Phase Diagrams for the Sequential Antiferroelectric-Feroelectric Phase Transitions

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Sequential phase transitions(polar-semipolar-antipolar phases)are discussed using Kittel's two sublattice models. Several phase diagrams are depicted in parameter space, which corresponds to the concentration vs temperature space. The phase diagrams are compared with one derived in the dipolar spin glass phase transition found in ADP-RDP mixed crystals.

§1 Introduction

In the ferroelectrics and antiferroelectrics, there are many experimental reports on the phase diagrams, which are usually drawn in the pressure-temperature space, or in the electric field-temperature space. [1-4]

Uchino and Nomura proposed the phenomenological theory of the solid solution systems between the ferroelectric $Pb(Fe_{2/3}W_{1/3})O_3$ and the antiferroelectric $Pb(M_{1/2}W_{1/2})O_3$ (M=Mn, Co, Ni), by Kittel's free energy expression for the two-sublattice model[1]. The sixth order term $P_a^6 + P_b^6$ of the polarizations was omitted in the proposed free energy, however, the agreements between the calculated phase diagram and the experimental ones were satisfactory. These solid solutions show only the ferroelectric phase at lower temperature in the all ranges of the mixed concentration. Since the sixth order term of the polarization was omitted in his proposed phenomenological theory, the semipolar phase was not relized as a stable state.

Benguigui has been proposed Kittel's free energy which has sixth order terms, and compared with the phase diagrams of the electric-temperature and the concentration-temperature phase diagrams[4]. In the phase diagrams of the solid solution of $Pb(Zr_x Ti_{1-x})_{0.7}Sn_{0.3}O_3$, successive phase transition from the ferroelectric to the antiferroelectric phase below 120℃ were observed. The qualitative analysis was given in the temperature-k phase diagrams, where k is the coefficient of the fourth order term $P_a P_b(P_a^2+P_b^2)$.

Although the solid solution of $Pb(Zr_x Ti_{1-x})_{0.7}Sn_{0.3}O_3$ has no ferrielectric phase, the phase diagram is of interest. Recently, we have shown that the semipolar-phase exists as a stable state with the same starting point of the free energy as one used by Benguigui. [5-7] Moreover we have reported the analytical method for drawing the phase diagrams, where we have shown the second order phase transition lines, the tricritical point (TCP), and the tetracritical point.

From the birefringence and dielectric measurements of $(RDP)_{1-x}(ADP)_x$ ($0 < x < 0.35$), Courtens reported that the crystal shows the glassy phase transition resemble to the spin-glass phase transition[8,9]. Iida and Terauchi have reported the measurement of X-ray diffraction and the dielectric constants[10]. Matsushita and Matsubara also discussed the phenomenological theory of this crystal[11,12]. The crystal RDP-ADP shows the sequential phase transitions ; ferroelectric-mixed phase-antiferroelectric-ferroelectric-dipolar glass phase-antiferroelectric phase.

In this report, we show the m'' vs temperature phase diagram in the antiferroelectric and the ferroelectric phase transitions, where m'' is a coefficient of the fourth power of the order parameter and propotional to k in Benguigui theory[5]. In the phase diagram, the stable semipolar phase appears around $m''=0$. This stable semipolar phase can be proposed as stable state by inducing the sixth order terms of the polarization. The phase transition from nonpolar to semipolar phase is of the first order, because two phases belonging to the different symmetry exist simultaneously at the transition point. When the parameter m'' is varied, the sequential phase transitions, from the antiferroelectric to the ferroelectric and or to the semipolar, and to the ferroelectric phase, which is similar to the case of RDP-ADP mixed crystal, are realized.

§2 Model and Results

Let us take the following free energy for the antiferroelectric phase transitions as in previuos papers[5-7]

$$a = (1+t)Q^2+tq^2-(m+m'+m'')Q^4-(m+m'-m'')q^4-2(3m-m')Q^2q^2+Q^6+q^6+15Q^2q^2(Q^2+q^2), \tag{1}$$

where Q and q are two order parameters defind as

$$Q=\frac{1}{\sqrt{2}}(P_a+P_b)$$
$$q=\frac{1}{\sqrt{2}}(-P_a+P_b), \tag{2}$$

P_a and P_b being sublattice polarizations, and t represents the temperature. The coefficients m, m', and m'' in (1) are the coefficients of the fourth order terms, which are related to the following fourth order dipolar terms, [5]

$$\left(\begin{array}{l} m \sim P_a^4+P_b^4 \\ m' \sim P_a^2+P_b^2 \\ m'' \sim P_aP_b(P_a^2+P_b^2) \end{array}\right). \tag{3}$$

These constants are assumed to be independent of temperatures, but may depend on the hydrostatic pressure, the uniaxial stress and the concentration of a mixed crystal.

From the equilibrium conditions

$$\partial a/\partial Q=\partial a/\partial q=0, \tag{4}$$

four stable phases are derived :

(1) Nonpolar : $Q=0,\ q=0,\ a_N=0,$

(2) Antipolar : $Q=0,\quad q^2=\frac{1}{3}\left\{(m+m'-m'')+\sqrt{(m+m'-m'')^2-3t}\right\}$

(3) *Polar* : $q\doteq 0,\ Q^2=\frac{1}{3}\left\{(m+m'+m'')+\sqrt{(m+m'+m'')^2-3(1+t)}\right\}$

(4) *Semipolar*: $Q\neq 0,\ q\neq 0.$

The stability condititions of these are that all the principal minors of the Hessian

$$|H_{Qq}| = \begin{vmatrix} \dfrac{\partial^2 a}{\partial Q^2} & \dfrac{\partial^2 a}{\partial Q\partial q} \\ \dfrac{\partial^2 a}{\partial q\partial Q} & \dfrac{\partial^2 a}{\partial q^2} \end{vmatrix} \tag{6}$$

is positve definite. The second order phase transition line is the locus of the Hessian:

$$|H_{Qq}| = 0. \tag{7}$$

The first order phase transition, however, is realized when the free energies of the different phases become identical. The transition temperatures from nonpolar phase to antipolar phase, and to the polar phase are given by equating the energies of these phases, that is, $a_{AP}=a_N=0$ and $a_P=a_N=0$, respectively. These transition temperatures t_{AP}^f and t_P^f are easily calculated as

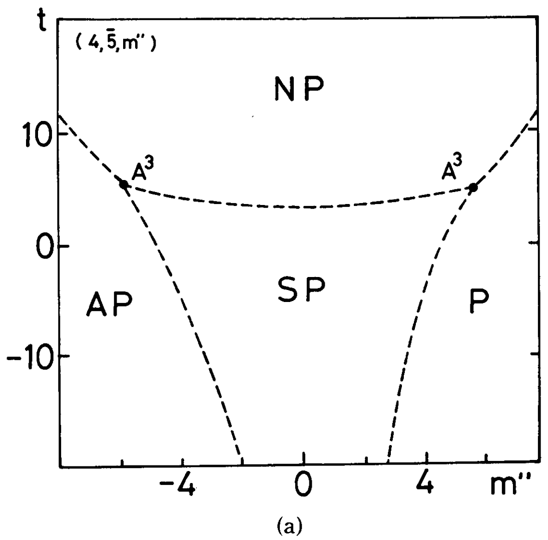
$$t_{AP}^f=\frac{1}{4}(m+m'-m'')^2 \tag{8}$$

and

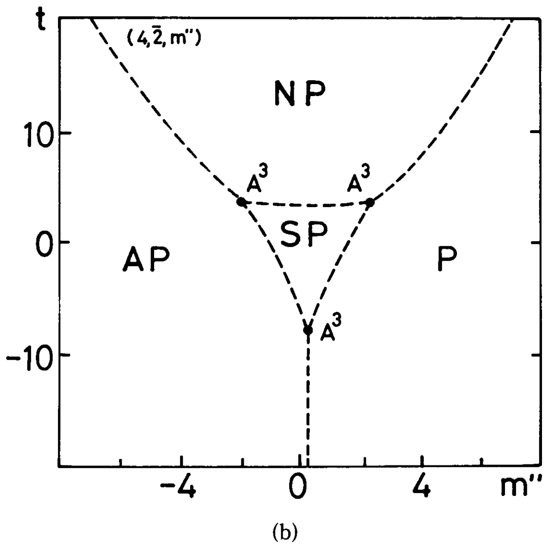
$$t_P^f=\frac{1}{4}(m+m'+m'')^2-1. \tag{9}$$

On the other hand, the second order transitions derived from (7) are given by $t_{AP}^s=0$ and $t_p^s=-1$, respectively. The coefficient of the second order terms vanishes at the temperature. The transition temperature from nonpolar to the semipolar phase is deduced from the tedious numerical calculations. The temperature of the transition from the antipolar to the polar phase is found by equating $a_{AP}=a_P$ as,

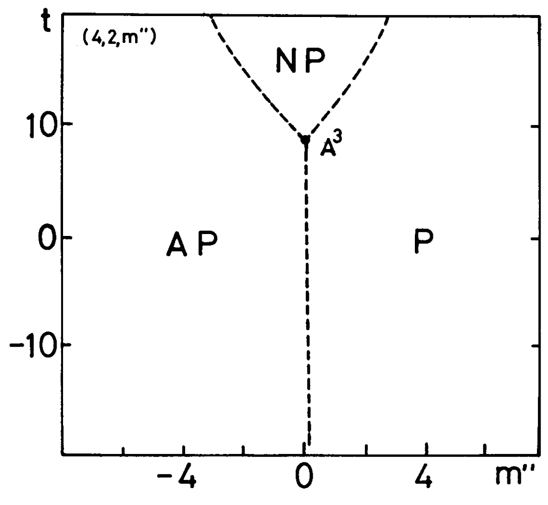
$$3(m+m'-m'')t-\frac{2}{3}(m+m'-m'')^3+2\left\{t-\frac{1}{3}(m+m'-m'')^2\right\}(m+m'-m'')^2-3t$$
$$=3(m+m'+m'')(1+t)-\frac{2}{3}(m+m'+m'')^3+2$$



(a)



(b)



(c)

Fig. 1 Calculated phase diagrams for the parameters (a) $(4, -5, m'')$ (b) $(4, -2, m'')$ and (c) $(4, 2, m'')$ Triple points are denoted by closed circles : A^3.

$$\left\{ 1+t-\frac{1}{3}(m+m'+m'')^2 \right\} (m+m'+m'')^2-3(1+t). \tag{10}$$

The stable semipolar phase is found by the solution under the equlibrium condition (4).
The dielectric susceptibility χ^{-1} are calculated by the equation

$$\chi^{-1}=\frac{\partial^2 a}{\partial Q^2}-\left(\frac{\partial^2 a}{\partial Q \partial q}\right)^2 \Big/ \frac{\partial^2 a}{\partial q^2} \tag{11}$$

§3 Phase Diagrams

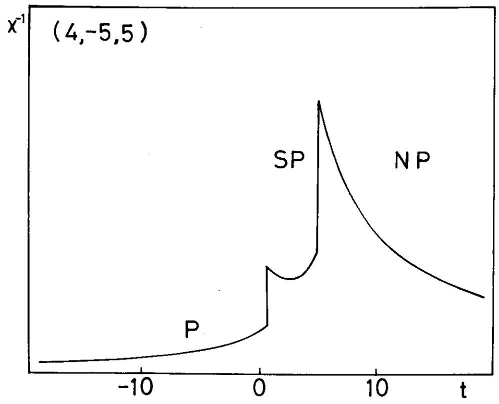
Figure 1 shows the $m''-t$ phase diagrams, where m and m' are fixed. In the case of $(4, -5, m'')$, where we denote the parameters as (m, m', m''), the semipolar phase appears at around $m''=0$. However, in the case of $(4, -2, m'')$, the semipolar phase are realized only in a small region, and at low temperature the semipolar phase change to antipolar or polar phase depending on m''. When the suitable parameter values of m'' is taken, the sequential phase transitions from the polar to the antipolar phase appear, which is the similar to the mixed crystal of RDP-ADP crystal[8-13]. Two or three triple points, which is denoted by A^3, occur at the temperature

$$t=\frac{1}{4}\left(\frac{1}{m''}-m''\right)^2 \tag{12}$$

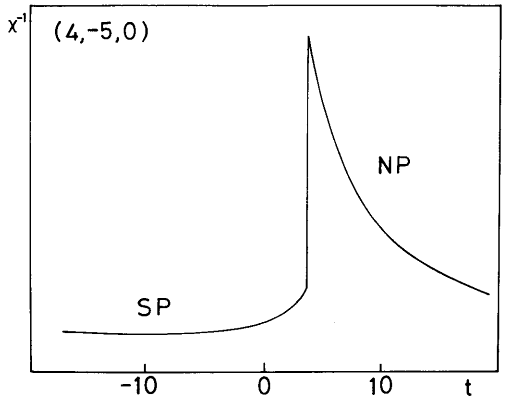
with the condition $m+m'=m''$, which is reduced by $t_{AP}{}^{f}=t_{P}{}^{f}$.

§4 Discussion

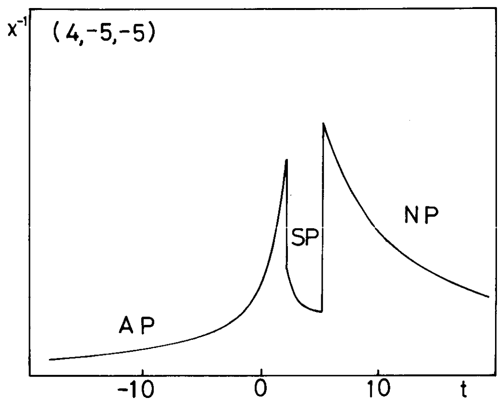
In the present paper, we have discussed the sequential phase transitions by changing the parameters of the fourth order term of kittel's type free energy functions written by two-sublattice polarizations. The pressure-temperature



(a) (4, −5,5)



(b) (4, −5,0)



(c) (4, −5, − 5)

Fig. 2 Calculated temperature dependences of the dielectric susceptibility in arbitrary unit.

phase diagram and the concentration temperature phase diagram in the mixed crystal are useful in the practical purpose for the study of the ferroelectrics.

The calculated phase diagram shows the semipolar phase around $m''=0$. The temperature dependence of the dielectric susceptivility χ^{-1} is different from the data observed in RDP-ADP crystal (Fig. 2).

Proposed model calculation for the pressure dependence of $PbZrO_3$ and the concentration dependence of the solid solution $Pb(Fe_{2/3}W_{1/3})O_3-Pb(M_{1/2}W_{1/2})O_3$ (M=Mn, Co, Ni) by Uchino and Nomura[1] showed the straight transition lines, however, our results show the curved transition lines, which are more satisfactory for the solid solutions of $PbZrO_3$ + 5 % Nb_2O_5 crystal as shown by Benguigui[4]. This may be reduced from the fact that this theory contains the term $P_a^6+P_b^6$ · In the actual case of RDP-ADP mixed crystal, the transition line from nonpolar to antipolar, or to the polar phase is curved one.

In order to analyse the dipolar-glass phase transition of the RDP-ADP crystal, we have to discuss the model Hamiltonian concerning the proton configurations tached to the PO_4 tertahedron with the ice-rule. Although Matushita and Matsubara showed the phase diagram for the RDP-ADP crystal[11,12], the temperature dependence of the dielectric constant is not given. Recently we also discussed the phase diagrams of the RDP-ADP crystals with the consideration of the proton configurations. [13]

Transition line between polar and antipolar intersect almost 180° at the triple point. The well known 180° rule at the triple point is expressed in the form : no stable phase may occupy more than 180° of angle at the triple point.[14,15] In multicomponent systems, for the case when two densities are used as independent variables, 180° rule takes on a stronger form which is known as Scheinemaker's rule. In our case, the phase diagram is depicted in the $m''-t$ plane, where m "is not a thermodynamically proper independent field variable, however, the 180° rule is satisfied. Our model free energy (1) has a convexity property required by the second law of thermodynamics, then it seems to be the reason that the 180° rule is satisfied.

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