

Theory of the superionic phase transition in CsHSO_4

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The superionic phase transition in cesium hydrodeuterosulfate is described as a transition due to a disordering of protons on hydrogen bonds. The strong short-range correlations of the protons and the linear relationship between the order parameter and the strain are taken into account.

Recent experiments¹⁻³ have revealed a new class of superionic semiconductors—acid sulfates and selenates—whose high ionic conductivity (on the order of 10^{-2} S/cm) results from a diffusion of protons.³⁻⁵ Neutron-diffraction studies⁵ have shown that the superionic transitions in CsHSO_4 (CHS) and $\text{CsD}_{0.7}\text{H}_{0.3}\text{SO}_4$ (CDS) is accompanied by a structural transition from a C_{2h}^2 monoclinic phase to a phase of higher symmetry. Optical studies⁶ indicate that the structural transition is a ferroelastic transition, $C_{2h} \rightarrow D_{4h}$, with a large spontaneous strain ($\sim 10^{-2}$) in the C_{2h} phase.

In this letter we propose an elementary theory for the superionic ferroelastic transition in the CHS crystal, which is the crystal that has been studied most thoroughly.^{1,4-6} Our theory is based on the Silsbee-Jüling-Schmidt model (see Ref. 7, for example), which incorporates the short-range proton correlations that are important in crystals with hydrogen bonds. In this regard, the theory is quite different from the standard phenomenological theories of superionic transitions (see Ref. 8, for example).

According to the structural data of Refs. 5 and 9, the hydrogen bonds in the CHS crystal form one-dimensional chains along the **b** monoclinic axis of the C_{2h}^2 phase below the transition temperature $T_c = 414$ K ($T_c = 412$ K in CDS). Another possible chain of hydrogen bonds—along the **c** axis—is not filled (in contrast with the structurally similar CsH_2PO_4 crystal). We assume that the superionic transition results from a disordering of the protons in the crystal along these two chains. At $T < T_c$, the number of “defects” is thus $n = n_x = 0$, with $n_y = 1 - n = 1$, while at $T > T_c$ it is $n = n_x = n_y = 1/2$, where $n_{x,y}$ are the average numbers of protons per bond along the $x \parallel \mathbf{c}$ and $y \parallel \mathbf{b}$ axes. Since the order parameters in the D_{4h} high-temperature phase, $\sigma = n_y - n_x = 1 - 2n$, transforms under the same irreducible representation as the strain $e_1 = (\epsilon_{yy} - \epsilon_{xx})/2$, we can write the following representation for the free energy density:

$$F = F_0 + \frac{1}{2} C_1 e_1^2 - \lambda e_1 \sigma + F(\sigma), \quad (1)$$

where the stiffness coefficient is $C_1 = 2(C_{11} - C_{12})$. From the equilibrium condition $\partial F / \partial e_1 = 0$, we find the relationship between the strain and the order parameter: $e_1 = (\lambda / C_1) \sigma$. The free energy of the proton subsystem, $F(\sigma)$, is calculated in the approximation of a four-particle cluster,⁷ in which the proton occupation numbers n^i on

the $\alpha = 1, 2, 3, 4$ bonds near the i -th SO_4 tetrahedron are determined by the relations $n_{1,3}^i = 1/2(1 + \sigma_{1,3}^i)$ along the y axis and $n_{2,4}^i = 1/2(1 - \sigma_{2,4}^i)$ along the x axis, where the pseudospin operator is $\sigma_\alpha^i = \pm 1$, and $\sigma = \langle \sigma_\alpha^i \rangle$.

After the equilibrium stain is eliminated from (1), we find the standard expression for the free energy in the Silsbee-Jüling-Schmidt model⁷ with the long-range constant $\gamma = \lambda^2/2C_1[\gamma \approx 25 \text{ K}/v_0$ for $C_1 \approx 10^7 \text{ dyn/cm}^2$, $e_1 \approx 2.7 \times 10^{-2}$, and $v_0 \approx 10^{22} \text{ cm}^{-3}$ (Ref. 5) is the volume per molecule]. Assuming that the number of defects consisting of three-proton configurations (for $n_1 = n_2 = n_3 = 1$, $n_4 = 0$, etc.) is small at room temperature, $n = \exp(-2W/T) \sim 10^{-5}$, we find the energy to be $W \approx 1500 \text{ K}$. Ignoring the contribution $L = \exp(-W/T_c)$, we find the following expression for the transition temperature:

$$T_c = \epsilon [\ln (2 / (2 \exp(\gamma / T_c) - 1))]^{-1}, \quad (2)$$

where ϵ is the excitation energy of the two-proton configuration (for $n_1 = n_2 = 1$, $n_3 = n_4 = 0$, etc.). Assuming $T_c = 414 \text{ K}$, we find $\epsilon \approx 250 \text{ K}$.

For the values found for the parameters of this model, the phase transition turns out to be a first-order transition of the Slater type with a jump in the order parameter, $\sigma(T_c^-) - \sigma(T_c^+) = 1$ [or in the "defect" concentration, $n(T_c^+) - n(T_c^-) = 1/2$] and a temperature difference $T_c - T_0 \approx 2.5^\circ$, where T_0 is the Curie temperature, at which the reciprocal of the susceptibility vanishes in terms of the field which is the conjugate of σ . The stiffness coefficient \tilde{C}_1 of the free crystal has an anomaly $\tilde{C}_1 = C_1 + \lambda^2/a(T - T_0^0) = C_1(T - T_0)/(T - T_0^0)$ at $T > T_0$, where T_0^0 is the Curie temperature at $\lambda = 0$: $T_0 = T_0^0 + \lambda^2/aC_1$. The jump in the entropy, $\Delta S \approx 0.52R$, turns out to be less than that observed,¹⁰ $\Delta S = 1.32R$, apparently because the contributions to the entropy from other degrees of freedom have been ignored. In particular, the contribution of the rotational jumps of the SO_4 groups, which undergo rapid reorienting motions above T_c (Ref. 3), have been ignored.

On the whole, this theory gives a reasonable description of the nature of the phase transition in the CHS and CDS crystals. To calculate the conductivity, we need to examine the kinetics of the protons upon the phase transition; this will require a separate study. On the other hand, the similarity between the superionic phase transitions in the acid sulfates and selenates suggests that this mechanism for the transition in CHS also operates in other compounds of this group, in particular, CsHSeO_4 , where we again observe a ferroelastic transition with a large spontaneous strain.¹¹ It would be very interesting to pursue the study of superionic phase transitions in these compounds, with the primary goal of determining the structure of the high-temperature phase and studying the elastic anomalies at the phase transition.

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