

structure was observed in Phase III. In the present calculation, however, the II-III transition and the long-period structure in Phase III are ignored for simplicity. The calculation only aims to interpret the experimental results qualitatively.

The Helmholtz free energy A given by Mitsui for a clamped crystal is⁴⁾

$$A = -\frac{\beta}{2}(P_1^2 + P_2^2) - \beta' P_1 P_2 - \frac{V}{\mu}(P_1 - P_2) + \frac{kTN}{4} \sum_{i=1}^2 \left\{ \left(1 + \frac{2P_i}{N\mu}\right) \ln \left(1 + \frac{2P_i}{N\mu}\right) + \left(1 - \frac{2P_i}{N\mu}\right) \ln \left(1 - \frac{2P_i}{N\mu}\right) - 2 \ln 2 \right\}, \quad (1)$$

$$G = -\frac{\beta}{2}(P_1^2 + P_2^2) - \beta' P_1 P_2 - \frac{V}{\mu}(P_1 - P_2) + \frac{\xi}{4}(P_1^4 + P_2^4) + \frac{\zeta}{2} P_1^2 P_2^2 + \frac{kTN}{4} \sum_{i=1}^2 \left\{ \left(1 + \frac{2P_i}{N\mu}\right) \ln \left(1 + \frac{2P_i}{N\mu}\right) + \left(1 - \frac{2P_i}{N\mu}\right) \ln \left(1 - \frac{2P_i}{N\mu}\right) - 2 \ln 2 \right\}. \quad (2)$$

According to Ishibashi and Takagi⁶⁾ eq. (2) is rewritten by introducing reduced quantities as;

$$g = -\frac{a_1}{2}(x_1^2 + x_2^2) - a_2 x_1 x_2 - (x_1 - x_2) + \frac{a_3}{4}(x_1^4 + x_2^4) + \frac{a_4}{2} x_1^2 x_2^2 + \frac{t}{2} \sum_{i=1}^2 \{ (1 + x_i) \ln(1 + x_i) + (1 - x_i) \ln(1 - x_i) \}, \quad (3)$$

where $g = 2(G + kTN \ln 2)/(NV)$, $x_1 = 2P_1/(N\mu)$, $x_2 = 2P_2/(N\mu)$, $t = kT/V$, $a_1 = \beta N\mu^2/(2V)$, $a_2 = \beta' N\mu^2/(2V)$, $a_3 = \xi N^3\mu^4/(8V)$, and $a_4 = \zeta N^3\mu^4/(8V)$.

The expansion coefficients a_i are generally dependent both upon reduced temperature t and upon hydrostatic pressure p as $a_i = a_i^{00} + a_i^{10}t + a_i^{01}p + a_i^{11}pt + \dots$. For simplicity, temperature dependence of a_i is neglected. The effect of hydrostatic pressure is more significant for the lower-order expansion coefficients. Possible pressure variation of a_1 affects mainly the pressure coefficients of transition points, and it is ignored in the present calculation since the calculation aims to demonstrate the p - T phase diagram only in a qualitative way. Then, the next lowest expansion coefficient a_2 is assumed to depend linearly upon pressure as

$$a_2 = a_2^{00} + a_2^{01}p. \quad (4)$$

The other coefficients are assumed to be constants.

The spontaneous sublattice polarizations x_1^s , x_2^s are obtained by solving

where P_1 and P_2 are sublattice polarizations, μ is the dipole moment of a molecular dipole unit, N is the number of the dipoles per unit volume. The parameter V measures the asymmetry of the potential at a dipole site.⁴⁾ As is well known the elastic Gibbs function for a free crystal contains higher order terms of P_i 's. Third order terms of P_i 's may be introduced because of existence of $(P_1 - P_2)$ term in eq. (1). However, in the present calculation the third order terms are neglected; this means that the asymmetry parameter V is assumed to be independent of lattice strains.* Then, the resultant elastic Gibbs function G is expressed to the fourth order terms of P_i 's as;

$$\frac{\partial g}{\partial x_1} = -a_1 x_1 - a_2 x_2 - 1 + a_3 x_1^3 + a_4 x_1 x_2^2 + t \cdot \tanh^{-1} x_1 = 0, \quad (5)$$

$$\text{and } \frac{\partial g}{\partial x_2} = -a_1 x_2 - a_2 x_1 + 1 + a_3 x_2^3 + a_4 x_1^2 x_2 + t \cdot \tanh^{-1} x_2 = 0, \quad (6)$$

simultaneously. The reduced ferroelectric and antiferroelectric polarizations P_F , P_A are expressed by

$$P_F = (x_1 + x_2)/2, \quad (7)$$

$$\text{and } P_A = (x_1 - x_2)/2, \quad (8)$$

respectively. The reduced dielectric susceptibility χ_F is obtained as

$$\chi_F^{-1} = \left(\frac{\partial^2 g}{\partial P_F^2} \right)_{E=0} = \left(\frac{\partial^2 g}{\partial x_1^2} + \frac{\partial^2 g}{\partial x_2^2} + 2 \frac{\partial^2 g}{\partial x_1 \partial x_2} \right)_{E=0} = -2(a_1 + a_2) + 4a_4 x_1^s x_2^s + (3a_3 + a_4) \{ (x_1^s)^2 + (x_2^s)^2 \} + t [\{ 1 - (x_1^s)^2 \}^{-1} + \{ 1 - (x_2^s)^2 \}^{-1}]. \quad (9)$$

* Inclusion of the third order terms did not cause a drastic alternation of the results.

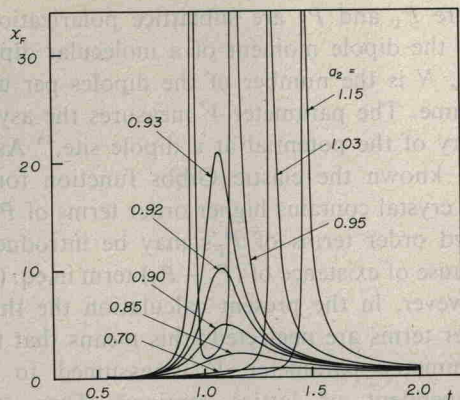


Fig. 8. Calculated reduced temperature t dependence of the dielectric susceptibility χ_F for various values of a_2 . $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

Starting from eq. (3) one may calculate using eqs. (5)–(9) the reduced values of dielectric susceptibility χ_F and spontaneous ferro- and antiferroelectric polarizations P_F^s , P_A^s as functions of t and a_i 's. The calculation was carried out numerically with an electronic computer FACOM 230-75 for various sets of a_i 's. Figure 8 shows the t -dependence of χ_F for different values of a_2 . Here the other parameters are fixed to be $a_1=0.45$, $a_3=-0.5$, and $a_4=-0.2$. When a_2 is less than 0.94, no phase transition takes place and the system is antiferroelectric throughout whole range of t . However, a broad peak of the susceptibility becomes progressively intense and sharp as a_2 increases. In a range $0.94 < a_2 < 1.0$, the dielectric susceptibility shows two anomalies, and a ferroelectric phase (denoted as F_1) is stabilized between them. When a_2 is larger than 1.0, second ferroelectric phase (F_2) is stable in a lower t region. As a_2 further increases the lower temperature peak of χ_F is masked by the direct transition between two ferroelectric phases. Since the parameter a_2 is assumed to be a linear function of pressure, Fig. 8 represents the temperature dependence of the susceptibility at various pressures corresponding to Figs. 1 and 2 for $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. Figure 9 shows the a_2 dependence of the inverse of the maximum susceptibility $1/\chi_F^{\text{max}}$ in a region of $a_2 < 0.94$ where ferroelectric phases are not stabilized. The inverse of the maximum susceptibility linearly decreases with increasing a_2 and tends to zero at $a_2=0.94$. Figure 9 qualitatively represents the observed behavior of $1/\epsilon_{\text{max}}$ vs

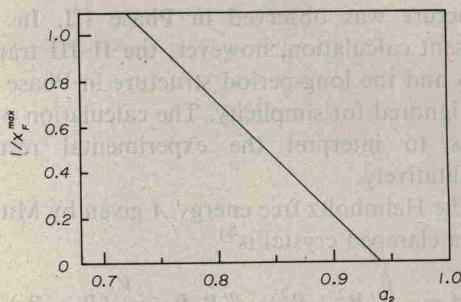


Fig. 9. Variation of the inverse of the maximum susceptibility $1/\chi_F^{\text{max}}$ with a_2 . $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

p of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ shown in Fig. 5. Figures 10 and 11 show t -dependence of the spontaneous ferro- and antiferroelectric polarizations P_F^s and P_A^s for different values of a_2 , respectively.

In the limit of the present approximation the transition between two ferroelectric states F_1 and F_2 is isomorphous one,⁸⁾ namely the symmetry of the crystal does not change during

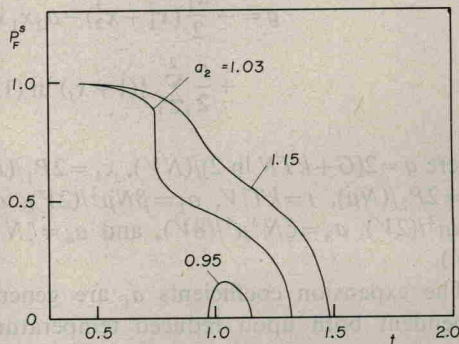


Fig. 10. Reduced temperature t dependence of the spontaneous ferroelectric polarization P_F^s for different a_2 . $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

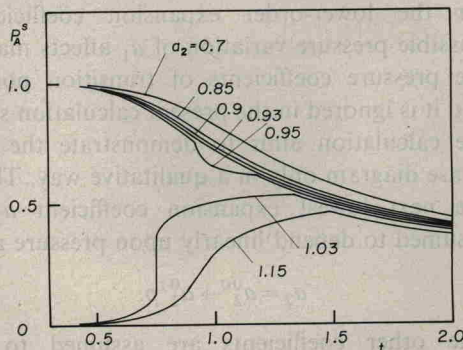


Fig. 11. Reduced temperature t dependence of the spontaneous antiferroelectric polarization P_A^s for different a_2 . $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.