[7] M. G. Priestley, Proc. Roy. Soc. A276, 258 (1963).

PROOF OF THE EXISTENCE OF TWO SHARPLY DISTINCT FERROELECTRIC PHASES IN $NaH_3(SeO_3)_2$

N. R. Ivanov, L. A. Shuvalov, R. M. Fedosyuk, and K. A. Pluzhnikov
Crystallography Institute, USSR Academy of Sciences
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Crystalline sodium hydroselenite $NaH_3(SeO_3)_2$ is a ferromagnetic with a Curie point at -79°C [1,2], and is presently under presistent investigation [3-6], but a number of its most important properties have not been disclosed so far. Yet the data presented below give grounds for assuming that $NaH_3(SeO_3)_2$ is one of the most interesting representatives of not only an isomorphic series of ferroelectric hydroselenites.

Large homogeneous single crystals of $NaH_3(SeO_3)_2$ were grown from the aqueous solution by the method of dropping the temperature, and had a Curie point T_C = -78.6° and a melting temperature 111 ± 0.5°C. Measurements of the low-frequency (800 cps) dielectric constant (Fig. 1) at a measuring-field intensity 10 V/cm were made for three mutually perpendicular cuts oriented parallel to the principal sections of the optical indicatrix: the crystal-physics directions were taken to be the principal axes of the indicatrix, so that the x, y, and z axes were directed respectively along the acute and obtuse bisectors and the normal to the plane of the optical axes. We measured the temperature dependence of the rotation of the indicatrix φ(T) about the y axis (Fig. 2) and the components of the spontaneous polarization.

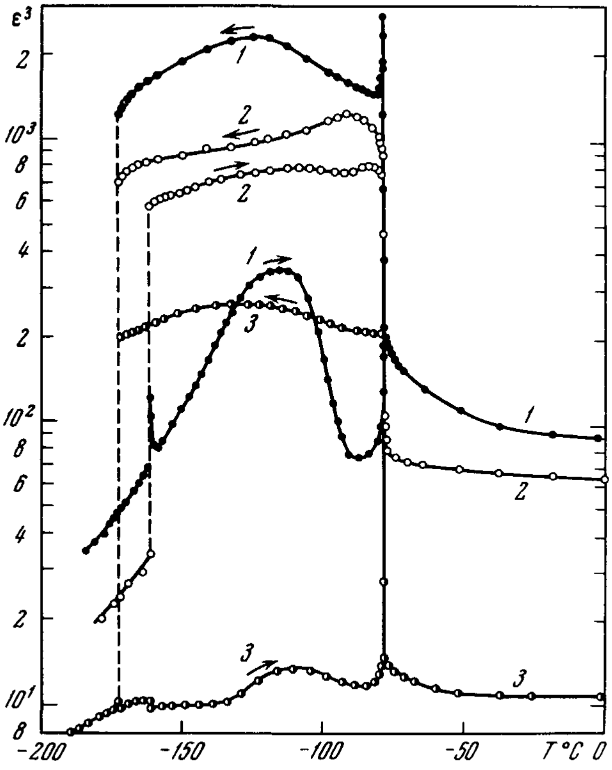


Fig. 1

The measurements have demonstrated quite obviously the presence of one more phase transition in $NaH_3(SeO_3)_2$ at -172.5°C, at which a jumpwise decrease takes place in the components of the dielectric constant. The transition has a temperature hysteresis of 10.5°. Consequently, the transition is of first order. A high value of ε is retained in the region -172.5°C < T < T_C, owing, as will be shown below, to the domain contribution. At -78.6°C the peak of the dielectric constant is exhibited only by the component ϵ_x (Fig. 1, curve 1). All the $\epsilon(T)$ curves (in Fig. 1, curve 2 for ϵ_y and curve 3 for ϵ_z) show a characteristic difference in the forward and backward directions if the temperature of the lower phase transition has been reached, and coincidence in the opposite case.

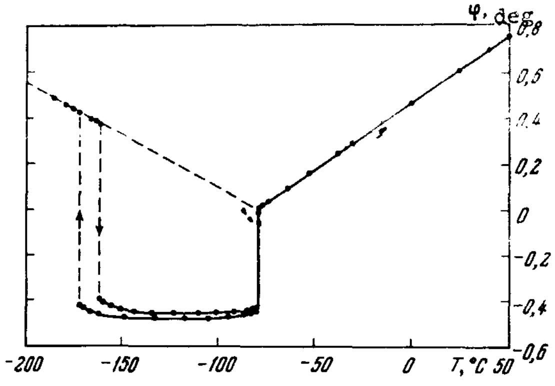


Fig. 2

The x component of the spontaneous polarization occurs at -78.6°C, increases rapidly but continuously, saturates very rapidly, and remains practically constant at 3.1 μC/cm^2 to the temperature of liquid nitrogen. The corresponding coercive field remains constant at 1.4 kV/cm only in the interval -80 - -170°C, exhibiting an unusually sharp rise at -172.5°C and reaching approximately 30 kV/cm at -180°C. The z component of the polarization amounts to only 0.2 μC/cm^2, and consequently the polarization component in the xz plane is close in direction to the acute bisector. At the same time, dielectric hysteresis loops are observed also in a direction which is not allowed in the symmetry class m, namely in the direction of the y axis, which is normal to the symmetry plane of the monoclinic paraelectric phase. The y component of the polarization occurring at -78.6°C increases rapidly and then remains practically constant at 3.8 μC/cm^2 to -172.5°C, at which temperature it vanishes abruptly. The corresponding coercive field increases rapidly near T_C to 1.4 kV/cm, and then, with decreasing temperature, it increases linearly to 3.9 kV/cm at -172.5°C. No hysteresis loop is observed in the y-cut below -172.5°C.

The angle of rotation of the indicatrix was registered polarimetrically by determining the change in the position of the extinction of the crystal. Above T_C and below -172.5°C (Fig. 2), $\varphi(T)$ is a linear function of the temperature (the thermo-optical effect [7]). It is interesting that the thermo-optical coefficient ξ_5^{σ} changes sign and magnitude as a result of the phase transition at -78.6°C (the plot of $\varphi(T)$ at low temperatures was extrapolated to T_C); all the remaining singularities of the $\varphi(T)$ curve must be attributed to spontaneous electro-optical and elasto-optical effects connected with the y-component of the polarization and corresponding to spontaneous deformation.

If an x-cut $NaH_3(SeO_3)_2$ plate is placed between crossed Nicol prisms in a position corresponding to extinction above T_C, then it will become almost completely transparent and cease to extinguish below T_C, and the temperature dependence of its optical transmission will correspond to the y component of the polarization P_y. Below -172.5°C, where P_y vanishes, the extinction of the plate is restored. The forward and backward variations of the transmission do not coincide directly, the transmission in the backward path being always smaller than in the forward path. For some samples it does not differ in practice from the transmission below -172.5°C. An external electric or mechanical action in this case increases the transmission irreversibly.

When the light propagates along the xz plane, effects of its directed scattering become clearly pronounced, appearing at the Curie point and vanishing at -172.5°C (the light is scattered in a direction perpendicular to the xz plane).

In the interval from -78.6 to -172.5°C one can observe the domain structure in cuts perpendicular to the xz plane by the ordinary polarization-optical method. Clear cut pictures of the domain structure were observed in the z-cut (Fig. 3). The angle of disorientation of the indicatrices is approximately 1°. A highly regular picture of domain walls, arranged parallel to the xz plane, is usually observed. However, a small part of the surface can be occupied by domains with 90° wall orientation relative to the xz plane.

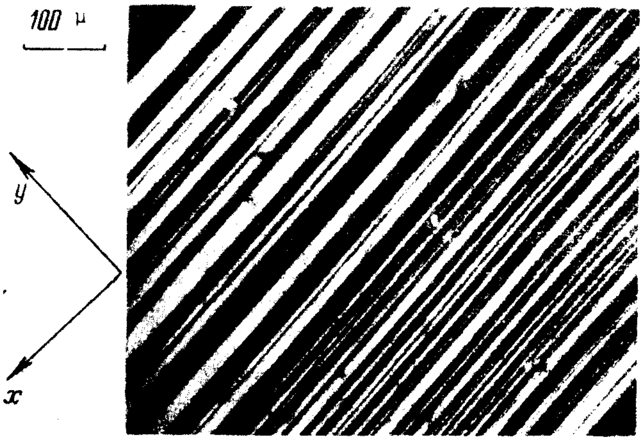
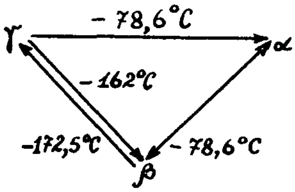


Fig. 3

An analysis of the obtained information has led us to the following conclusions.

1. $NaH_3(SeO_3)_2$ undergoes two phase transitions, one at -78.6°C (second order but close to first order) from the paraelectric α phase to the ferroelectric β phase with a change in symmetry $2/m \rightarrow 1$, and the other at -172.5°C (first order) from the β phase to the ferroelectric γ phase with a symmetry change $1 \rightarrow m$. Schematically the phase transitions can be represented in the form



2. In the absence of external action, the γ phase (or part of it) can remain metastable in the crystal in the range $-162°C < T < T_C$. An external electric field or mechanical action can transform the crystal to the β which is stable in this temperature region. The γ phase is apparently isostructural with the ferroelectric phase of $LiH_3(SeO_3)_2$, whereas the β phase is definitely not isostructural.

3. In the γ phase, the vector of spontaneous polarization lies in the xz plane (m plane), but in the β phase there appears a y component of the polarization, as a result of which the crystal becomes triclinic and two systems of antipolarized domains are produced in it. These systems are arranged in plane-parallel layers, between which mechanical stresses are produced.

4. As a result of these stresses and of the noncollinearity of the vector P_s in different domain systems, it becomes possible to display visually the trace of the domain structure, light reflection takes place from the boundaries of the layers, and the transmission of

the light by the crystal increases radically. All these effects are connected only with the y component of the polarization and are missing from the γ phase.

5. Since the motion of the domain walls takes place in a field of inhomogeneous mechanical deformation, an appreciable domain contribution to the dielectric constant is produced.

6. The difference between the effects brought about by the x and y polarization components, and the different behavior of these components themselves and of the coercive fields corresponding to them, offer definite evidence of two essentially different mechanisms for the occurrence of spontaneous polarization in $NaH_3(SeO_3)_2$. It is possible that only the x component of the polarization is connected with the transitions of the protons between the SeO_3^{2-} groups [6], and the y component, although stimulated by the occurrence of the x component, has a different mechanism which is apparently connected with the displacement of the Na^+ ion along the y axis.

[1] R. Pepinsky and K. Vedam, Phys. Rev. 114, 1217 (1959).
[2] F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.
[3] Y. Makita, J. Phys. Soc. Japan 19, 576 (1964); 20, 1567 (1965).
[4] R. Blinc, A. Jovanovic, A. Levstik, and A. Prelesnik, J. Phys. Chem. Solids 26, 1359 (1965).
[5] R. D. Blinc and D. Vovk, Phys. Lett. 19, 177 (1965).
[6] R. K. Khanna, J. C. Decius, and E. R. Lippincott, J. Chem. Phys. 43, 2974 (1965).
[7] N. R. Ivanov and L. A. Shuvalov, Kristallografiya 11, 614 (1966), Soviet Phys. Crystallography 11, in press.

CHANGE OF TOPOLOGY OF THE FERMI SURFACE OF CADMIUM UNDER PRESSURE

E. S. Itskevich and A. N. Voronovskii
Institute of High-pressure Physics, USSR Academy of Sciences
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The hole Fermi surface of cadmium in the second band constitutes a monster of the same type as in zinc, but it has qualitative differences: the arms of the monster, which are in the (0001) plane, are discontinuous [1], and according to the data of [2] the monster has also a contact with the edge of the Brillouin zone parallel to the [0001] axis, along the total length of the edge. In the third band of the electron-surface of cadmium there are no needles as in the case of zinc [1]. These differences are essentially due to the difference in the magnitude of the ratio of the lattice parameters c/a, which deviate somewhat more from ideal in the case of cadmium.

The differences in the shape of the Fermi surface of the two hexagonal metals give rise, first, to differences in the angular dependence of the electric resistivity $\rho(\theta)$ in strong magnetic fields: $\rho(\theta)$ of cadmium is characterized by the absence of a deep minimum at $\vec{H} \parallel [0001]$. In this minimum one observes in the $\rho(H)$ dependence of zinc saturation modulated