relation:  $\nu_{SO_4} / \nu_{SeO_4} = (I_{SeO_4} / I_{SO_4})^{1/2}$ . This means that in the harmonic approximation, assuming the same force constants in CHS and CHSe, one may ascribe the given bands to librations of the tetrahedrons  $SO_4$  and  $SeO_4$ , respectively. Since the tetrahedrons  $SO_4$  and  $SeO_4$  in the systems under investigation are connected by hydrogen bonds, the softening and broadening of bands with increasing temperature testify to a strong anharmonicity of librations of these tetrahedrons and disordering of protons on the hydrogen bonds.

In the energy region above 30 meV it is natural to relate the bands at 53 and 73 meV in CHS and at 40, 49 and 73 meV in CHSe with low-frequency vibrations of the oxygen tetrahedron, and more intensive bands at 100 and 165 meV in CHS and at 105 and 162 meV in CHSe with bending vibrations of protons on the hydrogen bonds out of plane of bonds with  $\gamma$  (OH)-vibrations and in plane with  $\delta$  (OH)-vibrations, respectively.

This interpretation is verified by measurements of IR spectra

in the CHS crystal <sup>/22/</sup>. There it has been established that 9 normal vibrational modes of the tetrahedron  $SO_4$  of  $A_1E$  and  $2F_2$  types are splitted into the following bands:  $\nu_2(E)=51$  meV,  $\nu_4(F_2)=70.4$ ;  $72.0$ ;  $73.9$  meV;  $\nu_1(A_1)=123$  meV;  $\nu_3(F_2)=145.1$ ;  $148.2$ ;  $155.0$  meV. In that work the frequencies:  $\nu_{\gamma(OH)}=106.0$  meV,  $\nu_{\delta(OH)}=156.8$ ;  $164.4$ ;  $170.5$  meV were ascribed to the bending vibrations of protons on the hydrogen bond.

The largest change occurs in the course of heating in the band of  $\gamma(OH)$  proton vibrations, which testifies to a significant change in the character of hydrogen bonds. A considerable broadening and softening occur also in the band of  $\delta(OH)$ . It is to be noted that if in CHS the changes in spectrum take place mainly in the region of superionic transition, in CHSe these changes take place mainly at 360 K, i.e. essentially lower than  $T_c$ .

In Fig. 10 we compare the functions  $G(\omega)$  for phases III and II in CHS at  $T = 123$  K and at a temperature slightly higher than the room temperature. Since phase III does not directly turn into the superionic phase, the analysis of its INS spectrum will be restricted only by the indication of a higher frequency of the spectral bands connected with the hydrogen vibrations in phase III as compared to phase II. This may point to a more strong coupling of protons in the lattice of phase III than that of phase II.

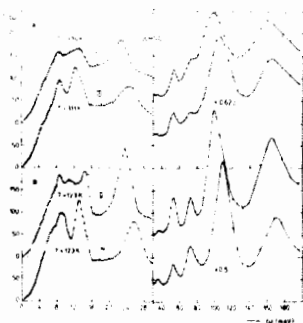


Fig. 10.  $G(\omega)$  for phases III and II of CHS.

### 3.2. Elastic incoherent scattering

An extra information on the phase transition mechanism may be found by studying the temperature dependence of quasielastic incoherent neutron scattering that should in main be connected with the diffusive motion of protons. According to measurements for the diffusion coefficient of protons in the superionic phase <sup>/4/</sup> we have  $D \approx 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which should lead to the width of the quasielastic peak  $\Gamma = DQ^2 \approx 10 \mu\text{eV}$  at  $Q = 2.4 \text{ \AA}^{-1}$ . Since the spectrometer resolution  $\Delta E = 0.6$  meV did not allow us to observe this broadening, we measured only the integral intensity of the elastic line in the energy interval  $\Delta E = 1.65$  meV in the INS spectrum.

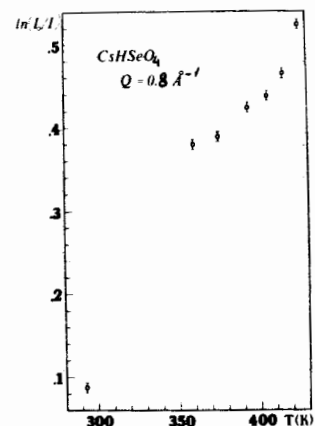


Fig. 11. The temperature dependence of  $\ln[L_0/I(T)]$  for CHSe.

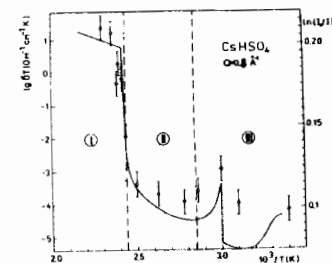


Fig. 12.

The dependence of  $\ln[L_0/I(T)]$  on the inverse temperature for CHS. Roman numerals denote the phases of CHS. The solid curve represents the dependence of conductivity on the inverse temperature (see <sup>/1/</sup>).

In Fig. 11 the temperature dependence of  $\ln[L_0/I(T)]$  for CHSe is shown for the scattering angle  $2\theta = 30^\circ$  ( $Q \approx 0.8 \text{ \AA}^{-1}$  at the center of the elastic line). Here  $L_0$  is the intensity of scattering at  $T_0 = 110$  K and  $I(T)$  the same at a given temperature  $T$ . The intensity of scattering is much decreasing in a temperature range near 360 K and then with heating it decreases only weakly even in the region of phase transition at 400 K. A somewhat different behaviour is observed for the intensity of scattering from the CHS powder shown in Fig. 12 as a function of the inverse temperature. A major growth of  $\ln[L_0/I(T)]$  takes place in the region of phase transition at 414 K and well correlates with  $\lg[\sigma(T) \cdot T]$  shown by a solid curve according to measurement of conductivity  $\sigma(T)$  <sup>/1/</sup>.

A significant decrease in the intensity of the elastic line in CHSe at 360 K and in CHS at 414 K may originate from the increase of the effective Debye-Waller factor and from the changing nature of motion of protons on hydrogen bonds. Indeed, the quasifree motion of protons arising at the jumps from one hydrogen bond to another may produce a quasielastic component with a large width  $\Gamma \sim (kT \cdot \hbar^2 Q^2 / 2m) \approx 8$  meV beyond the energy window  $\Delta E = 1.65$  meV which will diminish the integral intensity. A similar effect was observed in studying the hydrogen diffusion in vanadium. <sup>/23/</sup>

A further study of quasielastic scattering with the high resolution  $\Delta E \approx 10 \mu\text{eV}$  on the CHS and CHSe monocrystals and measurement

of the Q-dependence of that scattering would allow a more unambiguous interpretation of the change observed in quasielastic scattering.

#### 4. Theoretical model for superionic phase transition

The experimental data reported in the previous sections and obtained by other methods discussed in the Introduction permit one to consider the first-order superionic phase transition at  $T_c = 414$  K in CHS and at  $T_c \approx 400$  K in CHSe as an order-disorder phase transition for protons that induces the ferroelastic structural transformation from monoclinic to tetragonal phase. A relatively high activation energy for the proton diffusion in the superionic phase,  $E = 0.3 + 0.4$  eV, shows that the proton disordering at the tetragonal phase should occur by creating new O-H...O bonds between previously isolated H-bonded chains in the low temperature monoclinic phase. Since the number of possible hydrogen bonds in the crystal is twice that of protons, this disordering process can be easily performed.

According to crystallographic data<sup>16,15/</sup> in the low-temperature monoclinic phase of CHS hydrogen bonds are running one-dimensionally along  $\vec{b}$ -axis and there are no protons on the other possible chain of hydrogen bonds along  $\vec{c}$ -axis (compare with structurally similar crystal  $\text{CsH}_2\text{PO}_4$ ). Now assuming that in the high-temperature tetragonal phase average numbers of protons  $n_y$  and  $n_x$  on the hydrogen bonds running, respectively, along the  $y//\vec{b}$  and  $x//\vec{c}$  axes are the same:  $n_y = n_x$ , we can introduce the order parameter:

$$\sigma = n_y - n_x = \frac{1}{4N} \sum_{i\alpha\beta} \langle n_{i\alpha} - n_{i\beta} \rangle, \quad (2)$$

where  $i = 1 \dots N$ ,  $N$  is the total number of unit cells in the crystal ( $Z=4$ ),  $n_{i\alpha} = 0, 1$  and  $n_{i\beta} = 0, 1$  are the occupation numbers for protons in the  $\alpha = 1, 3, 5, 7$  and  $\beta = 2, 4, 6, 8$  positions in the unit cell on the hydrogen bonds along the  $y$  and  $x$  axes, respectively; the angular brackets  $\langle \dots \rangle$  mean the thermodynamical average.

By taking into account that the order parameter (2) is described by the same irreducible representation  $B_{1g}$  of the tetragonal point group  $4/mmm$  as the strain  $\sigma_i = \frac{1}{2}(\epsilon_{yy} - \epsilon_{xx})$  one can write down the free energy expansion for strains  $e_i$ ,  $e_4 = \epsilon_{yz}$ ,  $e_5 = \epsilon_{xz}$  in the form:

$$F = F(\sigma) + \frac{1}{2} C_1 e_i^2 + \frac{1}{2} C_E (e_4^2 + e_5^2) - \lambda e_i \sigma - \frac{1}{2} \beta \sigma (e_4^2 - e_5^2). \quad (3)$$

Here we introduce the elastic coefficients  $C_i = 2(C_{11} - C_{12})$ ,  $C_E = 4C_{44} = 4C_{55}$  and coupling constants  $\lambda$  and  $\beta$  for the order parameter (2) and strains. The strains  $(e_4, e_5)$  are described by the two-dimensional irreducible representation  $E_g$  of the point group  $4/mmm$ . The free energy  $F(\sigma)$  of the proton subsystem is calculated by taking into account short-range proton correlations on hydrogen bonds in the four-particle cluster approximation as in the Silsbee-Ueling-Schmidt model<sup>12,4/</sup>.

Minimizing  $F$  with respect to  $e_i$  and  $e_{4(5)}$ :  $\partial F / \partial e_i = 0$ ,  $\partial F / \partial e_{4(5)} = 0$ , one finds that the strain  $\sigma_i = (\lambda / C_1) \sigma$  is nonzero as soon as  $\sigma \neq 0$ , and the nonzero spontaneous strain  $e_4$  (while  $e_5 = 0$  for  $\beta > 0$ ) can be obtained at the first-order phase transition only when the condition  $C_E < \beta$  is fulfilled.

A further investigation of the free energy  $F(\sigma)$  (3) and an estimation of the model parameters for CHS<sup>16/</sup> shows that the phase transition in the proton subsystem is the first-order Slater-type phase transition with  $\sigma = 0$  at  $T > T_c$  and  $\sigma = 1$  at  $T = T_c^-$ . The susceptibility of the system at  $T > T_0$  (the Curie temperature) obeys Curie-Weiss law:  $\chi(T) \sim (T - T_0)^{-1}$ , and describes the softening of the elastic coefficient of a "free" crystal  $\tilde{C}_i(T)$ :

$$\tilde{C}_i(T) = C_i \frac{T - T_0}{T - T_0^0} \quad (4)$$

where  $T_0^0$  is the Curie temperature of a "clamped" crystal ( $e_i = \text{const}$ ). Estimations for the CHS crystal show that  $(T_0 - T_0^0) / T_0^0 \approx 0.18$  and  $(T_c - T_0) / T_0 \approx 5 \cdot 10^{-3}$ , or  $T_0 - T_0^0 \approx 65^\circ\text{C}$  and  $T_c - T_0 \approx 2.5^\circ\text{C}$ . The entropy change at phase transition  $\Delta S \approx 0.52R$  is considerably smaller than the experimental one  $\Delta S \approx 1.32R$ <sup>15/</sup>. This discrepancy is apparently due to the disregarding of all other degrees of freedom at phase transition, e.g. the thermal motion of  $\text{SO}_4$  groups (see Fig. 8).

The theory proposed provides quite a good qualitative description of the Slater-type superionic phase transition in CHS, CDS and CHSe crystals and elucidates the coupling between ferroelastic and superionic phase transitions.

#### 5. Conclusions

The studies of structural phase transitions in powder samples of  $\text{CsHSO}_4$  (CHS)  $\text{CsDSO}_4$  (CDS) and  $\text{CsHSeO}_4$  (CHSe) performed by the neutron diffraction and inelastic neutron scattering methods allow the following conclusions:

1. In the temperature range from 123 to 420 K there exist three phases (III-II-I) in the crystal CHS and only two phases (II-I) in the deuterated crystal CDS (the coefficient of deuterization  $x \geq 0.7$ )



(see Figs. 1 and 3). As has been shown later<sup>/15/</sup> phase III of CHS has a monoclinic lattice  $P2_1/c$  and phase II of CHS and CDS has also a monoclinic lattice  $P2_1/c$  but with another orientation of the axes<sup>/18/</sup>. The superionic transition to phase I, possibly of tetragonal symmetry, occurs from phase II.

2. In the temperature range from 110 to 425 K two phases are observed in the CHSe crystal (see Fig. 4). The diffraction spectrum at a room temperature is consistent with the monoclinic lattice parameters determined in<sup>/10/</sup> but contradicts the data of his work for the tetragonal phase (at  $T > 400$  K) (see also<sup>/15/</sup>).

3. The structural phase transition between superionic phase I and phase II in CHS and CDS occurs with a small hysteresis. Phase transition III-II in CHS has a considerable hysteresis and depends on the amount of water in the powder sample. The structural phase transition in CHSe starts long before the temperature of superionic transition so that in the temperature range from 360 to 400 K a two-phase region exists.

4. The integral intensity of the elastic line in INS spectra decreases in CHSe mainly in the temperature range below 360 K, and in CHS in the region of superionic transition (see Figs. 11 and 12).

5. INS spectra reveal a considerable change of the spectral density  $G(\omega)$  when passing to the superionic phase. A particularly strong broadening of peaks at 23 meV in CHS and CDS and at 21 meV in CHSe connected with librations of tetrahedrons  $SO_4$  ( $SeO_4$ ) and of the band near 100 meV in CHS and CHSe connected with  $\gamma$  (OH)-vibrations of protons points to disordering of protons in the transition to superionic phase. A major change of  $G(\omega)$  in CHS and CDS occurs in the region of superionic phase transition, and in CHSe considerably below  $T_c$  (see Figs. 5, 7-9).

A further more accurate determination of the structure of a high-temperature phase of the crystals CHS and CHSe and studies of neutron quasielastic scattering with a high resolution will provide a more complete picture of the mechanism of superionic transitions in this new class of solid electrolytes.

#### Acknowledgements

The authors express their deep gratitude to Mrs. N.M.Shchagina for preparing samples, Dr. A.M.Balagurov and Dr. A.I.Baranov for useful discussions, and to Mr. S.I.Bragin and Mr. W.Olejarczyk for a technical help in experiments.

#### References

1. Baranov A.I. e.a. Pis'ma Zh. Eksp. Teor.Fiz. (USSR), 1982, 36, p. 381.
2. Baranov A.I. e.a. Ferroelectrics Lett., 1984, 2, p. 25.
3. Moskvitch Ju.N., Sukhovski A.A., Rozanov O.V. Fiz. Tv.Tela (USSR) 1984, 26, p. 38.
4. Blinc R. e.a. phys.stat.sol., 1984, 123b, p. K83.
5. Komukae M. e.a. J.Phys.Soc. Japan, 1981, 50, p. 3187.
6. Itoh K., Ozaki T., Nakamura E. Acta Cryst., 1981, E37, p. 1908.
7. Ozaki T., Itoh K., Nakamura E. J.Phys. Soc. Japan, 1982, 51, p. 213.
8. Baranov A.I., Shuvalov L.A. and Schagina N.M. Kristallografia (USSR), 1984, 29, p. 1203.
9. Yokota S. e.a. J.Phys. Soc. Japan, 1982, 51, p. 199.
10. Yokota S. J.Phys.Soc. Japan, 1982, 51, p. 1884.
11. Belushkin A.V. e.a. JINR Communication, P14-84-612, Dubna (USSR), 1984.
12. Belushkin A.V. e.a. JINR Communication, P14-85-436, Dubna (USSR), 1985.
13. Balagurov A.M. e.a. Ferroelectrics, 1985, 64, p. 59.
14. Balagurov A.M. e.a. JINR Communication, 15-84-536, Dubna (USSR), 1984.
15. Balagurov A.M. e.a. JINR Communication, P14-85-472, Dubna (USSR), 1985.
16. Plakida N.M. Pis'ma Zh.Eksp.Teor. Fiz. (USSR), 1985, 41, p. 95.
17. Baluka G. e.a. JINR Communication, P13-84-242, Dubna (USSR), 1984.
18. Dilanyan R.A. e.a. Fiz. Tv.Tela (USSR), 1985, 27.
19. Olejnik S., White J.W. Nature Phys.Sc., 1972, 236, p. 15.
20. Pawley G.S. e.a. Solid St.Comm., 1971, 9, p. 1353.
21. Alexandrov K.S. e.a. Kristallografiya (USSR), 1980, 25, p. 1142.
22. Dmitriev V.P. e.a. Kristallografiya (USSR), 1985, 30, p. 6.
23. Lottner V., Heim A., Springer T. Z.Physik, 1979, B32, p. 157.
24. Silsbee H.B., Uehling E.A., Schmidt V.H. Phys.Rev., 1964, 133, p. A165.

Received by Publishing Department  
on November 15, 1985.

COMMUNICATIONS, JINR RAPID COMMUNICATIONS, PREPRINTS, AND PROCEEDINGS OF THE CONFERENCES PUBLISHED BY THE JOINT INSTITUTE FOR NUCLEAR RESEARCH HAVE THE STATUS OF OFFICIAL PUBLICATIONS.

JINR Communication and Preprint references should contain:

- names and initials of authors,
- abbreviated name of the Institute (JINR) and publication index,
- location of publisher (Dubna),
- year of publication
- page number (if necessary).

For example:

1. *Pervushin V.N. et al. JINR, P2-84-649, Dubna, 1984.*

References to concrete articles, included into the Proceedings, should contain

- names and initials of authors,
- title of Proceedings, introduced by word "In,"
- abbreviated name of the Institute (JINR) and publication index,
- location of publisher (Dubna),
- year of publication,
- page number.

For example:

*Kolpakov I.F. In: XI Intern. Symposium on Nuclear Electronics, JINR, D13-84-53, Dubna, 1984, p.26.*

*Savin I.A., Smirnov G.I. In: JINR Rapid Communications, N2-84, Dubna, 1984, p.3.*

Белушкин А.В. и др.

E14-85-811

Исследование спектра колебаний решетки и структурных фазовых переходов в суперионных проводниках  $\text{CsHSO}_4$  и  $\text{CsHSeO}_4$  методом рассеяния нейтронов

В работе представлены результаты исследования фазовых переходов и спектра колебаний решетки на поликристаллических образцах суперионных проводников  $\text{CsHSO}_4$  (CHS) и  $\text{CsHSeO}_4$  (CHSe) методами дифракции нейтронов /ДН/ и неупругого рассеяния нейтронов /НПН/ на импульсном реакторе ИБР-2. В кристаллах CHS обнаружены три различные фазы / III, II, I /, а в частично дейтерированных кристаллах  $\text{CsD}_{0.7}\text{H}_{0.3}\text{SO}_4$  (CDS) обнаружены только две фазы / II, I / в интервале температур 123-420 К. В случае CHS (CDS) структурный фазовый переход ферроэластического типа из моноклинной фазы II в вероятно тетрагональную фазу I происходит в узком температурном интервале около  $T_c = 414 \text{ K} / 412 \text{ K}$  для CDS /. В отличие от CHS в CHSe структурные изменения начинаются уже при температурах гораздо ниже  $T_c = 400 \text{ K}$ . В обоих кристаллах при переходе в суперионное состояние наблюдаются значительные изменения спектров НПНН: сильно уширяется полоса, отвечающая либрациям групп  $\text{SO}_4$  /или  $\text{SeO}_4$  / в CHS (CHSe),  $\gamma(\text{OH})$  изгибная мода колебания протонов смягчается и уширяется. Для объяснения экспериментальных результатов предложена теоретическая модель ферроэластического перехода при  $T_c$ , вызванного суперионным переходом порядок-беспорядок слэтеровского типа в системе протонов на водородных связях.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1985

Belushkin A.V. et al.

E14-85-811

Neutron Scattering Studies of Vibrational Spectra and Structural Transformations in Superionic Conductors  $\text{CsHSO}_4$  and  $\text{CsHSeO}_4$

The results of neutron diffraction (ND) and inelastic neutron scattering (INS) studies on phase transitions and vibrational spectra in powder samples of superionic conductors  $\text{CsHSO}_4$  (CHS) and  $\text{CsHSeO}_4$  (CHSe) at pulsed reactor ИБР-2 are reported. Three different phases (III, II, I) in CHS and only two phases (II, I) in partly deuterated crystal  $\text{CsD}_{0.7}\text{H}_{0.3}\text{SO}_4$  (CDS) are observed in the temperature range 123-420 K. The structural transformation of the ferroelastic type from monoclinic phase II to a possibly tetragonal phase I in CHS (CDS) at the superionic phase transition temperature  $T_c = 414 \text{ K} (412 \text{ K}$  for CDS) is rather sharp as compared to those in CHSe where the structural transformation starts far below  $T_c = 400 \text{ K}$ . Considerable changes in INS spectra at the superionic phase are observed in all crystals: a librational mode of  $\text{SO}_4$  (or  $\text{SeO}_4$ ) groups in CHS (CHSe) becomes rather broad and  $\gamma(\text{OH})$ -proton bending mode softens and broadens. To explain the experimental results, a theoretical model for ferroelastic transformation at  $T_c$  induced by the Slater order-disorder type superionic phase transition of protons on hydrogen bonds is proposed.

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

Preprint of the Joint Institute for Nuclear Research. Dubna 1985