

THE INFLUENCE OF UNIAXIAL PRESSURES ON BIREFRINGENCE OF $(\text{NH}_4)_2\text{SO}_4$ CRYSTALS

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We have studied the influence of the uniaxial mechanical load $\sigma_m \leq 200$ bar on the spectral (300–800 nm) and temperature (300–77 K) dependences of the birefringence Δn_i and the phase transition point of crystals $(\text{NH}_4)_2\text{SO}_4$. It is established that the uniaxial pressure does not change the character, but only the value of the dispersion $d\Delta n_i/d\lambda$. It is revealed that the simultaneous action of the pressures σ_x and σ_y leads to the appearance of a uniaxial isotropic state in $(\text{NH}_4)_2\text{SO}_4$ crystal. We have analyzed the spectral and temperature changes of the piezooptical constants. A significant baric shift of the ferroelectric phase transition point is observed.

along the Z axis, and the angle between two optical axes $2V = 60^\circ$ ($\lambda = 632.8$ nm) and 58° ($\lambda = 441.1$ nm) [9]. Studies of the influence of the uniaxial pressure on the spectral and temperature dependences of the birefringence Δn_i and the refractive indices n_i of crystals isomorphic to AS showed the significant baric sensitivity of the electron subsystem of these crystals, which was revealed in a considerable shift of the positions of the effective bands of UV and IR oscillators in the energy spectrum [10,11].

1. Introduction

Crystals of ammonium sulfate (AS) $(\text{NH}_4)_2\text{SO}_4$ are nonpolar at room temperature and belong to the space symmetry group $Pnma$ of the orthorhombic syngony. At $T_c = 223$ K, they transit to the polar state with the space symmetry group $Pna2_1$ [1,2]. The phase transition (PT) is accompanied by the significant jump of a deformation, and the spontaneous polarization P_c below T_c decreases and changes its sign near 85 K [3]. This testifies to the presence of several temperature-dependent contributions to P_c from different sublattices and to the compensation of these contributions near 85 K [4].

As compared with pure ferroelectrics such, for example, as triglycine sulfate, AS crystals manifest some specific properties. For example, the Curie–Weiss constant is very small ($C \sim 15.6$) and satisfies the Curie–Weiss law only in a narrow temperature interval near T_c . The value of P_c at $T < T_c$ ($P_c \sim 0.6$ mC/cm²) is also rather small and changes its sign below 85 K [5,6].

The structural studies of the para- and ferroelectric phases of AS crystals discovered elements in the structure which are ordered [6]. As the possible disordered elements, the groups NH_4 (1), NH_4 (2), and SO_4 were considered [7,8]. The authors concluded that SO_4 -tetrahedra in the paraphase have no two positions of equilibrium and move in a one-minimum potential with a quite high amplitude.

At room temperature, an AS crystal is optically biaxial and positive with the acute bisectrix directed

To our knowledge, the literature contains no studies of the influence of uniaxial pressures on the optical characteristics and the behavior of the PT point of AS crystals. Such pressures are of interest, because they allow one to selectively affect the corresponding groups of bonds and the corresponding structural units and to get an additional information for the analysis of mechanisms of the PT.

The purpose of the present work is to investigate the influence of the uniaxial pressure on the temperature and spectral changes of Δn_i and on the position of the PT point of AS crystals.

2. Experimental Procedure

$(\text{NH}_4)_2\text{SO}_4$ crystals were grown from an aqueous stoichiometric solution by the method of slow cooling and have the form of rhombic prisms with a large number of faces.

In the spectral range 250–850 nm, the dispersion Δn_i was studied by a change of the interference pattern of polarized rays which was registered with the help of a spectral device KSVU-23 with a modernized input unit. A specimen under study was placed in a cryostat in the diagonal position between crossed polarizers. On the passage of white light through such a system, the interference pattern arises in the focal plane of a spectrometer. Spectral minima of the pattern satisfy the condition

$$d(n_i - n_j) = k\lambda, \quad (1)$$

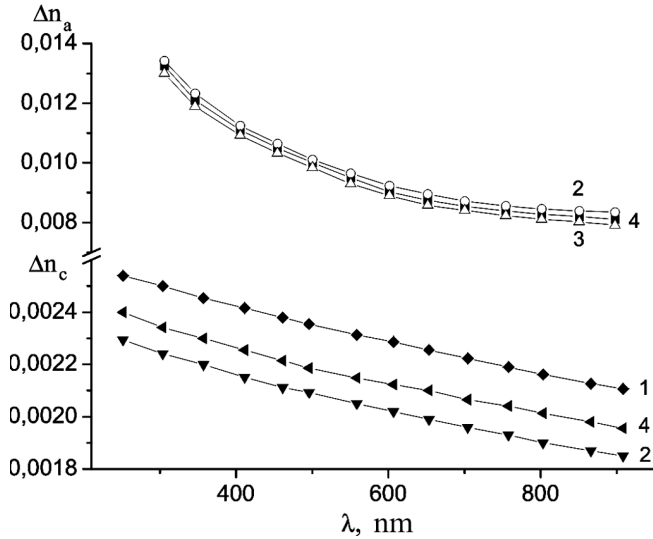


Fig. 1. Dispersion Δn_i of AS crystals at room temperature for different directions and values of the pressure: 1 - $\sigma_x = 100$ bar, 2 - $\sigma_y = 100$ bar, 3 - $\sigma_z = 100$ bar, 4 - $\sigma_m = 0$ bar)

where k is the order of the interference maximum; d is the specimen thickness along the path of a ray; and n_i and n_j are the refractive indices for the crystallophysical directions i and j . The order of the interference pattern was determined by the known values of the refractive indices and the thicknesses of specimens.

The spectral dependence of the transmission intensity of such a system is described by the well-known relation [12]

$$I = I_0 \sin^2 \frac{\pi}{\lambda} \Delta n_i d_i, \tag{2}$$

where I_0 is the incident light intensity on a specimen, and Δn_i is the birefringence in a transillumination direction. By the extrema of the interference pattern, we determined the spectral dependence of path difference (1) and Δn_i . At the uniaxial compression of a specimen, we observe a spectral shift of interference bands, which corresponds to a change of the thickness and Δn_i of the specimen in the light propagation direction. In this case, a baric change of Δn_i is given by the formula which follows from condition (1):

$$\Delta n_i(\lambda, \sigma_i) = k\lambda/d(\sigma). \tag{3}$$

The measurements were performed up to the pressure $\sigma_i \sim 200$ bar. The accuracy of measurements was $\delta\Delta n_i = 2 \times 10^{-5}$.

3. Results of the Experiment and Discussion

3.1. Birefringence

In Fig. 1, we present the dispersion Δn_i of the AS crystal at room temperature for three crystallophysical directions. As seen from the figure, the dispersion Δn_i of the AS crystal is normal ($d\Delta n_i/d\lambda < 0$), its anisotropy is significant, and the isotropic points in the given crystal are absent under the normal conditions.

The most significant changes of Δn_i are revealed for the crystallophysical directions X and Y : $d\Delta n_x/d\lambda = -5.2 \times 10^{-6}$ and $d\Delta n_y/d\lambda = -19.1 \times 10^{-6} \text{ nm}^{-1}$ in the spectral range 300–350 nm, and $d\Delta n_x/d\lambda = -1.2 \times 10^{-6}$ and $d\Delta n_y/d\lambda = -1.9 \times 10^{-6} \text{ nm}^{-1}$ in the spectral range 800–850 nm. Along the Z axis which corresponds to the polar direction of the AS crystal, Δn_i depends very slightly on the wavelength ($d\Delta n_x/d\lambda = -1.2 \times 10^{-8} \text{ nm}^{-1}$).

It is seen from Fig. 1 that the pressures σ_x and σ_y induce changes of the birefringence Δn_z which are different by value: $\delta(\Delta n_z) = 2.450 \times 10^{-4}$ and 1.72×10^{-4} ($\sigma_x = 200$ bar) and $\delta(\Delta n_z) = -1.660 \times 10^{-4}$ and -1.122×10^{-4} ($\sigma_y = 200$ bar) for $\lambda = 400$ and 700 nm, respectively. Curves $\Delta n_z(\lambda)$ are qualitatively invariable under the influence of the pressures, but their dispersion decreases under the pressure σ_x which leads to a decrease of Δn_z .

Similar dependences are observed also for Δn_x under the action of the pressures σ_y and σ_z . In this case, we have also different signs, different values and dispersion changes of Δn_x . But, on the whole, these changes are somewhat larger than those of Δn_z : $\delta\Delta n_x = 1.66 \times 10^{-4}$ and 1.58×10^{-4} for σ_y , and -1.84×10^{-4} and -1.24×10^{-4} for the pressures σ_z and $\lambda=400$ and 700 nm, respectively. Here, a value of the dispersion $d\Delta n_i/d(\lambda)$ is also changed.

The above-presented experimental data are described in terms of changes of the polarization constants of crystals of the group mmm ,

$$\begin{aligned} \Delta n_3(\sigma_{11}) &= (n_2 - n_1)' = \\ &= \Delta n_{30} - 1/2(n_{20}^3\pi_{21} - n_{10}^3\pi_{11})\sigma_{11}; \end{aligned} \tag{4}$$

$$\begin{aligned} \Delta n_3(\sigma_{22}) &= (n_2 - n_1)'' = \\ &= \Delta n_{30} - 1/2(n_{10}^3\pi_{22} - n_{20}^3\pi_{12})\sigma_{22}, \end{aligned} \tag{5}$$

and testify that the expressions in parentheses have different values and different signs. The shear stresses σ_{km} do not change the polarization constants $a_{ii} = \varepsilon_{ii}^{-1}$, and a rotation of the optical indicatrix φ_r which is

described by the constants π_{44} , π_{55} , or π_{66} , turns out insignificant ($\varphi = 0.5 - 1^\circ$).

Generally, it is established that the action of the uniaxial mechanical pressure along the X axis leads to both an increase of Δn_z and a decrease of Δn_y . At the pressure along the Y axis, the birefringence Δn_z decreases, and Δn_x increases. At the pressure along the Z axis, Δn_y increases, and Δn_x decreases.

The AS crystals satisfy the relations $\Delta n_z > \Delta n_y > \Delta n_x$ for the refractive indices and $\Delta n_x = \Delta n_z - \Delta n_y$, $\Delta n_y = \Delta n_z - \Delta n_x$, and $\Delta n_z = \Delta n_y - \Delta n_x$ for the birefringences. By analyzing the obtained results, one may conclude that, under the influence of the uniaxial mechanical pressure σ_m , the anisotropy of the optical indicatrix increases. Moreover, the following regularity earlier observed in a number of crystals of the A_2BX_4 group was confirmed: the action of pressures along mutually perpendicular directions leads to changes Δn_i different by value and modulus [10,11].

However, as seen from the plot, the simultaneous action of the pressures σ_x and σ_z leads to a decrease of Δn_x and an increase of Δn_z . By means of the extrapolation of the straight lines $\Delta n_i = f(\sigma_m)$ or by solving the equation

$$\Delta n_x(\sigma_y = 0) + b_1\sigma_y = \Delta n_y(\sigma_x = 0) - b_2\sigma_x, \quad (6)$$

it is established that, at pressures $\sigma_y \sim \sigma_x \sim 560$ bar, one will observe the equality $\Delta n_x \sim \Delta n_y \sim 1.076 \times 10^{-2}$ for an AS crystal, which corresponds to the isotropic state of the given crystal. That is, under the influence of the pressures σ_x and σ_y , it is possible to induce the simultaneous increase of the symmetry of the optical indicatrix for $(NH_4)_2SO_4$ crystal.

Using the well-known relations for the birefringence in AS crystals, we can write the following relation for the upper "pseudoisotropic point":

$$\Delta n_x(\sigma_y) = n_z - n_y \sim \Delta n_y(\sigma_x) = n_z - n_x. \quad (7)$$

It corresponds to the equality of the refractive indices n_x and n_y .

A similar situation was earlier revealed for $LiRbSO_4$ crystals, where the intersection of the curves $\Delta n_a(\lambda)$ and $\Delta n_c(\lambda)$ was observed at the pressure $\sigma_z = 200$ bar and the light wavelength $\lambda \sim 423$ nm, which corresponds to the "pseudoisotropic point" [13].

Using the obtained spectral and temperature dependences of the birefringence under the influence of uniaxial pressures along the principal crystallophysical directions, we calculated the spectral and temperature dependences of the combined piezooptical constants π_{im}^0

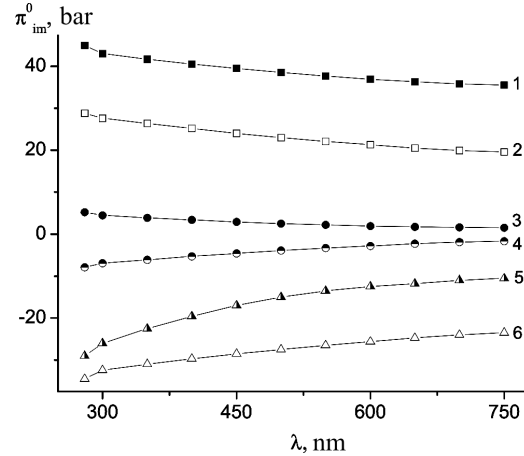


Fig. 2. Dispersion of the combined piezooptical constants of an AS crystal at $T = 295$ K: 1 - π_{23}^0 ; 2 - π_{31}^0 ; 3 - π_{12}^0 ; 4 - π_{13}^0 ; 5 - π_{32}^0 ; 6 - π_{21}^0

of AS crystals (Figs. 2 and 3). To this end, we applied the relation

$$\pi_{im}^0 = \frac{2\delta\Delta n_i}{\sigma_m} - 2\Delta n_i s_{im}, \quad (8)$$

where $\delta\Delta n_i$ is the induced change of the birefringence in the light propagation direction along the crystallographic axis i under the compression of the specimen along the axis m . The second term accounts for changes of the sizes of the crystals along the axis i , and s_{im} is the coefficient of elastic ductility. It is seen from Fig. 2 that the moduli of the constants π_{im}^0 increase with decrease in the incident light wavelength $\partial\pi_{im}^0/\partial\omega > 0$. The positive and negative signs of the piezoconstants π_{im}^0 correspond, respectively, to the increase and decrease of the birefringence under the action of the pressure. It is seen that the constants π_{im}^0 have different temperature dependences in the para- and ferroelectric phases. For example, all the constants π_{im}^0 in the paraphase increase in modulus with decrease in the temperature ($|\partial\pi_{im}^0/\partial T| < 0$), except for the constant π_{23}^0 . In the ferroelectric phase, the constants π_{21}^0 , π_{32}^0 , π_{23}^0 , and π_{12}^0 decrease, as the temperature decreases, whereas the other constants grow. The PT from the paraphase into the ferroelectric phase is accompanied by jump-like changes of all piezoconstants π_{im}^0 . The largest changes were revealed for the constants π_{31}^0 and π_{32}^0 .

The significant anomalies of the piezoconstants π_{im}^0 in the vicinity of the PT are caused by that the piezooptical effect in ferroelectric crystals is determined by the "proper" piezooptical and secondary electrooptical

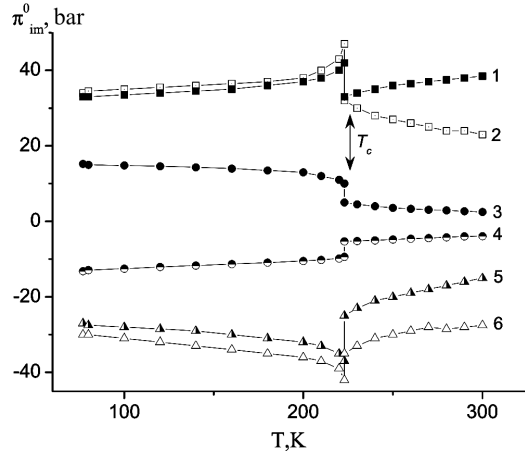


Fig. 3. Temperature dependences of the combined piezooptical constants of an AS crystal for $\lambda = 500$ nm: 1 - π_{23}^0 ; 2 - π_{31}^0 ; 3 - π_{12}^0 ; 4 - π_{13}^0 ; 5 - π_{32}^0 ; 6 - π_{21}^0

contributions $d\Delta n_i/dP_c$. The electrooptical contribution is determined by the following. Due to the dependence of the spontaneous polarization on the temperature and a displacement of the function $P_c(T)$ along the axis of temperatures under the action of the uniaxial pressure σ_m , the spontaneous polarization changes by some value δP_c . This causes, in its turn, an additional electrooptical change of the birefringence

$$\pi_{im}^* = 2 \frac{d\Delta n_i}{d\sigma_m} = 2 \left[\left(\frac{d\Delta n_i}{d\sigma_m} \right)_{icm} + \frac{d\Delta n_i}{dP_c} \frac{dP_c}{dT} \frac{dT}{d\sigma_m} \right], \quad (9)$$

where $(d\Delta n_i/d\sigma_m)_{icm}$ is the contribution of the ‘‘proper’’ piezooptical effect to the combined difference π_{im}^* and, since

$$\pi_{im}^0 = \pi_{im}^* + 2\Delta n_i s_{im}, \quad (10)$$

also to π_{im}^0 .

We now estimate the contribution of the electrooptical effect (EOE). To this end, by applying the available dependence of the spontaneous polarization on the temperature of an AS crystal [14] and the below-given experimental results for the baric shift of the PT point $dT_c/d\sigma_m$, we evaluated the temperature course of the spontaneous polarization under the action of a uniaxial pressure. In this case, we assumed that the shape of the curve $P_c(T)$ is invariable under the influence of σ_m , which is true in the case of hydrostatic pressure [15]: a pressure up to 6 kbar does not affect the molecular mechanism of polarization of ferroelectric crystals and only shifts the Curie point along the temperature coordinate axis due to a change of the number of dipoles per unit volume.

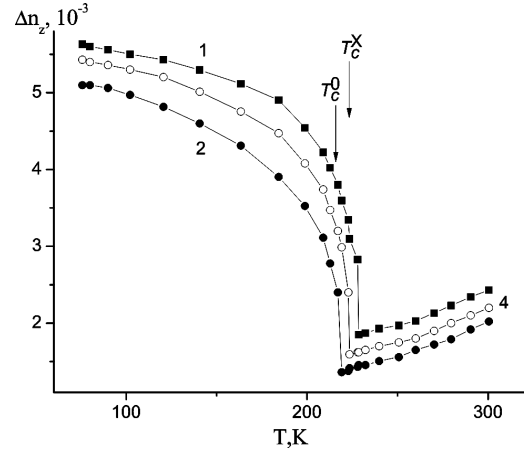


Fig. 4. Temperature dependence of the birefringence Δn_z of crystals $(\text{NH}_4)_2\text{SO}_4$ for $\lambda = 500$ nm at various pressures: 1 - σ_x ; 2 - σ_y ; 4 - $\sigma = 0$

These dependences allow us to determine the increments of the spontaneous polarization δP_c and δP_c^2 at certain pressures σ_m . Having determined the values of $d\Delta n_i/dP_c^2$ with regard for the obtained values of δP_c^2 , we calculated the increments of the secondary electrooptical birefringence $\delta\Delta n_i = d\Delta n_i/dP_c^2 \cdot \delta P_c^2$. Formula (9) yields the contribution of the secondary electrooptical effect to the piezooptical constants of AS crystals.

It was established that the EOE gives the greatest contribution to changes of the piezooptical constants ($\sim 85\text{--}90\%$) in the vicinity of the PT. On the movement from the PT point to the depth of the ferroelectric phase, the contribution from the EOE becomes insignificant and equals $\sim 10\text{--}15\%$. These results well agree with those obtained as the difference between π_{im}^0 in the ferroelectric phase and the extrapolated data from the paraelectric phase.

3.2. Baric shift of the phase transition point in the AS crystal

In Figs. 4 and 5, we show the temperature dependences of the birefringence Δn_z and Δn_y of crystals $(\text{NH}_4)_2\text{SO}_4$ for $\lambda = 500$ nm at various pressures. It is seen that, while approaching the PT point from the side of higher temperatures, Δn_z decreases, whereas Δn_y increases, and $d\Delta n_z/dT = 7.66 \times 10^{-6} \text{ K}^{-1}$, $d\Delta n_y/dT = -6.27 \times 10^{-6} \text{ K}^{-1}$. The PT is accompanied by the jump-like growth of the corresponding values of birefringence: $\delta\Delta n_z \sim 8.8 \times 10^{-4}$ and $\delta\Delta n_y \sim 8.1 \times 10^{-4}$. The further decrease of the temperature leads to an increase of the birefringence. In this case, Δn_z saturates near 100 K

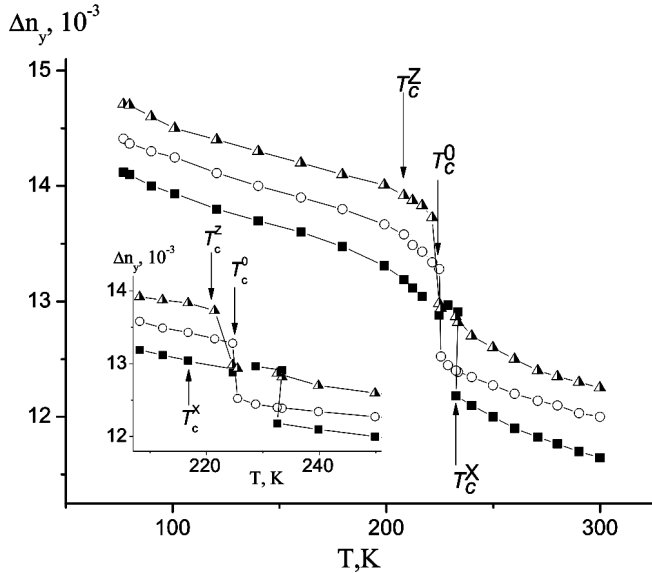


Fig. 5. Temperature dependence of the birefringence Δn_y of crystals $(\text{NH}_4)_2\text{SO}_4$ for $\lambda = 500$ nm at various pressures: 1 – σ_x ; 2 – σ_z ; 3 – σ_y ; 4 – $\sigma = 0$ (the insert shows temperature changes of $\Delta n_y(T)$ in the vicinity of the phase transition)

and then is practically invariable with variations of the temperature.

The action of uniaxial pressures along different crystallophysical directions causes the relevant changes of the birefringence in modulus. However, the character of both the temperature changes $d\Delta n_i/dT$ and the values of jumps $\delta\Delta n_i$ on the PT is not changed basically. A significant change of the PT point position is observed. For example, the uniaxial pressure σ_x shifts the PT point to higher temperatures ($T_c^X = 228.0$ K), and the uniaxial pressures along the Z and Y axes shift the PT point to lower temperatures ($T_c^Y = 216.5$ K, $T_c^Z = 218.8$ K). In this case, we determined the following baric coefficients of a shift of the PT point for the AS crystal: $\partial T/\partial\sigma_x \cong +0.024$ K/bar, $\partial T/\partial\sigma_y \cong -0.021$ K/bar and $\partial T/\partial\sigma_z \cong -0.046$ K/bar, and the summary coefficient of a baric shift of the PT point (analog of hydrostatic pressure) $\partial T/\partial p \cong -0.043$ K/bar. This agrees with data obtained by the method of differential-thermic analysis of the phase $p-T$ -diagram of an AS crystal at hydraulic pressures up to 6 kbar. In this case, it was established that the Curie point linearly shifts in the limits of a hydraulic pressure up to 6 kbar to the region of lower temperatures with a coefficient of -4.1 K/kbar [16].

We will relate the revealed baric shift of the PT point of AS crystals under the action of pressures to changes in the crystal structure. It is known that the crystal structure at room temperature is described by the

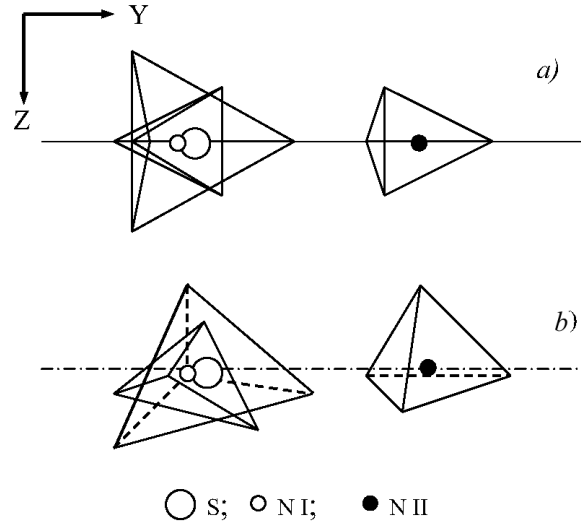


Fig. 6. Projection of an elementary cell of AS onto the YZ plane in the para- (a) and ferroelectric (b) phases

space symmetry group $Pnma$. In Fig. 6, we present the projection of an AS crystal structure onto the YZ plane. In this case, the tetrahedral groups SO_4 are somewhat distorted, and two tetrahedra NH_4 behave themselves as two different dipoles, NH_4 (I) and NH_4 (II). To analyze the structure of an AS crystal, one introduces the vector A^N directed between the nitrogen atom and the hydrogen atom H(1) normally to the XY plane, in which atoms H(2), H(3), and H(4) are positioned. The hydrogen atom H(1) is the most unstable in tetrahedra NH_4 . Therefore, the motion of the bond N-H(1) can be qualitatively related to the deformed tetrahedron NH_4 . At room temperature, the axes A^N for NH_4 (I) and NH_4 (II) are positioned in the XY plane. This fact indicates that the plane containing three hydrogen atoms is normal to the XY plane and oscillates near the position of equilibrium.

Generally, the AS crystal structure in the paraphase can be considered as a partially disordered state relative to small rotations of groups SO_4 , NH_4 (I), and NH_4 (II) mainly around the pseudohexagonal Z axis.

The ordering of structural elements on the ferroelectric transition consists, in particular for sulfate groups, in small displacements which are accompanied by rotations of a group [7]. The temperature dependence of the rotation angles of SO_4 groups and the ordering parameter for ammonium groups in one of the orientations correlate with each other. At the same time

those authors considered that SO_4 ions are not elements of the structure which are ordered, because the rotation angles of the group depend on the temperature. The spontaneous polarization of the crystal is created due to the ordering of the dipole moments of ammonium groups. These moments for NH_4 (1) and NH_4 (2) are antiparallel and different in magnitude [17].

It is considered that the PT in an AS crystal is a transition of the particular type [18]. As distinct from a PT of the type of displacement, where dipole moments P_i arise below T_c , and transitions of the ordering type, where the dipole moments P_i existing above T_c only change the orientation, we are faced with a distortion of the molecular ion itself in AS. That is, the PT in a given crystal is mainly defined by SO_4 groups which change collectively their orientation, positions, and values of a distortion at T_c , by determining a partial ordering of ammonium groups which conserve the possibility to reorient themselves below T_c . In this case, the number of rotations of tetrahedra SO_4^{2-} around all three axes of the structure grows, but this occurs mainly around the X axis. In this case, the tetrahedron is “frozen” in one of the orientational state placed by it in the paraphase. In this case, the spontaneous polarization of the crystal is composed “ferrimagnetically” of the noncompensated moments of sublattices which depend on the temperature in different ways.

If the character of the influence of an external field coincides with that of the influence caused by a decrease of the temperature on the crystal structure, then the thermodynamic equilibrium at the PT occurs at higher temperatures. In the opposite case, the PT temperature will shift to the side of lower temperatures. Since the PT in the ferroelectric phase is accompanied by an increase of the turn of a tetrahedron SO_4 around the Z axis, the uniaxial pressure along this axis “clamps” the tetrahedron, i.e. it decelerates its return to the symmetric state and, therefore, causes a decrease of the temperature required for the destruction of such a state. Respectively, the lower temperatures are needed for the PT to occur at such uniaxial pressure.

The rotation of a tetrahedron SO_4^{2-} of the AS crystal at the PT happens in the XY plane. A shift of the PT to the side of lower temperatures under the action of the pressure σ_y is related, obviously, to that the action direction of σ_y is opposite to that of the rotation of a tetrahedron SO_4^{2-} around the Z axis. That is, the pressure σ_y “decelerates” the rotation of a tetrahedron, and, respectively, the condition of thermodynamical equilibrium will be satisfied at lower temperatures. The action direction of the pressure σ_x

coincides with that of the rotation of a tetrahedron SO_4^{2-} at the PT. Therefore, it “accelerates” the transition in the ferroelectric phase; in this connection, the PT will occur at higher temperatures which “compensate” the mechanical ordering.

4. Results and Conclusions

1. We have studied the spectral and baric dependences of Δn_i of crystals $(\text{NH}_4)_2\text{SO}_4$. It is shown that the dispersion $\Delta n_i(\lambda)$ of an AS crystal is normal and sharply increases on approaching the absorption edge. It is established that the uniaxial pressure does not change the character but only the values of the dispersions $d\Delta n_i/d\lambda$ and temperature dependences of $d\Delta n_i/dT$.

2. It is revealed that the simultaneous action of the pressures σ_x and σ_y leads to the appearance of a new isotropic state in the crystal $(\text{NH}_4)_2\text{SO}_4$ at the light wavelength $\lambda = 500$ nm and the pressure $\sigma_z \sim \sigma_x \sim 560$ kbar, which is manifested in the equality of the birefringences Δn_x and Δn_y .

3. We have calculated the spectral and temperature dependences of the piezooptical constants of AS crystals. It is established that the constants π_{im}^0 vary significantly under changes of the light wavelength and the temperature. We have revealed the considerable jump-like changes of the constants π_{im}^0 in the vicinity of the PT, which is caused by the influence of a uniaxial pressure on the spontaneous polarization of the crystal. The contributions caused by the EOE to changes of the piezoconstants π_{im}^0 are estimated as follows: the EOE gives the largest contribution (~ 85 – 90%) in the vicinity of the PT; while moving from the PT point to the depth of the ferroelectric phase, its contribution becomes insignificant (~ 10 – 15%).

4. It is revealed that uniaxial pressures shift the ferroelectric PT point into different temperature regions, which is caused by the influence of a uniaxial pressure on the crystal structure, namely on the rotation of tetrahedra SO_4^{2-} which defines the PT in crystals $(\text{NH}_4)_2\text{SO}_4$, and on a partial reorientation of tetrahedra NH_4 .

1. A. Jonh and M.Mc. Ginnety, *Acta Crystallogr.* **28**, 2845 (1972).
2. A.J. Berg and F. Tuinstra, *Acta Crystallogr.* **34**, 3177 (1972).
3. M. Miyake and S. Iwai, *Phys. Chem. Miner.* **7**, 211 (1981).
4. H. Arnold and W. Kurtz, *Ferroelectrics* **25**, 557 (1980).
5. A. Onodera, H. Fujishita, and Y. Shiozaki, *Solid St. Commun.* **27**, 463 (1978).
6. A. Bard and S. Awad, *J. Phys. Chem. Solids.* **45**, 351 (1984).

7. A. Sawada, Y. Takagi, and Y. Ishibashi, *J. Phys. Soc. Japan.* **34**, 748 (1973).
8. A. Onodera, Y. Sugata, and Y. Shiozaki, *Solid St. Commun.* **27**, 243 (1978).
9. N.A. Romanyuk, V.M. Gaba, and Z.M. Ursul, *Ukr. Fiz. Zh.* **33**, 1381 (1988).
10. M.O. Romanjuk and V.Yo. Stadnyk, *Condensed Matter Physics* **20**, 711 (1999).
11. V.Yo. Stadnyk and M.O. Romanyuk, *Ferroelectrics* **317**, 255 (2005).
12. M.O. Romanjuk, *Crystalloptics* (IZMN, Kyiv, 1997) (in Ukrainian).
13. V.Yo. Stadnyk, M.O. Romanyuk, and L.T. Karplyuk, *Ukr. Fiz. Zh.* **49**, 808 (2004).
14. H.G. Unruh, E. Sailer, and H. Hussinger, *Solid State Commun.* **25**, 871 (1978).
15. K. Imai, *J. Phys. Soc. Japan.* **38**, 836 (1975).
16. I.N. Polandov, M.E. Levin, and V.P. Mylov, *Zh. Fiz. Khim.* **46**, 491 (1972).
17. K. Hasebe, *J. Phys. Soc. Japan.* **50**, 1266 (1981).
18. Y.S. Jain, P.K. Baipai, and R. Bhattacharjee, *J. Phys. C.: Solid State Physics* **19**, 3789 (1986).

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ВПЛИВ ОДНОВІСНИХ ТИСКІВ
НА ДВОПРОМЕНЕЗАЛОМЛЕННЯ КРИСТАЛІВ $(\text{NH}_4)_2\text{SO}_4$

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Резюме

Досліджено вплив одновісного механічного навантаження $\sigma_m \leq 200$ бар на спектральну (300–800 нм) й температурну (300–77 К) залежність двоприменезаломлення Δn_i та точку фазового переходу кристалів $(\text{NH}_4)_2\text{SO}_4$. Встановлено, що одновісний тиск не змінює характеру, а лише величину дисперсії $d\Delta n_i/d\lambda$. Виявлено, що одночасна дія тисків σ_x і σ_y приводить до виникнення одновісного ізотропного стану в кристалі $(\text{NH}_4)_2\text{SO}_4$. Проаналізовано спектральні й температурні зміни п'єзооптичних констант. Виявлено значне баричне зміщення точки сегнетоелектричного фазового переходу.