

function of P_m in the antiferroelectric phase are given by substituting P_n^2 in eq. (3.b) for P_n^2 in eq. (2) and E in eq. (3.a) as follows;

$$W \equiv F - cp^2/2 = -(f - u - gp)^2/8\xi + (2f - u - gp)P_m^2/2 - \xi P_m^4 - EP_m \quad (11)$$

$$E = (2f - u - gp - 4\xi P_m^2)P_m. \quad (12)$$

By putting eq. (10) into P_m in eq. (12), the electric field at P_{ma} (or critical field E_a) is

$$E_a = (2f - u - gp)^{3/2}/3\sqrt{3\xi}. \quad (13)$$

This critical field E_a is also a maximum value of E shown by eq. (12).

The electric field dependence of the permittivity at a given pressure is obtained on eliminating P_m and P_n from eqs. (3.b), (4) and (12) as follows;

$$E = (2f - u - gp - 4/\epsilon)\sqrt{(2f - u - gp - 1/\epsilon)/27\xi} \quad (14)$$

(iii) Under strong bias field; At the moment E exceeded a critical value E_a , the state changes from the antiferroelectric phase to the induced phase. In the induced phase, $P_m \neq 0$ and $P_n = 0$, and the stable region for P_m is obtained by applying the conditions [$f > 0$ and $\xi > 0$] into eq. (3.c) as follows;

$$P_m^2 > (f - u - gp)/3\xi \equiv P_{mi}^2, \quad (15)$$

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

From eqs. (2) and (3.a), the free energy and the electric field in this phase are

$$W \equiv F - cp^2/2 = (u + gp + f)P_m^2/4 + \xi P_m^4/8 - EP_m \quad (16)$$

$$E = (u + gp + f + \xi P_m^2)P_m/2. \quad (17)$$

The electric field at P_{mi} (or critical field E_i) is obtained by putting eq. (15) into P_m in eq. (17) as follows;

$$E_i = (2f + u + gp)\sqrt{f - u - gp}/3\sqrt{3\xi}. \quad (18)$$

The point (E_i, P_{mi}) is also a point of intersection for eqs. (12) and (17).

By elimination of P_m from eqs. (4) and (17), the electric field dependence of the permittivity at a given pressure is

$$E = (u + gp + f + 1/\epsilon)\sqrt{(2/\epsilon - u - gp - f)/27\xi}. \quad (19)$$

In order to show numerically the various characteristics for antiferroelectrics of the second order transition, we assume constants to be $u = 8 \times 10^8$ m/F, $g = -4 \times 10^7$ m/F·kbar, $f = 4 \times 10^8$ m/F and $\xi = 8 \times 10^{12}$ m⁵/F·C². Figure 2 shows curves calculated by putting these values into eqs. (12), (17), (11) and (16). The curves ① and ② are for the antiferroelectric phase, and ③ and ④ are for the induced phase. The points o, q, q', r, s and s', etc. on the [energy vs. polarization] curves ① and ② correspond to the points O, Q, Q', R, S and S', etc. on the [field vs. polarization] curves ③ and ④, respectively. The state changes suddenly from the paraelectric phase to the antiferroelectric phase with increasing pressure at $p_c = 10$ kbar, and this phase transition belongs to the type(a) of Fig. 1. The region between the point O(O, O) and Q(E_a, P_{ma}) on the curve ① shows the stable state as seen by eq. (10), while the region between O and S(E_i, P_{mi}) on the curve ③ shows the unstable state as seen by eq. (15). When the electric field E increases

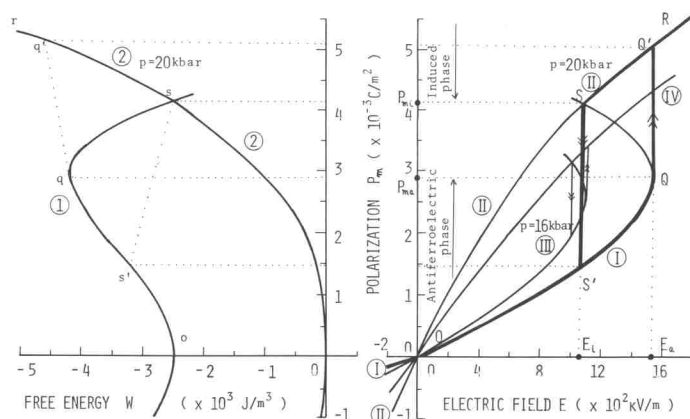


Fig. 2. Double hysteresis loops between electric field and polarization for antiferroelectrics of the second order transition.

along the curve ①, the polarization P_m jumps up from the point Q to the point Q'. Such a phase transition is explained to take place by the reason that the free energy at the point q' is lower than the energy at the point q ($E = E_a$ at both Q and Q').

When E decreases along ②, P_m drops down from the point S to S', and the transition from the induced phase to the antiferroelectric phase takes place here.

Figure 2 is called "double hysteresis loop", and the critical field E_a seen in it increases with increasing pressure by comparing the curve of 20 kbar with that of 16 kbar.

Figure 3(a) shows the pressure dependences of the relative permittivity ϵ_r under various electric fields in the paraelectric phase calculated from eq. (5), in the antiferroelectric phase calculated from eqs. (8) and (14) and in the induced phase calculated from eq. (19), and shows the pressure dependence of the antiferroelectric polarization calculated from eq. (7). Figure 3(b) shows the electric field dependences of ϵ_r under various pressures in the antiferroelectric phase calculated from eq. (14), and in the induced phase calculated from eq. (19). It is found from Fig. 3(a) that ϵ_r in the antiferroelectric phase decreases with increasing pressure and its decreasing rate increases with increasing E . Moreover, it is found from Fig. 3(b) that ϵ_r in the induced phase decreases with increasing E , while ϵ_r in the antiferroelectric phase increases with increasing E , and that the pressure contributes to expand the region of the antiferroelectric phase.

2.2.2 First order transition

The Gibbs free energy is given by neglecting terms in polarization of order higher than 6, so eq. (2) shows the free energy for the first order transition.

(i) Under no bias field; In this case, $P_m = 0$ under $E = 0$, and the following relations must be satisfied at the transition pressure p_c ;

$$[F]_{P_m=P_n=0, E=0} = [F]_{P_m=0, E=0}$$

$$\text{and } [\partial F / \partial P_n]_{P_m=0, E=0} = 0.$$

By putting eq. (2) into the above relations, the square of antiferroelectric polarization at p_c is

$$P_{nc}^2 = -2\xi/\zeta. \quad (20)$$

Now, eq. (2) shows that, if $\zeta < 0$, the free energy of antiferroelectrics gets lower with increasing polarization and the state must be the most stable at infinite polarization. This is unreasonable, so $\zeta > 0$. By applying this condition into eq. (20), $\xi < 0$.

The conditions [$\zeta > 0$ and $\xi < 0$] are important for the first order transition. The transition pressure is obtained by putting P_{nc}^2 given by eq. (20) into P_n^2 in the relation $[\partial F / \partial P_n]_{P_m=0, E=0} = 0$ and by using eq. (6) as follows;

$$p_c = (f - u + h/2)/g = p_0 + 2f/g + h/2g, \quad (21)$$

where $h = \xi^2/\zeta$.

by solving eq. (3.b) for P_n^2 ,

$$P_n^2 = -(4\xi/3\zeta)\{1 + \sqrt{1 + 3(f - u - gp)/2h}\}. \quad (22)$$

By putting P_n^2 given by eq. (22) into P_n^2 in eq.

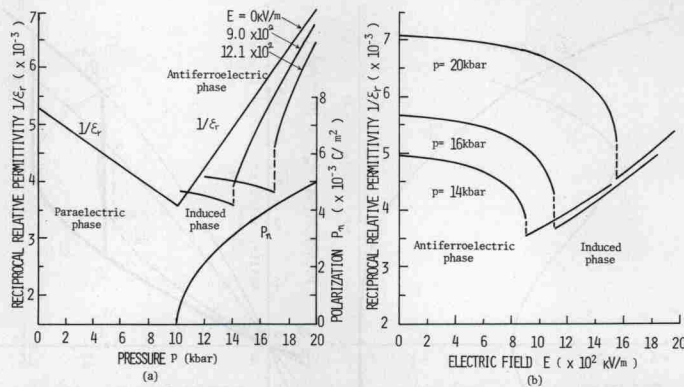


Fig. 3. (a) Pressure dependence of the reciprocal of the relative permittivity and spontaneous polarization, and (b) electric field dependence of the reciprocal of the relative permittivity for antiferroelectrics of the second order transition.