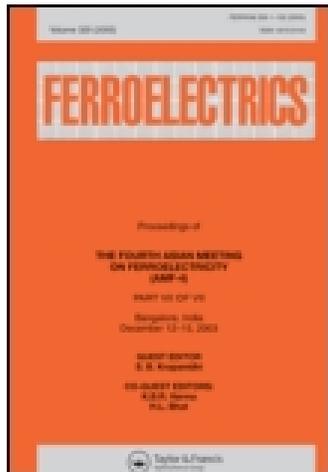


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PROPERTIES OF NH_4HSO_4 AND RbHSO_4 SINGLE CRYSTALS NEAR THEIR CURIE POINTS

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The accurate measurements of the properties of NH_4HSO_4 and RbHSO_4 were carried out. A statistical theory of the ferroelectric transitions is proposed.

Ferroelectricity of NH_4HSO_4 (AHS) and RbHSO_4 (RHS) has been known for a long time.¹⁻³ The previous measurements of dielectric permeability and heat capacity were conducted either by express methods^{1,2} or on powder samples.³ Therefore, only approximate data about phase transitions of the crystals are available.

The accurate thermal, dielectrical and optical investigations of AHS and RHS were carried out in the temperature range 130°-300°K. Single crystals of AHS and RHS were grown from aqueous solutions

by evaporation methods. Dielectric permeability (ϵ_c) and heat capacity (C_E) were measured simultaneously on the ferroelectric *c*-cut plates at the vacuum adiabatic calorimeter. Heat capacity was studied for electrically shorted samples to avoid a diffusion of C_E -anomalies near Curie points.⁴ Spontaneous polarization was determined from the hysteresis loops.

The temperature behaviour of C_E , ϵ_c and a normalized polarization P_s/P_s^{max} are shown on Figure 1a-d. Transition points of the crystals are: $T'_c = 271^\circ$

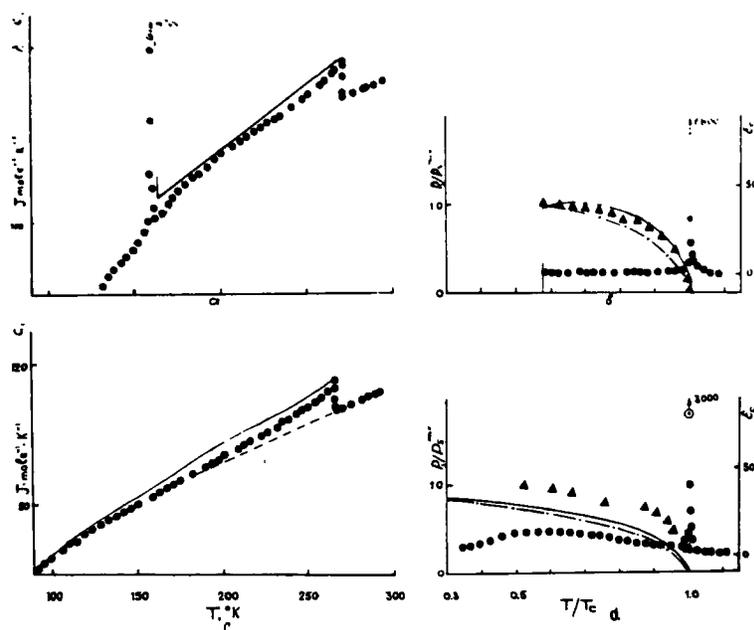


FIGURE 1 Temperature dependences of heat capacity C_E , dielectric permeability ϵ_c and spontaneous polarization P_s/P_s^{max} of AHS (a, b) and RHS (c, d). - - - - mf, — cluster approximation.

TABLE I
Principal thermodynamical characteristics of AHS and RHS

	AHS			RHS		
	Experiment	Theory		Experiment	Theory	
		mf	Clusters		mf	Clusters
$T_c', ^\circ\text{K}$	270.93	271	271	264.5	265	265
$\Delta S_1, \text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	1.66 ± 0.37	2.18	1.46	0.91 ± 0.08	4.95	4.25
$\Delta C, \text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	12.2 ± 0.3	9.8	5.97	9.0 ± 0.2	15.6	11.6
C, grade	206	266	279	131	237	231
$P_s \cdot 10^{-6} \text{C} \cdot \text{sm}^{-2}$	0.81	0.81	0.81	0.45	0.45	0.45
$T_c'', ^\circ\text{K}$	159.3	159.3	159.3	—	—	—
$\Delta S_2, \text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	6.7	11.7	4.75	—	—	—

and $T_c'' = 159^\circ\text{K}$ for AHS and $T_c = 264.6^\circ\text{K}$ for RHS. The growth of ΔC_E value in the paraelectric phase near T_c follows the logarithmic type curve. The Curie-Weiss law is fulfilled for ϵ_c in $T_c' + 0.05^\circ \leq T \leq T_c' + 3.5^\circ$ for AHS and $T_c + 0.05^\circ \leq T \leq T_c + 4.0^\circ$ for RHS. The main thermodynamical characteristics determined from the experiments are collected in Table I.

Temperature changes of birefringence $\Delta n_i (i=1, 2, 3)$ were measured by Senarmont compensator for $\lambda = 6328 \text{ \AA}$. Δn_i are linearly dependent on T in paraelectric phases. Breaklike change takes place at T_c' and T_c respectively and then Δn_i changes non-linearly for both crystals. According to the phenomenological theory⁵ the increases of Δn_i are proportional to P_s^2 below T_c and T_c' . The measurements of the induced electro-optical constants were possible only for RHS crystals because of the appreciable conductivity of AHS samples.⁶ The anomalies of the induced constants in the electric field parallel to the c -axis follow the dielectric ones.

Statistical theory of ferroelectricity in AHS was proposed earlier.⁶ Structural results of Nelmes⁷ were used in the model. It was supposed that P_s appearance was due to ordering of $S1_D$ groups which were moving in an asymmetric double well potential. The model, which is equivalent to that of Rochelle salt, is discussed in detail by Vaks,⁸ and the Hamiltonian is

$$H = -\frac{1}{2} \sum_{ij} J_{ij} (\sigma_i^{z1} \sigma_j^{z1} + \sigma_i^{z2} \sigma_j^{z2}) - \sum_{ij} K_{ij} \sigma_i^{z1} \sigma_j^{z2} - \Delta \sum_i (\sigma_i^{z1} - \sigma_i^{z2}) - pE \sum_i (\sigma_i^{z1} + \sigma_i^{z2}), \quad (1)$$

J and K are the effective interaction constants belonging to equal and different sublattices $S1_D'$ and $S1_D''$ respectively; Δ is the measure of the asymmetry of

the local crystalline potential. E is the external electric field; p is the effective dipole moment.

Thermodynamical properties of AHS at molecular field (mf) approximation were discussed in Ref. 6. RHS crystals according to Ref. 5 were considered as isomorphous to AHS. Calculated values for both crystals are given in Table I. In order to explain phase transition in AHS at T_c'' it was necessary to assume the temperature dependence of J .⁶

Later the thermodynamics of the phase transitions was investigated in cluster approximation. The simplest clusters of two particles in $S1_D'$ and $S1_D''$ sublattices were chosen for the $J > 0$ case. The interaction between sublattices was described in the mf approximation. In this case the free energy becomes

$$f = F/J + K = -t \{ \ln 2 [l^{-1} + lch2\beta(\gamma - a\eta + \xi)] + \ln 2 [l^{-1} + lch2\beta(\gamma - a\eta - \xi)] \} + t \ln 2ch\beta(\gamma - v\eta + \mu\xi) + t \ln 2ch\beta(\gamma - v\eta - \mu\xi) + \frac{a+1}{2} (\xi^2 - \eta^2), \quad (2)$$

where

$$\beta = \frac{1}{t}, \quad t = \frac{T}{J+K}, \quad a = \frac{K-J}{K+J}, \quad \gamma = \frac{\Delta}{K+J},$$

$$\xi = \frac{1}{2} [\langle \sigma^1 \rangle + \langle \sigma^2 \rangle], \quad \eta = \frac{1}{2} [\langle \sigma^1 \rangle - \langle \sigma^2 \rangle]$$

and brackets mean thermal averages. The values ξ and η can be obtained from the equations

$$\begin{aligned} sh\beta\gamma ch\beta\omega\eta ch\beta\omega\xi - ch\beta\gamma sh\beta\omega\eta ch\beta\omega\xi \\ = l^{-2} [sh\beta\gamma ch\beta v\eta ch\beta\mu\xi + ch\beta\gamma sh\beta v\eta ch\beta\mu\xi], \\ ch\beta\gamma ch\beta\omega\eta ch\beta\omega\xi - sh\beta\gamma sh\beta\omega\eta sh\beta\omega\xi \\ = l^{-2} [sh\beta\gamma sh\beta v\eta sh\beta\mu\xi + ch\beta\gamma sh\beta v\eta sh\beta\mu\xi]. \end{aligned} \quad (3)$$

Here:

$$l = e^{[\beta(1-a)]/2}, \quad \nu = \frac{1}{2}(3a - 1), \quad \mu = \frac{1}{2}(3 - a),$$

$$\omega = \frac{1}{2}(1 + a).$$

Thermodynamical values of C_E and P_s/P_s^{\max} are given in Table I and on Figure 1a-d. The best parameters of the model are $K = 326.5$ and 260°K , $J = 88.5$ and 57°K , $\Delta = 339$ and 234°K for AHS and RHS respectively. This approximation describes the phase transitions without assumption on temperature dependence of J .

The proposed microscopical model is valid for the qualitative description of the phase transitions AHS and RHS. Thus the orientational ordering in SO₄ sublattices could be regarded as the leading mechanism

of the trigger-type phase transition in the family of ferroelectrics.

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† Note added on proof