

***P-T* phase diagram of a proton superionic conductor CsHSO₄**

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The effect of hydrostatic pressure up to 2.0 GPa on the proton conductivity and phase transitions in a CsHSO₄ crystal is studied. Several high-pressure phases, including two superionic phases, have been detected.

It has recently been established that several crystals belonging to the family of alkali hydrosulfates and alkali hydroselenates exhibit phase transitions to the superionic state.^{1–3} Although the protons are responsible for the conductivity in these crystals, its sharp increase (several orders of magnitude) in the superionic phase seems to be caused by the disordering of hydrogen bonds. As a result, the protons acquire the ability of translational motion with a low activation energy (~ 0.33 eV).^{2–4} Optical⁵ and neutron-diffraction⁶ studies have shown that the structures of superionic and low-conductivity phases are highly unstable. Of particular interest in this regard are the studies of the effect of hydrostatic pressure on the stability of the superionic state and on the proton conductivity in superionic acid sulfates.

In the present letter we report a study of the *P-T* phase diagram of CsHSO₄ in the temperature range 20–200 °C and hydrostatic-pressure range up to 2 GPa. The measurements of isothermal and isobaric conductivity curves were carried out using *a*-cut wafers at a frequency of 20 kHz. As the electrodes we used a “Degussa” silver paste. The phase transitions were detected by the *TA* and piezometry methods.

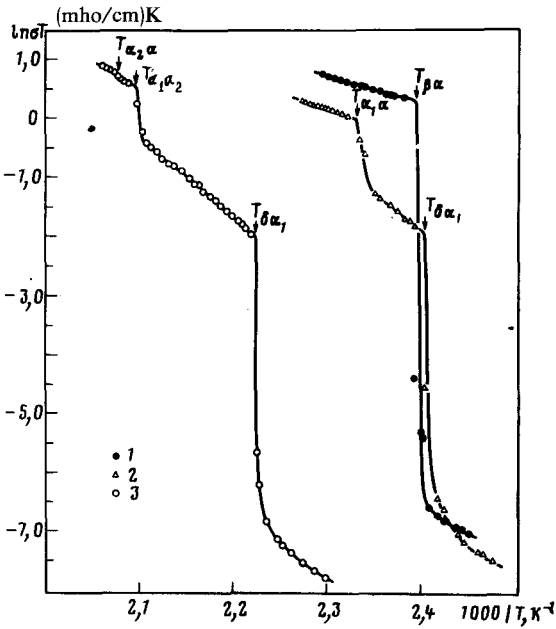


FIG. 1. Isobaric curves for $\ln \sigma_a T = f(1/T)$ in a CsHSO_4 crystal. 1— $P = 0.39$ GPa; 2— $P = 1.21$ GPa; 3— $P = 1.79$ GPa.

At atmospheric pressure and temperatures $T \lesssim 60^\circ\text{C}$, the stable phase in CsHSO_4 is the low-conductivity γ -phase ($\sigma_a \sim 10^{-8} - 10^{-6}$ mho/cm). At $T \simeq 60^\circ\text{C}$, the crystal undergoes a phase transition to another low-conductivity β -phase and at $T = 139^\circ\text{C}$ it undergoes a transition to the superionic α -phase.^{1,2} A superionic phase transition, $\beta \leftrightarrow \alpha$, is a first-order phase transition¹ which is accompanied by a slight thermal hysteresis (of order 4°) and by a significant change in the entropy, $\Delta S_{\alpha\beta} = 11.01$ J/mole-deg (Ref. 7).

At $P \lesssim 1.1$ GPa, the shape of the $\sigma_a(T)$ curves remains essentially the same (curve

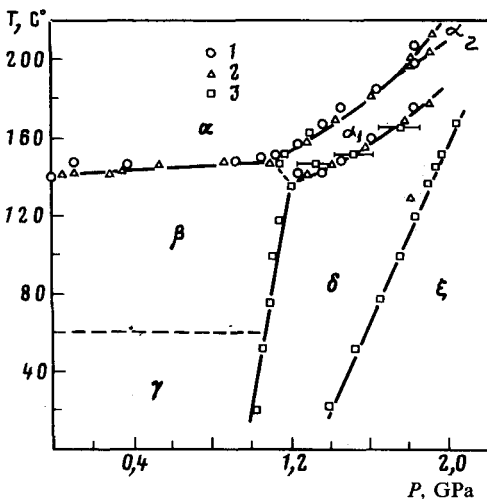


FIG. 2. P - T phase diagram of a CsHSO_4 crystal constructed from the following data: 1—conductivity; 2—pressure-temperature curves; 3—piezometry.

1 in Fig. 1), while $T_{\alpha\beta}$ increases slightly with pressure (Fig. 2) ($dT_{\alpha\beta}/dP = 5 \pm 3$ deg/GPa). The change in the crystal volume as a result of this phase transition is inordinately small ($\Delta V_{\alpha\beta}/V_{\beta} \simeq 0.08\%$). This change in the volume can be calculated from the Clausius-Clapeyron equation. At $P > 1.1$ GPa, the $\alpha \leftrightarrow \beta$ phase-transition line splits with the appearance of the intermediate superionic α_1 -phase (Fig. 2), whose conductivity (σ_a) is slightly lower than that of the α -phase (curve 2 in Fig. 1) and whose activation energy is higher than that of the α -phase. Preliminary results show that the proton activation volume in the α -phase is significantly different from that in the α_1 -phase: it is 0.1–1 cm³/mole in the α -phase and 7–9 cm³/mole in the α_1 -phase. This circumstance shows that the activation volume, an effective quantity for mobile protons, is not determined by the ionic radius but instead by the relaxation of the ions around this radius. At $P > 1.75$, there appears yet another superionic phase, α_2 , whose conductivity is only slightly lower than that of the α -phase (curve 3 in Figs. 1 and 2).

New polymorphic modifications (the δ and ξ phases in Fig. 2), with low conductivities, $\sigma_a < 10^{-7}$ mho/cm, are also induced at pressures $P \gtrsim 1$ GPa. The phase transitions $\beta \leftrightarrow \delta$ and $\delta \leftrightarrow \xi$ are accompanied by significantly greater changes in the volume ($\Delta V_{\beta\delta}/V_{\beta} = 2.0 \pm 0.1\%$ and $\Delta V_{\delta\xi}/V_{\xi} = 0.9 \pm 0.1\%$), but their thermal effects are weaker than those occurring in a $\beta \leftrightarrow \alpha$ superionic transition. Since a $\gamma \leftrightarrow \beta$ phase transition is characterized, as was pointed out elsewhere,^{1,6} by retarded kinetics, we cannot determine its displacement with pressure by repeating the heating and cooling cycles. The proposed $\gamma \leftrightarrow \beta$ phase-transition line is represented by the dashed line in the P - T phase diagram (Fig. 2).

The variety of phases with different proton conductivities can apparently be explained not only by the open structure of CsHSO₄, in which the protons in the short hydrogen bonds can be ordered, but also by the rearrangement or disordering of these bonds. Since all crystals of the group with the general formula MeHAO₄ (Me = Cs, Rb, NH₄, . . . Pb, A = S, Se, . . . P) have similar structures, we can expect that the rest of the crystals of this group also have some form of polymorphism in the superionic state.

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