AN EXPLANATION OF ANOMALOUS OPTICAL BEHAVIOUR OF THE IMPROPER FERROELECTRIC $Gd_2(MoO_4)_3$

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Typical features of the electric field dependences of an order parameter and of polarization in improper ferroelectrics are discussed. The anomalous optical hysteresis observed in the improper ferroelectric $Gd_2(MoO_4)_3$ is shown to be explained by them.

A ferroelectric phase does not necessarily result from a phase transition having the polarization as order parameter (Indenbom[1]). Boracites [2] are an example of such a ferroelectric, KDP and GMO are others. Dvořák [3-5] has called such ferroelectric improper and has given a phenomenological theory for them. Although correct in principle, it still does not reveal some of the peculiar features of these crystals. One of the authors (J. K.) [6] has therefore proposed a modification that permits a classification of the improper ferroelectrics according to the strength of the coupling between the polarization and the order parameter and explains the anomalous dielectric and electro-mechanical properties of some improper ferroelectrics. Here we wish to show that the unusual optical behaviour of GMO, found recently by Nakamura and Kumada [7], can be explained bt the same theory.

For our present purposes the following approximation to the free energy of the crystal will be sufficient

$$A = \tfrac{1}{2}B(T-T_\theta)\theta_3^2 + \tfrac{1}{4}\gamma\theta_3^4 + \tfrac{1}{2}\omega P_3^2 + \tfrac{1}{2}s_{11}(X_1^2+X_2^2) - \tfrac{1}{2}b_{31}(X_1-X_2)P_3 - Q_{31}(X_1+X_2)P_3^2 - \tfrac{1}{2}h_{31}(X_1-X_2)\theta_3 - R_{31}(X_1+X_2)\theta_3^2 + f\theta_3 P_3 .$$

The temperature-dependent order parameter θ_3 is coupled to the stresses X_1 and X_2 and, by a negative constant f, to the polarization; ω, the reciprocal dielectric permittivity, and γ are positive, and the transition is of second order. The equilibrium conditions for the machanically free crystal are

$$E_3 = f\theta_3 + \omega P_3, \qquad \theta = \beta(T-T_\theta) + \gamma\theta_3^3 + fP_3 .$$

These equations have non-zero spontaneous solutions θ_S, P_S if $T < T_0 = T_\theta + (f^2/\omega\beta)$.

The characteristic features of an improper ferroelectric depend directly on the magnitude of f/ω. For small values of f/ω, peculiar properties should be observed; boracites and GMO are in this case. Of course, $P_S \ll \theta_S$, and also the θ- and P- permittivities in weak electric fields

$$\eta_\theta = -\frac{f}{\omega}\frac{1}{\beta(T-T_0)}, \qquad \eta_P = \frac{1}{\omega} + \frac{f^2}{\omega^2}\frac{1}{\beta(T-T_0)}$$

have sharp peaks in the close vicinity of T_0. The E-dependence of θ_3 and P_3 are given in fig. 1.

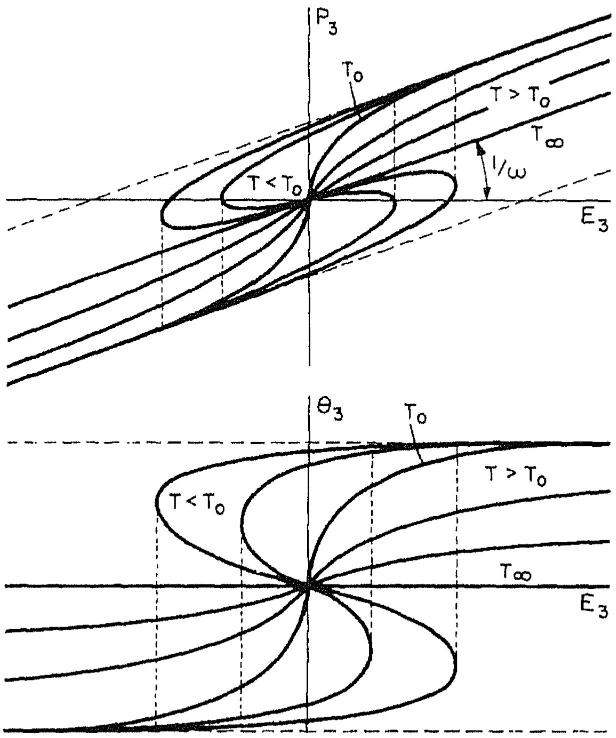

Fig. 1. Hysteresis of θ_3 and of P_3.

The θ_3 - E_3 hysteresis loop is square, with field independent saturation; the P_3 - E_3 loop is not square and the saturation line has a positive slope: $1/\omega$. Above T_0, the field dependence of θ_3 disappears immediately, while $P_3 = (1/\omega)E_3$. This different field dependence must manifest itself in an unusual behaviour of all physical properties that can be expressed as a difference of terms depending on θ_3 and terms depending on P_3. A typical example is the temperature dependence of pure shear in Fe-I-boracite [8]. The birefringence of GMO is another example.

According to Nakamura et al., the spontaneous birefringence Δn^{S}_{xy} perpendicular to the polar axis decreases with an increase of E_3 (the direction of P_S being the + direction). Now

$$\Delta n_{xy} = n_o^3\{(r'_{13} + b_{31}\ \Pi_{44})P_3 + (u'_{13} + h_{31}\ \Pi_{44})\theta_3\} = \Delta n_P + \Delta n_\theta \ .$$

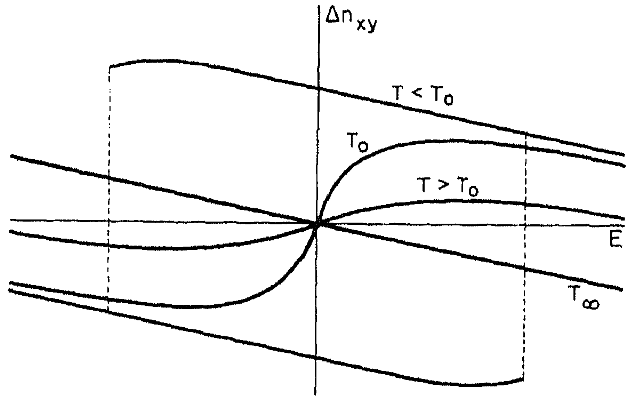

Fig. 2. Hysteresis of Δn_{xy}.

Here n_0^3 is the ordinary refractive index, r'_{13} is an electro-optic coefficient of the clamped crystal, u'_{13} the corresponding coefficient for θ_3, and Π_{44} an electro-elastic coefficient. These coefficients are approximately independent of temperature; Δn_{xy} is the sum of Δn_θ and Δn_P, terms proportional to θ_3 and P_3 respectively. If Δn_θ and Δn_P have opposite signs and $|\Delta n_\theta| > |\Delta n_P|$, which is quite a plausible condition, then Δn_{xy} depends on E_3 as shown in fig. 2, where an arbitrary small value of f has been chosen. Such an unusual optical hysteresis is observed in GMO and must always occur in the conditions assumed here; more extensive measurements of Δn_{xy} both in para-electric and ferroelectric states would reveal the features shown in fig. 2.

References

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