

Structural phase transition in a surface layer of cesium deuteriosulfate single crystals

A. A. Lomov, N. V. Shitov, V. A. Bushuev, and A. I. Baranov
Moscow Institute of Fine Chemical Engineering, 117571, Moscow

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At 122 °C, a structural phase transition occurs in CsDSO₄ single crystals with a {100} surface orientation. This transition occurs in a layer 10–20 nm thick. The average size of the regions of coherent scattering is 20 μm. The angular disorientation of these regions is 7°.

The research on the defective structure of surface layers of single crystals by the standard methods^{1,2} has recently been joined by active research on various cooperative phenomena at surfaces, in particular, surface phase transitions. For example, a study of ferroelastic single crystals of the protonic conductors CsHSO₄ and CsDSO₄ (CDS)

has revealed an anomalously large increase (by four or five orders of magnitude) in the surface conductance at a sample temperature T_s about 20°C below T_b , the temperature of the bulk superionic phase transition. The qualitative similarity between these anomalies in T_s and T_b led Baranoc³ to suggest a structural phase transition in a surface layer of the CDS. However, there has been no direct confirmation of changes in the crystal structure near the surface.

So far, the structural studies have been limited to bulk phase transitions of these hydrosulfates.^{4,5} One reason is that standard x-ray diffractometry is relatively insensitive to ultrathin layers, ~ 5 nm thick. Another difficulty is that electron-diffraction methods are destructive. According to x-ray structural analysis,⁴ the bulk superionic phase transition in CDS is accompanied by a raising of the symmetry from monoclinic, $P2_1/c$, to tetragonal, $I4_1/amd$, and this phase transition is simultaneously a ferroelastic transition. One might expect some corresponding structural changes in a surface layer at T_s .

In this paper we are reporting a study of a near-surface phase transition in a CDS single crystal by the high-resolution method of three-crystal x-ray diffractometry. The method is based on an angular analysis, at a resolution $\approx 1''$, of the intensity of the x rays reflected by the test crystal during an angular scan of an analyzer crystal.⁶ The experiments were carried out on transparent, colorless single crystals of $\text{CsH}_{1-x}\text{D}_x\text{SO}_4$ ($x = 0.7$) grown from a CsDSO_4 solution under static conditions during slow evaporation of the solvent.

The test samples, platelets $7 \times 5 \times 1.5$ mm in size, were cleaved along $\{100\}$ cleavage planes from the interior of the crystal. We studied the (200) reflection of $\text{CuK}\alpha_1$ radiation over the angular interval $\pm 2000''$ of the deviation ($\alpha = \theta - \theta_B$) of the sample from the exact Bragg angle ($\theta_B = 12.22^\circ$ at $T = 20^\circ\text{C}$). High-quality silicon single crystals [the (111) reflection] were selected for use as monochromator and analyzer. A preliminary study showed that the CDS samples are high-quality single crystals with a dislocation density $\approx 8 \times 10^4 \text{ cm}^{-2}$. The x-ray diffraction was carried out in a nitrogen atmosphere immediately after the cleavage of the samples, at various temperatures (from 20°C to 128°C). The surface component of the conductance was measured simultaneously. The temperature was regulated within $\pm 0.1^\circ$.

Figure 1 shows the angular distribution of the reduced intensity of the main diffraction-reflection peak, $\tilde{I}(\alpha) = I(\alpha) \cdot \alpha^2 / I_0$, found from the spectra measured by three-crystal x-ray diffractometry for various sample temperatures. Here I_0 and $I(\alpha)$ are the intensities of the incident and reflected beams, respectively. When the sample is heated from $T = 20^\circ\text{C}$ to $T = 128^\circ\text{C}$, no substantial change occurs in the angular distribution $\tilde{I}(\alpha)$ except near $\alpha \approx 1600''$. At these angles, we find a clearly expressed maximum (curve 2), which is evidence of the appearance of an additional diffractive scattering. Figure 2 shows corresponding examples of spectra measured by three-crystal x-ray diffractometry which illustrate the behavior of the diffractive scattering as a function of the temperature. When a sample is heated to 128°C , we observe a peak in the spectrum (Fig. 2b) which corresponds to an additional diffractive reflection. On the other hand, only the background component of the scattering is found at room temperature (Fig. 2a) or when the sample is cooled to 110°C (Fig. 2c). Points A, B, and C in Fig. 3 show the corresponding temperatures at which the diffraction mea-

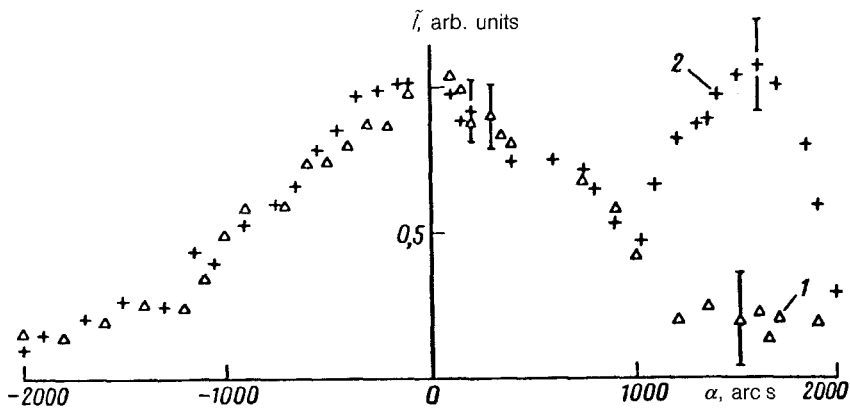


FIG. 1. Angular distribution of the reduced intensity, $\bar{I}(\alpha)$, of a diffraction reflection from a CDS crystal. 1— $T = 20^\circ\text{C}$; 2— $T = 128^\circ\text{C}$. [(200) reflection; $\text{CuK}\alpha_1$ radiation].

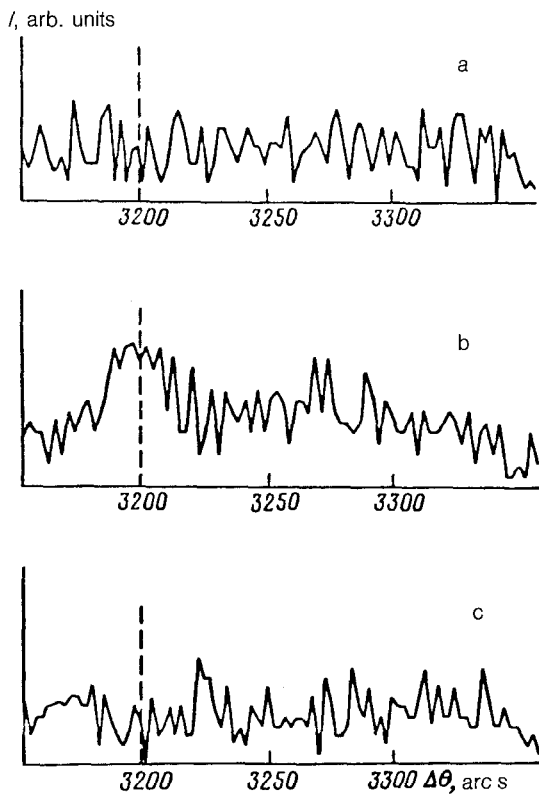


FIG. 2. Parts of spectra measured by the method of three-crystal x-ray diffractometry corresponding to an angular deviation $\alpha = 1600''$ of the sample. The vertical lines show the positions of the main peak, $\Delta\theta = 2\alpha$. a— $T = 20^\circ\text{C}$; b— $T = 128^\circ\text{C}$; c— $T = 110^\circ\text{C}$ (after cooling from 128°C to 90°C and then heating to 110°C).

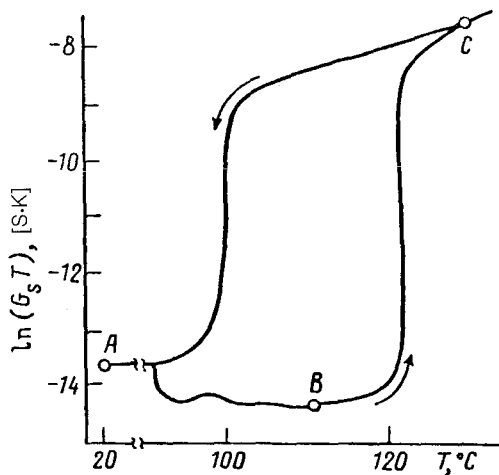


FIG. 3. Temperature dependence of surface component of the conductance, G_s , for CDS samples cleaved along $\{100\}$ cleavage planes.

measurements were carried out. This figure shows the temperature dependence of the surface component of the conductance, which exhibits a sharp jump at $T_s = 122^\circ\text{C}$. We wish to stress that the changes in the spectra found with the three-crystal x-ray diffractometer and in $C_s(T)$ are reversible.

The angular position of the peak in the additional diffractive scattering observed at $T = 128^\circ\text{C}$ was analyzed. The thermal expansion of the crystal was taken into account.⁵ The results show that this peak coincides with the (112) Bragg reflection which corresponds to reflection from a tetragonal phase. The orientation of the four-fold \tilde{c}_T axis of the tetragonal cell is parallel to the \tilde{c}_m^* of the monoclinic phase. This result agrees well with the sharp increase in the conductance at $T_s = 122^\circ\text{C}$, which is 17°C below the bulk phase transition. The simultaneous presence of a strong diffraction reflection at $\alpha \approx 0$ is evidence that the structural phase transition has not yet occurred in the interior of the crystal.

We can work from the broadening of the main peaks in the spectra measured at $T = 128^\circ\text{C}$ by three-crystal x-ray diffractometry in the region $\alpha = 50\text{--}200''$ to find the dislocation density in the surface layer of the sample.⁷ We find $N_d \sim 4 \times 10^5 \text{ cm}^{-2}$. In other words, this density is almost five times the corresponding density at room temperature. The bulk superionic transition in CDS is known⁴ to be accompanied by large ferroelastic deformations ($\geq 10^{-2}$). The increase in N_d near T_s is apparently due to spontaneous deformations which arise in the surface region as a result of the phase transition. The increase in the dislocation density N_d in the surface layer may also be a consequence of a stress at a boundary between structures corresponding to a tetragonal phase (in the surface layer) and a monoclinic phase (in the interior). Analyzing the intensity and width of the additional peak on curve 2 in Fig. 1, we conclude that the effective thickness of the layer in which the phase transition occurs is 10–20 nm. The average size of the blocks (i.e., of the regions of coherent scattering) is about 20 μm in this case, and the angular disorientation of the blocks is $\approx 7''$.

In summary, the results found in this study show that CDS single crystals with a

{100} surface orientation undergo a superionic phase transition in a layer with a thickness on the order of 10–20 nm at a temperature of 122 °C. The observed anomaly in the surface component of the conductance is thus due to specifically structural changes in the cesium deuteriosulfate single crystal near the surface.

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¹B. A. Nesterenko and O. V. Sintko, *Physical Properties of Atomically Clean Semiconductor Surfaces*, Nauk. Dumak, Kiev, 1989.

²E. Vlieg, J. F. van der Veen, S. J. Gurman *et al.*, *Surf. Sci.* **210**, 301 (1989).

³A. I. Baranov, V. V. Sinitsyn, E. G. Ponyatovskii, and L. A. Shuvalov, *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 186 (1986) [*JETP Lett.* **44**, 237 (1986)].

⁴B. V. Merinov, A. I. Baranov, L. A. Shuvalov, and B. A. Maksimov, *Kristallografiya* **32**, 86 (1987) [*Sov. Phys. Crystallogr.* **32**, 47 (1987)].

⁵R. A. Dilanyan and V. Sh. Shekhtman, *Fiz. Tverd. Tela (Leningrad)* **29**, 3577 (1987) [*Sov. Phys. Solid State* **29**, 2049 (1987)].

⁶A. M. Afanas'ev, P. A. Aleksandrov, and R. M. Imamov, *X-Ray Diagnostics of Submicron Layers*, Nauka, Moscow, 1989.

⁷N. V. Shitov, A. A. Lomov, V. A. Bushuev *et al.*, *Fiz. Tverd. Tela (Leningrad)* **33**, 3625 (1991) [*Sov. Phys. Solid State*].

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