$$E = \frac{1}{3} \left(\frac{1}{\epsilon} + \frac{2}{\epsilon_2} \right) \left\{ \frac{1}{3\xi} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_2} \right) \right\}^{\frac{1}{2}} \tag{15}$$

Here

$$1/\epsilon_2 = u + gp = g(p - p_0) \tag{16}$$

$1/\epsilon_2$ is constant under the given temperature & pressure. The eq. (15) indicates the electric field dependence of the permittivity in ferroelectric phase under constant pressure, and it is found that the permittivity decreases with increasing electric field. In the special case, the permittivity at no electric field is expressed by putting zero into E of eq. (15) and by using eq. (16) as follows;

$$\epsilon = - \epsilon_2/2 = 1/2g(p_0 - p)$$

Therefore, the permittivity at no electric field depends on pressure & coefficient g.

2.2.2   First order transition

When the following two conditions are satisfied in the case of the first order transition, the spontaneous polarization is present at the transition pressure(p_c).

(I)   The free energy of ferroelectric phase must be equal to that of paraelectric phase at the transition pressure(p_c). Accordingly, from eq. (2), the relation

$$\left[\; F(p, P) \; \right]_{\substack{p=p_c \\ P=P_s=0}} = \left[\; F(p, P) \; \right]_{\substack{p=p_c \\ P=P_s}}$$

must be satisfied. That is,

$$u + gp_c + \frac{1}{2} \xi P_s^2 + \frac{1}{3} \zeta P_s^4 = 0 \tag{17}$$

holds good.

(II)   The free energy of ferroelectric phase must have the minimized value with polarization. Accordingly, from eq. (2), the relation

$$\left[\partial F/\partial P \right]_{\substack{p=p_c \\ P=P_s}} = 0$$

must be satisfied. That is,

$$u + gp_c + \xi P_s^2 + \zeta P_s^4 = 0 \tag{18}$$

holds good. Combining eq. (17) and eq. (18), and eliminating ($u + gp_c$), the square of the spontaneous polarization at the transition pressure is expressed as follows;

$$P_s^2 = -3\xi/4\zeta > 0, \quad \text{therefore} \ \xi\zeta < 0 \tag{19}$$

On the other hand, the spontaneous polarization in paraelectric phase does not exist. Hence, the spontaneous polarization changes discontinuously at the transition pressure. This is the character of the first order transition. The following expression is obtained by putting the P_s^2 of eq. (19) into that of eq. (17);

$$p_c = p_0 + 3\xi^2/ 16g\zeta \tag{20}$$

Here, the p_0 is given by $p_0 = -u/g > 0$, and p_c is the transition pressure as mentioned above.

Schematic pressure variation of Ps & $1/\epsilon$ for the first order transition is shown in Fig. 2.

Fig. 2(a) corresponds to the transition from paraelectric phase to ferroelectric phase at p_c with increasing pressure, and Fig. 2(b) corresponds to the transition from ferroelectric phase to paraelectric phase. In Fig. 2(a), the following conditions exist; $p_0 > p_c$, $g < 0$ from paraelectric phase and $u > 0$ because of $p_0 = -u/g > 0$. By putting these relations into eq. (20), the relation $\zeta > 0$ is obtained and then $\xi < 0$ is obtained from eq. (19). In Fig. 2(b), the following conditions exist; $p_c > p_0$, $g > 0$ from paraelectric phase and $u < 0$ because of $p_0 = -u/g > 0$ (corresponding to, for example, $BaTiO_3$). By putting these relations into eq. (20), the relation $\zeta > 0$ is obtained and then $\xi < 0$ is obtained from eq. (19), too. Therefore, in the case of the first order transition, these relations $\zeta > 0$ & $\xi < 0$ hold good.

Let's obtain the spontaneous polarization in ferroelectric phase under above conditions. The square of the spontaneous polarization is obtained from eq. (8) & $P_s \neq 0$ as follows;

$$P_s^2 = -\frac{\xi}{2\zeta} \left\{ 1 + \sqrt{1 - \frac{4\zeta}{\xi^2}(u + gp)} \right\} \tag{21}$$
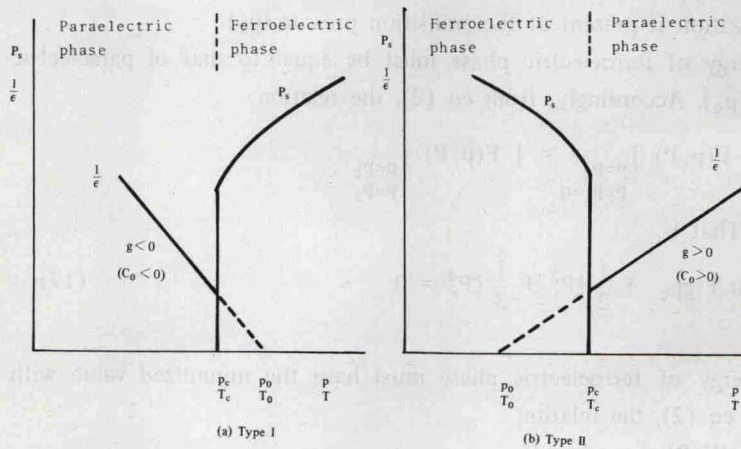

Fig. 2.   Schematic temperature & pressure variations (type I, type II) of the spontaneous polarization & the reciprocal permittivity for the first order transition.

The eq. (21) shows the fact that the square of the spontaneous polarization varies according to irrational function with pressure. The reciprocal permittivity is obtained by putting P_s^2 of eq. (21) into that of eq. (4);

$$\frac{1}{\epsilon} = -4(u + gp) + \frac{\xi^2}{\zeta}\left\{ 1 + \sqrt{1 - \frac{4\zeta}{\xi^2}(u + gp)} \right\} \tag{22}$$

The value of the reciprocal permittivity $1/\epsilon_{cf}$ in ferroelectric phase at the transition pressure(p_c) is expressed by putting p_c of eq. (20) into p of eq. (22);

$$1/\epsilon_{cf} = 3\xi^2 / 4\zeta$$

The value of the reciprocal permittivity $1/\epsilon_{cp}$ in paraelectric phase at the transition pressure is obtained by putting p_c of eq. (20) into p of eq. (5);