

Phase transitions in surface layers of hydrosulfate crystals

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(Submitted 8 July 1986)

Pis'ma Zh. Eksp. Teor. Fiz. **44**, No. 4, 186–189 (25 August 1986)

The surface layers of certain alkali hydrosulfate single crystals undergo phase transitions which are accompanied by appreciable anomalies of the surface conductivity. In CsHSO_4 and CsDSO_4 these transitions precede a volume transition to the superionic state and in NH_4HSO_4 and RbHSO_4 they precede their melting.

The effect of the surface component of the conductivity G_s on the accuracy of determining the volume conductivity G_v of ionic crystals has been established experimentally quite well. An important point here is that the difference in the temperature dependences of G_s and G_v is essentially only a quantitative difference. In the present letter we report the observation of a qualitative difference in the anomalies of $G_s(T)$ and $G_v(T)$ in alkali hydrosulfate crystals, indicating that these are phase transitions in the surface layers of these crystals.

Hydrosulfate crystals with a general formula MeHSO_4 ($\text{Me} = \text{NH}_4, \text{Rb}, \text{Cs}$) are proton conductors.^{1,2} In NH_4HSO_4 (AHS) and RbHSO_4 (RHS) the proton conductivity is no greater than 10^{-6} S/cm, whereas in CsHSO_4 (CHS) and in its deuterated analog CsDSO_4 (CDS) at $T = T_{\text{II-I}}$ the superionic phase transitions^{2,3} are accompanied by an increase in the conductivity to 10^{-3} – 10^{-2} S/cm, which is essentially the same conductivity as that in the melts of these salts.

The volume conductivity G_v was measured in an experimental arrangement in which a guard ring was used.⁴ The total conductivity, $G_t = G_v + G_s$, was determined from measurements without a guard ring. For the test samples the conductivity measured between the central electrode and the guard ring was the parameter of the surface layer with an effective thickness no greater than 10^{-4} – 10^{-5} cm. This conductivity was assumed to be G_s . At the frequency of 0.01 Hz the measurements of G_v , G_t , and G_s were carried out with an electrometer and at frequencies 30 Hz – 1 kHz they were carried out using a bridge method. The electrodes and a guard ring made from a silver paste were deposited on x -, y -, and z -cut wafers of thickness $d \approx 0.022$ – 0.2 cm and area $S \approx 0.7$ – 1 cm². The temperature was stabilized to within $\pm 0.1^\circ$.

As can be seen in Figs. 1 and 2, at temperatures above a certain temperature T_s , characteristic for each crystal, the temperature dependences of G_t are qualitatively different from the temperature dependence of the specific volume conductivity $\sigma_v = G_v d / S$. Clearly, an anomaly near T_s and T_{s_2} in this case is experienced only by the surface component of G_s . We have studied here in greater detail the anomalies in the conductivity near T_{s_1} . Within accuracy to ($\pm 1^\circ$), T_{s_1} does not depend on the indices of the principal faces of the sample, on the surrounding medium, or on the pressure ($10^{-5} \leq P \leq 5$ atm); it also does not depend on the thickness of the surface or its ma-

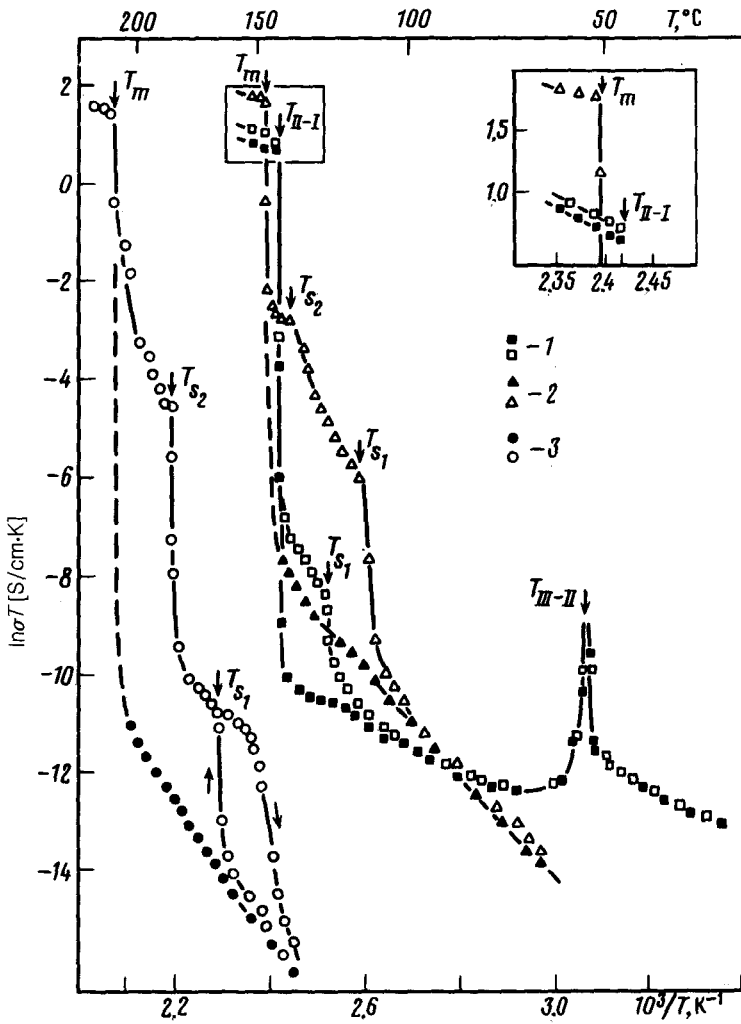


FIG. 1. The dependences $\sigma_v = f(1/T)$ (black symbols) and $\sigma_i = f(1/T)$ (light symbols) measured at a frequency of 1 kHz in air. 1—x-cut CHS; 2—z-cut AHS; 3—z-cut RHS. The thermal hysteresis is shown only for RHS.

chining quality. The last factor, however, has an appreciable effect on the $G_s(T)$ and $G_i(T)$ anomalies. These anomalies are most sharply defined in samples which are freshly cleaved in the cleavage plane. Figure 2 shows that at $T = T_{s_1}^+$, G_s of CDS increases by more than three orders of magnitude. The superionic volume phase transitions in CDS and CHS or the melting of AHS and RHS cause approximately the same increase of G_v (Ref. 2). Upon cooling the crystals, the temperature dependences $G_s(T)$ exhibit a thermal hysteresis, $T_{s_1}^+ - T_{s_1}^- \approx 20$ K, for all crystals that were tested. Table I gives the values for $T_{s_1}^+$, $T_{s_2}^+$, T_{I-II} , and for the melting points T_m .

Studies of the $G_s(T)$ dependences for CDS in air, in argon, and in a vacuum

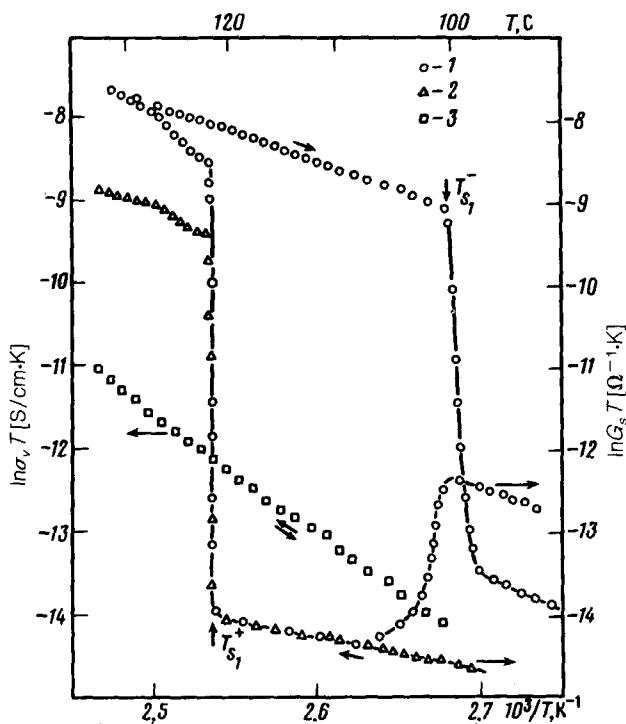


FIG. 2. The dependences $G_s = f(1/T)$ (1,2) and $\sigma_v = f(1/T)$ (3) for x-cut CDS samples measured at a frequency of 0.1 Hz in argon. 1—sample was placed in dry air for ~ 30 min before taking the measurements; 2—the same sample, after placing it in air with $\sim 30\%$ moisture for 24 hours.

($P \approx 10^{-4}$ atm) showed that below $T = 373$ K the value of G_s is essentially independent of the surrounding medium but is sensitive to the moisture content in it. From curves 1 and 2 in Fig. 2 we see that the values of G_s of a sample held in moist air for several hours at $T < 373$ K after being cleaved are considerably higher than those of a sample held in dry air after being cleaved. At $T \approx 373$ K the value of G_s of the first sample decreases sharply and then begins to follow the $G_s(T)$ curve of the second sample. These results are evidence that at $T < 373$ K water is adsorbed at the surface and that at $T \approx 373$ K it is rapidly desorbed. At $T = T_s$, the anomalies in the depen-

TABLE I.

Crystal	$T_{s_1}^+$, K	$T_{s_2}^+$, K	T_{I-II}	T_m , K
RbHSO ₄ (RHS)	434	455	—	481
NH ₄ HSO ₄ (AHS)	386	412	—	420
CsHSO ₄ (CHS)	395	468	414	486
CsDSO ₄ (CDS)	395	468	412	478

dence $G_s(t)$ should therefore be linked with the phase transformation in the surface layer of a crystal rather than with the adsorbed layer. We should note that the higher value of the conductivity G_s at $T > T_{s_1}$ (Fig. 2) for samples with an originally adsorbed layer of water seems to be attributable to its incomplete desorption at $T > 373$ K. Similar features in the behavior of $G_s(T)$ have also been observed in other crystals.

The anomaly in $G_s(T)$ at T_{s_1} , characteristic of superionic volume phase transitions (or melting), the presence of a thermal hysteresis ($T_{s_1}^+ \neq T_{s_1}^-$), and the reproducibility of this anomaly in the subsequent cycles of lowering and raising the temperature collectively confirm that a phase transition occurs in the surface layers of the crystal. As the preliminary optical studies have shown, an increase in G_s at T_{s_2} is accompanied by the formation of a $> 10^{-5}$ -cm-thick macroscopic film of the melt on the surface of the samples. At $T = T_{s_1}$ the surface phase transitions may also be the transitions of the melting-solidification type. Since the conductivity of the melts of these salts lies within the limits 10^{-2} – 10^{-1} S/cm, the thickness of the surface layer, in which these surface phase transitions occur, is estimated to be on the order of several lattice constants.

We wish to thank N. M. Shchagin, R. M. Fedosyuk, Z. V. Bobrov, and S. V. Redin for furnishing the crystals and also A. V. Tregubchenko for assistance in carrying out certain experiments.

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⁴L. B. Harris, *J. Appl. Phys.* **41**, 1883 (1970).

Translated by S. J. Amoretty