

Phenomenological Treatment of Antiferroelectric Transition under Hydrostatic Pressure

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By applying Kittel's antiferroelectric polarizations (P_a and P_b) and Cross' ferroelectric polarization P_m and antiferroelectric polarization P_n to the free energy function for ferroelectrics under hydrostatic pressure, the Gibbs function for antiferroelectrics under hydrostatic pressure is given in terms of the pressure, polarization and electric field. On the basis of this energy function, dielectric properties such as the pressure dependence of permittivity or spontaneous polarization and the electric field dependence of permittivity are clearly explained, and the so-called double hysteresis loop under hydrostatic pressure is explained fairly well for antiferroelectrics of the second and the first order transitions. Moreover, these analyses are confirmed to be appropriate by comparing with the experimental results for antiferroelectric Pb_2MgWO_6 , etc.

§1. Introduction

Kittel reported the phenomenological analysis for antiferroelectrics by applying a sublattice model¹⁾ to Devonshire's theory.²⁾ This sort of analyses is generally not for pressure dependence, but for temperature dependence of dielectric properties.

In this paper, the phenomenological analysis for antiferroelectrics under hydrostatic pressure is described. First, the free energy function for antiferroelectrics under hydrostatic pressure is expressed by introducing terms of pressure into the Gibbs free energy function and by transforming the Kittel's two spontaneous polarizations [P_a , P_b] of sublattices into the Cross' ferroelectric polarization P_m and antiferroelectric polarization P_n . Next, some dielectric characteristics such as pressure dependence of the permittivity or the spontaneous polarization and the electric field dependence of the permittivity are related for the first and the second order transition, and the double hysteresis loop between the electric field and the polarization is fairly elucidated under hydrostatic pressure. Finally, the above analyses are compared with the experimental results for antiferroelectric Pb_2MgWO_6 ,³⁾ etc. to confirm the appropriateness.

§2. Phenomenological Analysis

When the hydrostatic pressure is applied to antiferroelectrics whose state is non-piezoelectric in the paraelectric phase, the Gibbs func-

tion taken to the sixth order in polarization is expressed on the basis of the free energy function for ferroelectrics under hydrostatic pressure⁴⁾ as follows;

$$\begin{aligned}
 F(p, P_a, P_b) &= \frac{1}{2}cp^2 + \frac{1}{2}(u+gp)(P_a^2 + P_b^2) + fP_aP_b \\
 &\quad + \zeta(P_a^4 + P_b^4) + \zeta(P_a^6 + P_b^6) - E(P_a + P_b),
 \end{aligned}
 \tag{1}$$

where expansion coefficients c , u , g , f , ζ and ζ are phenomenological constants being dependent on temperature, and E is the electric field in antiferroelectrics.

According to Cross, non-observable polarizations P_a and P_b are transformed into the ferroelectric polarization $P_m = P_a + P_b$ (observable) and the antiferroelectric polarization $P_n = P_a - P_b$ (non-observable),⁵⁾ so eq. (1) yields

$$\begin{aligned}
 F &= \frac{1}{2}cp^2 + \frac{1}{4}\{(u+gp)(P_m^2 + P_n^2) + f(P_m^2 - P_n^2)\} \\
 &\quad + \frac{1}{8}\zeta(P_m^4 + P_n^4 + 6P_m^2P_n^2) \\
 &\quad + \frac{1}{32}\zeta(P_m^6 + P_n^6 + 15P_m^4P_n^2 + 15P_m^2P_n^4) \\
 &\quad - EP_m.
 \end{aligned}
 \tag{2}$$

In order to minimize the free energy F , the following conditions must be satisfied;

$$\partial F/\partial P_m = 0 \quad (3.a), \quad \partial F/\partial P_n = 0 \quad (3.b)$$

$$\begin{aligned}
 \partial^2 F/\partial P_m^2 > 0, \quad \partial^2 F/\partial P_n^2 > 0 \quad \text{and} \\
 (\partial^2 F/\partial P_m^2)(\partial^2 F/\partial P_n^2) - (\partial^2 F/\partial P_m \partial P_n)^2 > 0.
 \end{aligned}
 \tag{3.c}$$

In general, the permittivity $\varepsilon = \varepsilon_0 \varepsilon_r = \kappa + \varepsilon_0$, where ε_0 is the vacuum permittivity, ε_r is the relative permittivity and κ is the dielectric susceptibility. In case of $\varepsilon \gg \varepsilon_0$ seen in ordinary antiferroelectrics, $\varepsilon \doteq \kappa \equiv \partial P_m / \partial E$.

By putting E in eq. (3.a) into this relation, the reciprocal of the permittivity is

$$\frac{1}{\varepsilon} = \frac{1}{2}(u + gp + f) + \frac{3\xi}{2}(P_m^2 + P_n^2) + \frac{15\xi}{16}(P_m^4 + 6P_m^2 P_n^2 + P_n^4). \quad (4)$$

2.1 Paraelectric phase

Since $P_a = 0$ and $P_b = 0$ in this phase, $P_m = P_n = 0$.

By putting the above relations into P_m and P_n in eq. (4), the reciprocal of the permittivity is

$$\frac{1}{\varepsilon} = (u + gp + f)/2. \quad (5)$$

This equation shows that the reciprocal of the permittivity is proportional to pressure at a given temperature. From eq. (5), the characteristic pressure $p_0 = [p]_{1/\varepsilon=0}$ is

$$p_0 = -(u + f)/g. \quad (6)$$

2.2 Antiferroelectric phase

2.2.1 Second order transition

In this case, the Gibbs free energy is given by neglecting in eq. (2) terms in polarization of order higher than 4, and by putting zero into ξ in eqs. (1)–(4).

(i) Under no bias field; Since $P_a = -P_b$ under $E = 0$, $P_m = 0$ and by putting the above relations into eq. (3.b),

$$P_n^2 = (f - u - gp)/\xi. \quad (7)$$

The eq. (7) shows that the square of the spontaneous polarization of a sublattice is proportional to pressure.

By putting P_n^2 given by eq. (7) into P_n^2 in eq. (4), the reciprocal of the permittivity is

$$\frac{1}{\varepsilon} = 2f - u - gp. \quad (8)$$

The eq. (8) shows that the reciprocal of the permittivity is a linear function of pressure with the slope of $-g$ at a given temperature, and its slope is, in comparison with eq. (5), twice of the slope in the paraelectric phase.

At the transition pressure p_c , the following re-

lations must be satisfied; $[F]_{P_m=P_n=0, E=0} = [F]_{P_m=P_n=0, E=0}$ and $[\partial F / \partial P_n]_{P_m=P_n=0, E=0} = 0$.

By putting eq. (2) into the above relations, p_c is

$$p_c = (f - u)/g. \quad (9)$$

By putting p_c given by eq. (9) into eqs. (5) and (8), both the reciprocal of the permittivity in the paraelectric phase and that in the antiferroelectric phase are the same form $1/\varepsilon = f > 0$ at $p = p_c$. It is interesting fact that the permittivity for antiferroelectrics of the second order transition is a finite value $1/f$ at p_c while the permittivity for ferroelectrics of the second order transition is infinite value at p_c .⁴⁾

The schematic pressure dependences of P_n^2 and $1/\varepsilon$ for the second order transition are shown in Fig. 1(a) and (b). Figure 1(a) corresponds to the transition from the paraelectric phase to the antiferroelectric phase with increasing pressure, and the relation $f - u - gp > 0$ holds good by combining the conditions [$g < 0$ and $p > p_c$] as seen in Fig. 1(a)] and eq. (9). Figure 1(b) corresponds to the transition from the antiferroelectric phase to the paraelectric phase, and the same relation holds good by combining the conditions [$g > 0$ and $p < p_c$] as seen in Fig. 1(b)] and eq. (9).

By putting the above relation into eq. (7), $\xi > 0$ for antiferroelectrics of the second order transition.

(ii) Under bias field; In this case, $P_n \neq 0$ and $P_m \neq 0$ under the applied electric field E . Then the stable region for P_m is found by substituting P_n^2 in eq. (3.b) for P_n^2 in eq. (3.c) and by using conditions [$f > 0$ and $\xi > 0$] as follows;

$$P_m^2 < (2f - u - gp)/12\xi \equiv P_{ma}^2, \quad (10)$$

where P_{ma} is a limiting value of P_m .

The free energy F and the electric field E as a

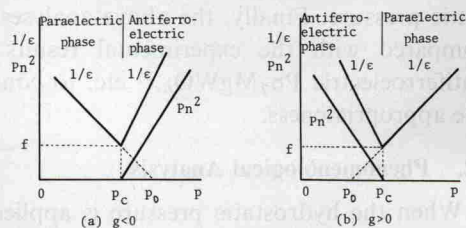


Fig. 1. Second order transition with pressure (no applied field).