Superion conductivity and phase transitions in $CsHSO_4$ and $CsHSeO_4$ crystals

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The phase transitions at $T_{\mathrm{tr}_1} = 414$ and 397 K for $CsHSO_4$ and $CsHSeO_4$, respectively, are transitions to a state with an anomalously high ion conductivity, $\sigma_a \approx 10^{-2}$ mho/cm. In a broad critical region $2° \lesssim T - T_{\mathrm{tr}_1} \lesssim 50°$ in the low-temperature phase, the ion conductivity exhibits the behavior $\sigma_a \sim (T - T_{\mathrm{tr}_1})^{-\gamma}$ with $\gamma \simeq 1.3$–1.65.

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Crystals of the alkali hydrosulfates and hydroselenates with the general formulas $MeHSO_4$ and $MeHSeO_4$ are the object of active research because of their ferroelectric and ferroelastic properties. In principle, these crystals could also be good proton conductors because of their particular structure (only two of the four oxygen atoms per molecule participate in the formation of *H* bonds,[1,2] so that the number of protons is half the number of possible proton sites). According to Refs. 3 and 4, the conductivity of $CsHSO_4$ and $CsHSeO_4$ crystals at room temperature is in fact quite high: 10^{-8}–10^{-6} mho/cm.

In this letter we report measurements of the conductivity of $CsHSO_4$ and $CsHSeO_4$ crystals over the temperature range 290–480 K and the frequency range 30 Hz–1 MHz. The measurements were carried out with wafers $6 \times 6 \times 1$ mm in size, oriented perpendicular to the *a* axis. The electrodes were made of Degussa silver paste.

The measurements show that the phase transition in $CsHSO_4$ at $T_{\mathrm{tr}_1} = 414$ K is a transition to a superion state (Fig. 1) with an anomalously high ion conductivity. The values of σ_a at 10 kHz at $T_{\mathrm{tr}_1} < T \lesssim 470$ K are in the range 10^{-3}–10^{-2} mho/cm, and the dielectric function is $\epsilon_a \simeq 5 \times 10^4$–$10^4$ esu. At $T = 293$ K at this frequency we find $\sigma_a \approx 10^{-6}$ mho/cm and $\epsilon_a \approx 10$ esu. The frequency dependence of σ_a and ϵ_a over the range 30–10^6 Hz is typical of ion conductors with electrodes which are essentially irreversible with respect to the major carriers: As the frequency increases, σ_a increases, while ϵ_a decreases. Furthermore, ϵ_a goes negative in the superion phase at frequencies above 300 kHz; this effect has been observed previously in several superion crystals.[5] As mentioned earlier, protons are apparently primarily responsible for the observed conductivity. The electron conductivity in this case should be negligible even at $T < T_{\mathrm{tr}_1}$, since the gap width in crystals which are transparent in the visible part of the spectrum is usually greater than 4–5 eV.

It can be seen from Fig. 1 that in addition to the transition to the superion state there are two structural phase transitions in $CsHSO_4$ as it is heated: at $T_{\mathrm{tr}_3} = 300$ K and $T_{\mathrm{tr}_2} = 330$ K. These transitions are accompanied by relatively small changes in σ_a. We do not, however, detect the phase transition at $T = 373$ K mentioned in Ref. 3.

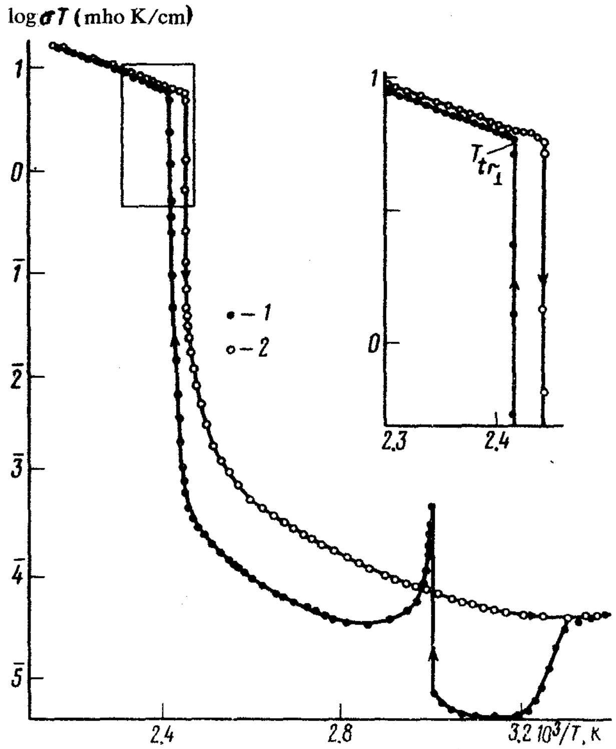

FIG. 1. Dependence of $\log(\sigma_a T)$ on the reciprocal of the temperature for a $CsHSO_4$ crystal according to measurements at 10 kHz. 1—Heating; 2—cooling.

In the superion phase the dependence $\sigma_a(T)$ is described well by the equation

$$\sigma_a T = A_a \exp\left(-\frac{V}{T}\right) \tag{1}$$

with $V_a = 0.33 \pm 0.01$ eV and $A_a = 10^4$ mho deg/cm. Below T_{tr_1}, however, in the interval $2^\circ \lesssim T_{\mathrm{tr}_1} - T \lesssim 60^0$, the dependence $\sigma_a(T)$ is not exponential but a power law (Fig. 2):

$$\sigma_a \sim (T_{\mathrm{tr}_1} - T)^{-\gamma}. \tag{2}$$

The values $\gamma = 1.65$ and 1.34, obtained during cooling and heating, respectively, are quite close to the values of the critical index for the generalized susceptibility in systems with a short-range interaction.[6]

In the immediate vicinity of T_{tr_1} ($T - T_{\mathrm{tr}_1} \lesssim 2^\circ$), the conductivity σ_a changes by two orders of magnitude, but since this phase transition is characterized by a slow kinetics, we are not able to distinguish the jump $\Delta\sigma_a$ at T_{tr_1} from the critical change in $\sigma_a(T - T_{\mathrm{tr}_1})$. Nevertheless, we can assert that the difference between the value of T_{tr_1} chosen as explained in the inset in Fig. 1 and the temperature at which the low-temperature phase suffers an absolute loss of stability does not exceed 1.5–2°. Further

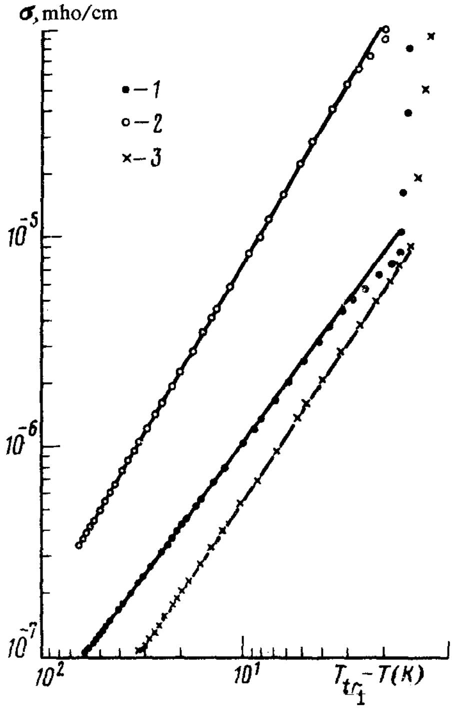

FIG. 2. Dependence of $\log\sigma_a$ on $\log(T-T_{tr_1})$ for $CsHSO_4$ (curves 1 and 2) and for $CsHSeO_4$ (curve 3) at 10 kHz. 1, 3—Heating; 2—cooling.

evidence that this is a second-order phase transition comes form the small thermal hysteresis: $\Delta T\approx 5°$.

A phase transition to a superion state also occurs in $CsHSeO_4$ at $T_{tr_1} = 398$ K (curves 1 and 2 in Fig. 3). Above T_{tr_1} the dependence $\sigma_a(T)$ is exponential, like (1) with $V_a = 0.35 \pm 0.02$ eV and $A_a = 1.4\times 10^4$ mho deg/cm. Below T_{tr_1} the dependence $\sigma_a(T)$ at $1.5 < T_{tr_1} - T \lesssim 35°$ is described by power law (2) (Fig. 2) with $\gamma = 1.42$ and 1.57 during heating and cooling, respectively. At $T_{tr_1} - T > 35°$, the dependence $\sigma_a(1/T)$ can be approximated by exponential function (1) with $V = 0.60 \pm 0.02$ eV and $A_a = 1\times 10^4$ mho deg/cm. In certain cases, yet another phase transition is observed during heating of $CsHSeO_4$, at $T_{tr_2} = 370$ K (curve 3 in Fig. 3).

There is also an interesting effect that occurs after a partial thermal decomposition of $CsHSeO_4$, which begins at $T \gtrsim 480$ K. As can be seen from Fig. 3 (curves 4 and 5), the curves of $\sigma_a(1/T)$ measured after the partial decomposition of the samples are different, but the temperature T_{tr_1} is essentially the same. As the decomposition proceeds, the curves of $\sigma_a(1/T)$ measured during cooling degenerate into exponential function (1) with $V = 0.67 \pm 0.02$ eV. For the dotted curve in Fig. 3 we have $A_a = 6\times 10^6$ mho deg/cm. This exponential dependence can naturally be associated with the part of the sample which is damaged during the decomposition. However, the

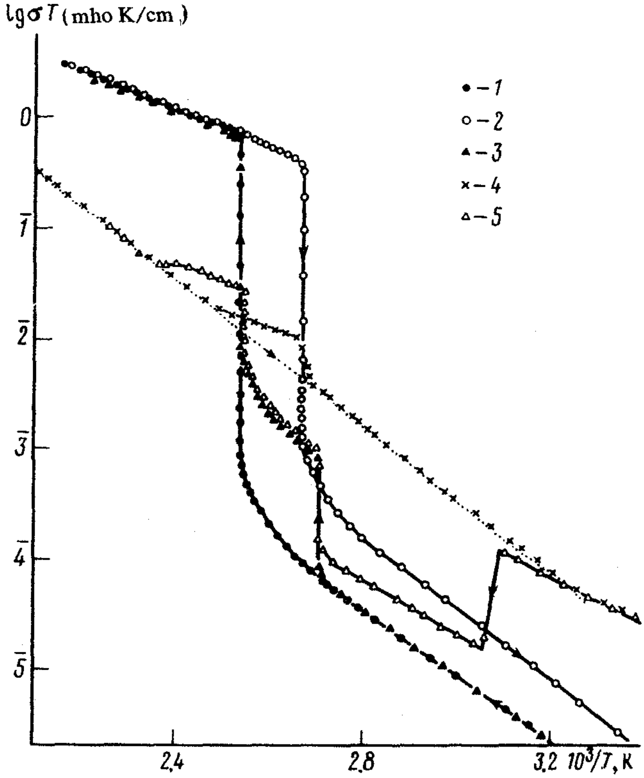

FIG. 3. Dependence of $\log(\sigma_a T)$ on the reciprocal of the temperature. 1–3—For a $CsHSeO_4$ crystal which has not undergone thermal decomposition; 4, 5—after partial thermal decomposition. 1, 3, 5—Heating; 2, 4—cooling. The measurement frequency is 10 kHz.

fundamental differences between the curves of $\sigma_a(1/T)$ during cooling and heating observed at lower temperatures (curves 4 and 5 in Fig. 3) indicate that the conductivity σ_a measured in these cases cannot be thought of as simply the sum of the contributions from the damaged and undamaged parts of the sample.

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