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 is[4]

$$A=-\frac{\beta}{2}(P_1^2+P_2^2)-\beta' P_1P_2-\frac{V}{\mu}(P_1-P_2)+\frac{kTN}{4}\sum_{i=1}^{2}\left\{\left(1+\frac{2P_i}{N\mu}\right)\ln\left(1+\frac{2P_i}{N\mu}\right)+\left(1-\frac{2P_i}{N\mu}\right)\ln\left(1-\frac{2P_i}{N\mu}\right)-2\ln 2\right\}, \quad (1)$$

where $P_1$ and $P_2$ are sublattice polarizations, $\mu$ 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;

$$G=-\frac{\beta}{2}(P_1^2+P_2^2)-\beta' P_1P_2-\frac{V}{\mu}(P_1-P_2)+\frac{\xi}{4}(P_1^4+P_2^4)+\frac{\zeta}{2}P_1^2P_2^2+\frac{kTN}{4}\sum_{i=1}^{2}\left\{\left(1+\frac{2P_i}{N\mu}\right)\ln\left(1+\frac{2P_i}{N\mu}\right)+\left(1-\frac{2P_i}{N\mu}\right)\ln\left(1-\frac{2P_i}{N\mu}\right)-2\ln 2\right\}. \quad (2)$$

According to Ishibashi and Takagi[6] eq. (2) is rewritten by introducing reduced quantities as;

$$g=-\frac{a_1}{2}(x_1^2+x_2^2)-a_2x_1x_2-(x_1-x_2)+\frac{a_3}{4}(x_1^4+x_2^4)+\frac{a_4}{2}x_1^2x_2^2+\frac{t}{2}\sum_{i=1}^{2}\{(1+x_i)\ln(1+x_i)+(1-x_i)\ln(1-x_i)\}, \quad (3)$$

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 $a_i=a_i^{00}+a_i^{10}t+a_i^{01}p+a_i^{11}pt+\cdots$. 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

$$\frac{\partial g}{\partial x_1}=-a_1x_1-a_2x_2-1+a_3x_1^3+a_4x_1x_2^2+t\cdot\tanh^{-1}x_1=0, \quad (5)$$

and

$$\frac{\partial g}{\partial x_2}=-a_1x_2-a_2x_1+1+a_3x_2^3+a_4x_1^2x_2+t\cdot\tanh^{-1}x_2=0, \quad (6)$$

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

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

and

$$P_A=(x_1-x_2)/2, \quad (8)$$

respectively. The reduced dielectric susceptibility $\chi_F$ is obtained as

$$\chi_F^{-1}=\left(\frac{\partial^2 g}{\partial P_F^2}\right)_{E=0}=\left(\frac{\partial^2 g}{\partial x_1^2}+\frac{\partial^2 g}{\partial x_2^2}+2\frac{\partial^2 g}{\partial x_1\partial x_2}\right)_{E=0}=-2(a_1+a_2)+4a_4x_1^sx_2^s+(3a_3+a_4)\{(x_1^s)^2+(x_2^s)^2\}+t[\{1-(x_1^s)^2\}^{-1}+\{1-(x_2^s)^2\}^{-1}]. \quad (9)$$

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

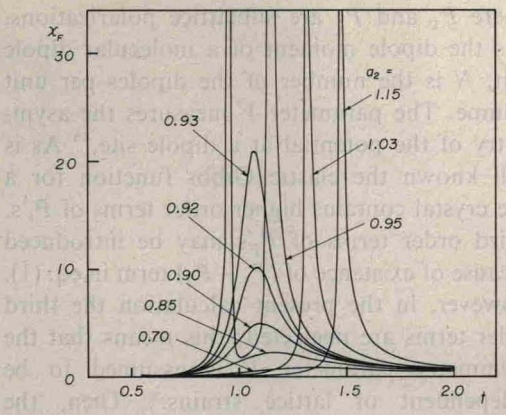


Fig. 8. Calculated reduced temperature $t$ dependence of the dielectric susceptibility $\chi_F$ for various values of $a_2$. $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

Starting from eq. (3) one may calculate using eqs. (5)–(9) the reduced values of dielectric susceptibility $\chi_F$ 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 $\chi_F$ 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 $\chi_F$ 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 $(NH_4)_3H(SO_4)_2$. Figure 9 shows the $a_2$ dependence of the inverse of the maximum susceptibility $1/\chi_F^{max}$ 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 $1/\varepsilon_{max}$ vs

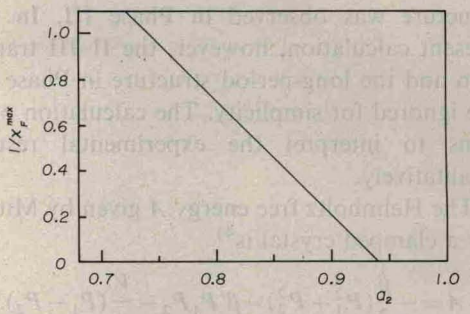


Fig. 9. Variation of the inverse of the maximum susceptibility $1/\chi_F$ with $a_2$. $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

$p$ of $(NH_4)_3H(SO_4)_2$ shown in Fig. 5. Figures 10 and 11 show $t$-dependence of the spontaneous ferro- and antiferro-electric 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

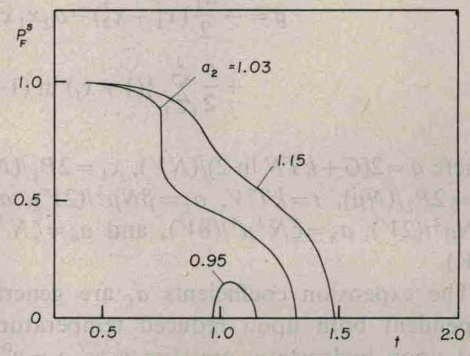


Fig. 10. Reduced temperature $t$ dependence of the spontaneous ferroelectric polarization $P_F^s$ for different $a_2$. $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

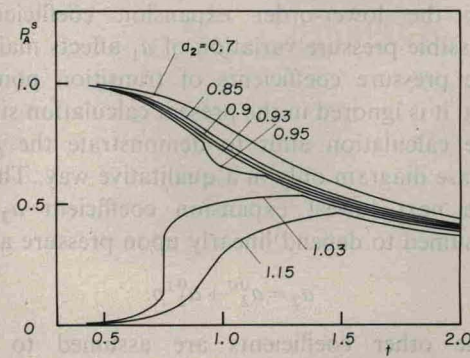


Fig. 11. Reduced temperature $t$ dependence of the spontaneous antiferroelectric polarization $P_A^s$ for different $a_2$. $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.