

Superplasticity of $C_5H_5SO_4$ crystals in the superionic phase

L. F. Kirpichnikova and A. A. Urusovskaya

Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

V. I. Mozgovoï

Khar'kov State University, 310077 Khar'kov, Ukraine

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The results of optical polarization studies and of mechanical tests on $C_5H_5SO_4$ crystals in the superionic phase are presented. The indicators of superplasticity of the crystals are determined. © 1995 American Institute of Physics.

In the last few years there has been great interest in superionic hydrosulfate crystals in which a structural phase transition into a high-temperature phase is accompanied by a sharp increase (by several orders of magnitude) in the proton conductivity.^{1,2} Two first-order phase transitions occur in $C_5H_5SO_4$ (CHS) crystals. III ($P2_1/m$) — II ($P2_1/c$) — I ($J4_1/amd$),^{1,3} and the phase transition III — II occurs with a large displacement of some atoms and orientation reversal of the system of hydrogen bonds.⁴ The superionic phase transition, which occurs at 414 K, is associated with the raising of the symmetry and with dynamic disordering of the system of hydrogen bonds. According to the data of Ref. 5, the transition is accompanied by the appearance of block structure in the superionic phase. Experimental studies by the method of inelastic and quasielastic neutron scattering,^{6,7} as well as theoretical studies^{8,9} have made a large contribution to the understanding of the nature and mechanism of superionic phase transition.

In Ref. 10 it was determined that at room temperature CHS crystals exhibit high plasticity by means of twinning of a stripe domain structure (001). We showed that the application of a shear stress produces a more complicated domain structure with {100}-type domain walls; this corresponds to tetragonal symmetry of the high-temperature phase.¹¹ We also showed that the mechanical properties of the crystals in phase III are strongly anisotropic: The crystals are anomalously plastic under shear stresses e_{13} and e_{31} and brittle under compression along the twofold axis. The combination of a large spontaneous shear deformation and almost complete reversibility of the twinning processes occurs only in phase III. In phase II the crystal becomes brittle and stressed.

Our objective in the present work was to investigate the plastic properties of CHS crystals in the superionic phase I.

Mechanical tests were performed on $2.5 \times 3 \times 10$ mm bars, to which the load was applied on a deformation machine at a rate of 10^{-4} s^{-1} . Oriented samples, to which a compressive stress was applied, were also investigated on a special thermal stand by an optical polarization method; the temperature was stabilized within $5 \times 10^{-2} \text{ K}$.

Figure 1 shows the deformation curves for bars of three different orientations. All

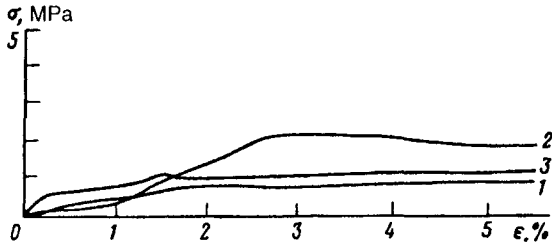


FIG. 1. Deformation curves for a CHS crystal at 420 K. The compression axis is parallel to [001] (curve 1), [100] (2), and [010] (3).

curves are fairly smooth and are characterized by a low yield point. The deformation occurs with weak strain hardening and reaches large values; there is virtually no anisotropy of plasticity. After the mechanical tests the samples become cloudy, opaque, and strongly deformed. It is impossible therefore to observe in a polarization microscope any crystallographic elements of plastic deformation by studying the samples after the tests.

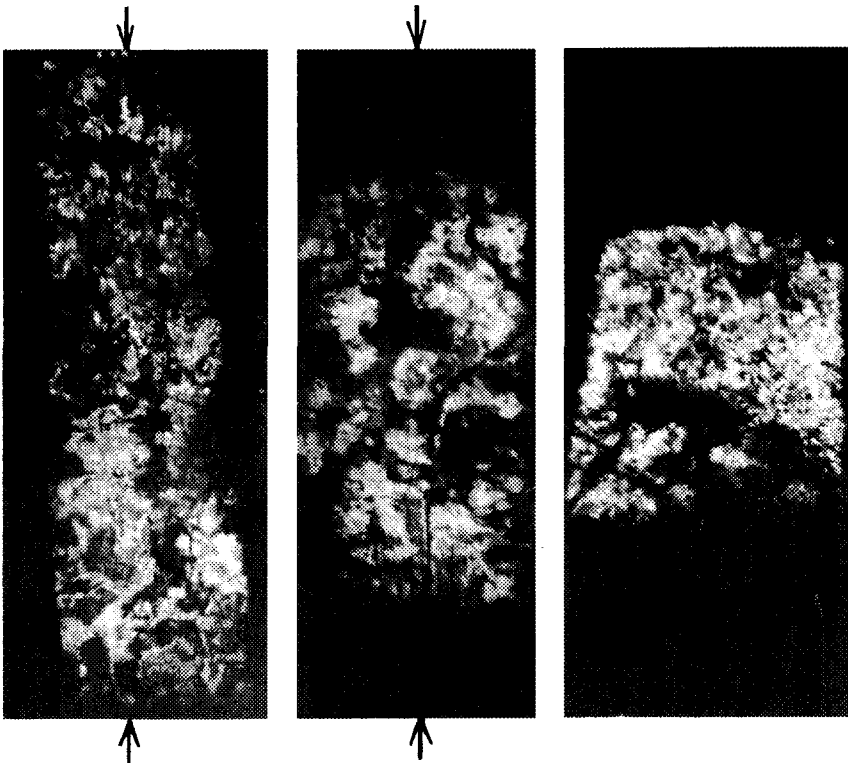


FIG. 2. Change produced in the shape of a (010)-cut sample of a CHS crystal by a gradually increasing (0.2–5 MPa) compressive stress applied along the [001] direction at 420 K.

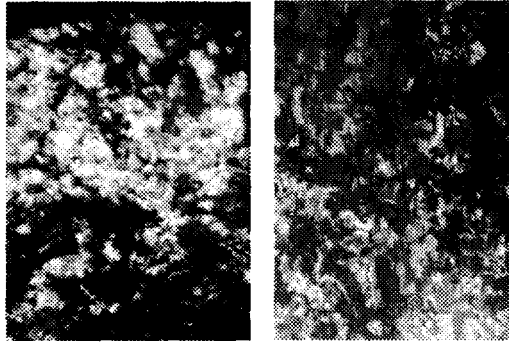


FIG. 3. Change produced in the form of the boundaries of the regions which are observed in the superionic phase by changing the position of the analyzer polaroid at 420 K on the (010)-cut of CHS crystals.

We have therefore performed optical polarization investigations on samples with different orientations on a special thermal stand under the action of different stresses. Our measurements showed that the samples deform easily in the superionic phase, and that their shape and dimensions change substantially (Fig. 2). A long, thin rod can be easily shortened, curved, and transformed into a small ball, just as clay or plasticine, by applying small stress. The brightly colored regions that appear in the superionic phase, as it turned out, are not blocks, as suggested in Ref. 5, since the boundaries of these regions change when the polaroids are rotated (Fig. 3). Therefore, the high plasticity cannot be associated to the presence of a block structure. In our opinion, the anomalously high plasticity is due to the high mobility and migration of the protons and the resulting mechanical instability of the structure. For example, the data of Ref. 7 show that the dynamic disordering of the H bonds results in orientational disordering of the SO_4 tetrahedra in the superionic phase. The orientation reversal of these tetrahedra can be substantial, depending on the positions of the hydrogen bond. As a result, the structure of the crystal is easily deformed under small loads.

We underscore the fact that superplasticity in the superionic phase I is of a different nature, and that it is substantially different from the plasticity in the ferroelectric-elastic phase III. In phase III the plastic deformation occurs by means of twinning [within $\pm(\beta - 90^\circ)$, where β is the angle of monoclinicity of the crystal lattice] under the action of a shear stress; it is almost completely reversible and anisotropic. In the intermediate phase II the crystals are brittle and stressed. In the superionic phase I the crystal manifests superplasticity in virtually all crystallographic directions; Deformation occurs under small loads with weak strain hardening and it is irreversible.

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