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**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;

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

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

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

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

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

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

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

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 ζ 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

$$1/\varepsilon = 2f - u - gp. \quad (8)$$

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

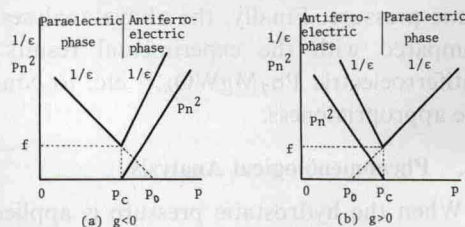


Fig. 1. Second order transition with pressure (no applied field).

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

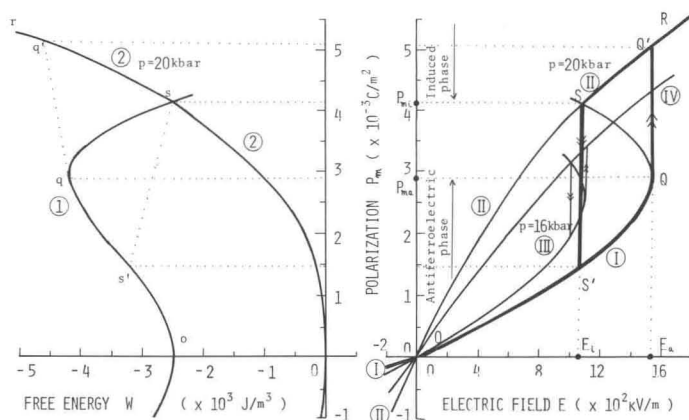


Fig. 2. Double hysteresis loops between electric field and polarization for antiferroelectrics of the second order transition.

along the curve (I), 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 (II), 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.

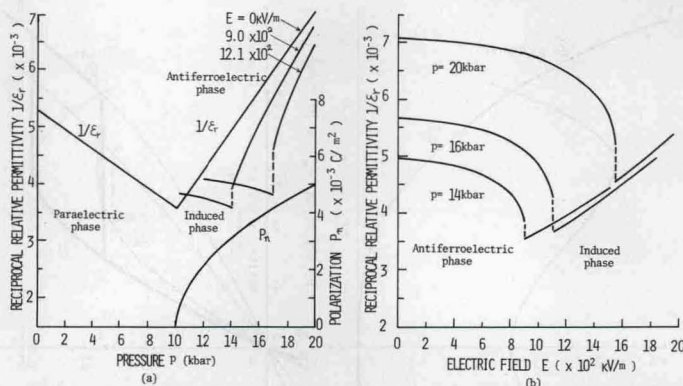


Fig. 3. (a) Pressure dependence of the reciprocal of the relative permittivity and spontaneous polarization, and (b) electric field dependence of the reciprocal of the relative permittivity for antiferroelectrics of the second order transition.

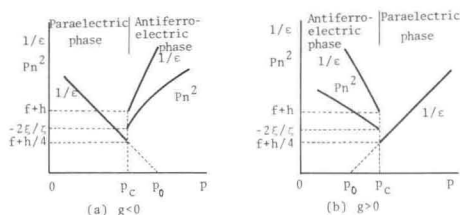


Fig. 4. First order transition with pressure (no applied field).

(4), the reciprocal of the permittivity is

$$\frac{1}{\epsilon} = 3f - 2(u + gp) + (4h/3) \left\{ 1 + \sqrt{1 + 3(f - u - gp)/2h} \right\}. \quad (23)$$

The permittivity at p_c in the paraelectric phase ϵ_{cp} and the permittivity at p_c in the antiferroelectric phase ϵ_{ca} are obtained by putting p_c given by eq. (21) into p in eqs. (5) and (23) respectively, so the ratio K of ϵ_{cp} to ϵ_{ca} is

$$K = \epsilon_{cp}/\epsilon_{ca} = (1 + h/f)/(1 + h/4f). \quad (24)$$

The schematic pressure dependences of $1/\epsilon$ and P_n^2 for the first order transition are shown in Fig. 4(a) and (b). Figure 4(a) corresponds to the transition from the paraelectric phase to the antiferroelectric phase with increasing pressure, and Fig. 4(b) corresponds to the transition from the antiferroelectric phase to the paraelectric phase.

(ii) Under bias field; In this case, $P_m \neq 0$ and $P_n \neq 0$ under the electric field E . Then, relations $[F$ vs. $P_m]$, $[E$ vs. $P_m]$ and $[1/\epsilon$ vs. $E]$ are obtained analytically or numerically by putting P_n^2 in eq. (3.b) into P_n^2 in eqs. (2)–(4).

(iii) Under strong bias field; As in the case of the second order transition, at the moment E exceeded a critical value E_a , the state changes from the antiferroelectric phase to the induced phase. In this phase, $P_m \neq 0$ and $P_n = 0$.

So, from eqs. (3.a), (4) and (2), the relations $[E$ vs. $P_m]$, $[E$ vs. $\epsilon]$ and $[F$ vs. $P_m]$ are

$$E = \frac{1}{2}(u + gp + f + \xi P_m^2 + 3\zeta P_m^4/8)P_m \quad (25)$$

$$E = \frac{1}{5} \left[2(u + gp + f) + \frac{1}{\epsilon} - \frac{4}{5}h \left\{ 1 + \sqrt{1 - 5 \left(u + gp + f - \frac{2}{\epsilon} \right) / 6h} \right\} \right] \times \sqrt{-\frac{4\xi}{5\zeta} \left\{ 1 + \sqrt{1 - 5 \left(u + gp + f - \frac{2}{\epsilon} \right) / 6h} \right\}} \quad (26)$$

$$W \equiv F - \frac{1}{2}cp^2 = -\frac{1}{4} \left(u + gp + f + \frac{3}{2}\xi P_m^2 + \frac{5}{8}\zeta P_m^4 \right) P_m^2. \quad (27)$$

Analytical results for antiferroelectrics of the first order transition obtained numerically by putting $u = 9.48 \times 10^8$ m/F, $g = -5.62 \times 10^7$ m/F·kbar, $f = 2.08 \times 10^8$ m/F, $\xi = -3.31 \times 10^{11}$ m⁵/F·C² and $\zeta = 2.65 \times 10^{14}$ m⁹/F·C⁴ into eqs. (22), (23) and (25), etc. are as follows; (1) Double hysteresis loops like Fig. 2 are obtained between the electric field and the polarization under various pressures ($p = 13, 15$ and 18 kbar). The critical field E_a seen in a loop increases with increasing pressure at a given temperature, while E_a increases with decreasing temperature at atmospheric pressure.⁷⁾ (2) The electric field dependence of the relative permittivity ϵ_r under various pressures ($p = 13, 15$ and 18 kbar) is similar to Fig. 3(b), and is, in the antiferroelectric phase, qualitatively compatible with Okada's experimental result at atmospheric pressure.⁸⁾

§3. Application of the Analysis to the Experimental Result

This analysis was applied to the experimental result for polycrystalline Pb_2MgWO_6 belonging to the type of Fig. 4(b). Solid lines in Fig. 5 show the pressure dependences of the reciprocal of the relative permittivity $1/\epsilon_r$ under various temperatures measured by Polandov,³⁾ and $1/\epsilon_r$ increases linearly with pressure in the paraelectric phase (above $p_c = 1.14$ kbar). From

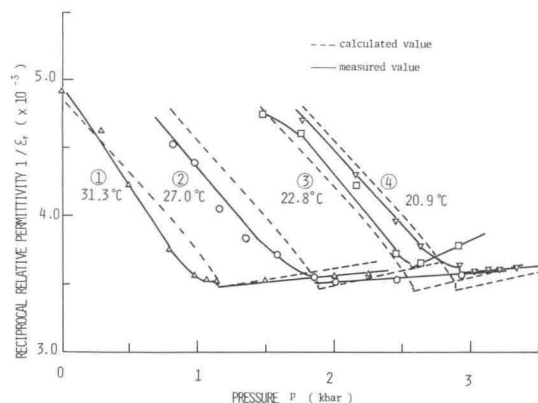


Fig. 5. Application of the analytical result to the experimental result for antiferroelectric Pb_2MgWO_6 belonging to the first order transition (after Polandov).

the curve ① in Fig. 5, the slope of $1/\epsilon$ to p in the paraelectric phase $g=5.32 \times 10^7$ m/F·kbar, the characteristic pressure $p_0=-13.7$ kbar and $K=3.52/3.48=1.01$ are found. By substituting this value of K for eq. (24), $h/f=0.016$. By substituting the above values for eq. (21), $f=3.93 \times 10^8$ m/F and $h=6.29 \times 10^6$ m/F.

According to Polandov, the temperature (T) dependence of p_c is $p_c=\alpha-\beta T$, where $\alpha=6.34$ kbar and $\beta=1.66 \times 10^{-1}$ kbar/°C. By elimination of p_c from this equation and eq. (21), and by substitution of $C(T-T_1)$ for u in eq. (21) (because Curie-Weiss' law is satisfied), $C=8.80 \times 10^6$ m/F·°C and $T_1=-6.32$ °C.

The dotted lines in Fig. 5 show the pressure dependences of $1/\epsilon_r$ under various temperatures in the paraelectric phase and the antiferroelectric phase calculated by putting all the estimated constants into eqs. (5) and (23), and agree approximately with the solid lines which show measured values.

§4. Conclusion

By applying the Kittel's antiferroelectric model and the Cross' polarizations to the free energy function for ferroelectrics under hydrostatic pressure, the Gibbs function for antiferroelectrics under hydrostatic pressure was given in terms of pressure, polarization and electric field. And antiferroelectric phenomena such

as the Curie-Weiss' law on pressure in the paraelectric phase, pressure dependence of the permittivity or the spontaneous polarization in the antiferroelectric phase, electric field dependence of the permittivity and double hysteresis loops under various pressures could be successfully explained on the basis of this energy function.

The analytical results were applied to the experimental results not only for Pb_2MgWO_6 , but also for PbZrO_3 ⁹⁾ reported by Samara and $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ reported recently by authors,⁶⁾ and were confirmed to be useful to explain antiferroelectric phenomena under hydrostatic pressure.

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Fig. 5. Pressure dependence of the inverse dielectric constant $1/\epsilon_r$ for the antiferroelectric phase of Pb_2MgWO_6 . The solid lines show measured values and the dotted lines show calculated values.