

Fig. 2 shows the pressure dependence of transition temperatures determined at decreasing and increasing temperature, $T_{\text{tr}}^{\text{PF}}$ and $T_{\text{tr}}^{\text{FP}}$, respectively, for three samples. Deviations of the transition temperature at non-zero pressure, ΔT_{tr} , from that at $p = 0$ are plotted instead of absolute values. From Fig. 2 (the curves 1 and 2) it follows that $\partial T_{\text{tr}}^{\text{PF}}/\partial p = \partial T_{\text{tr}}^{\text{FP}}/\partial p = +3.35 \times 10^{-3}$ deg/bar and that the temperature hysteresis of 0.5 deg is pressure-independent.

We shall, first, try to discuss the experimental data on the basis of the thermodynamic potential of proper ferroelectrics, which can be written as an expansion in powers and products of stress and polarization. The pressure influence is expressed in the electrostrictive terms. Using this potential the pressure dependences of the measured quantities can be calculated [5, 9]:

$$\left(\frac{\partial \varepsilon}{\partial p}\right)_{\substack{p=0 \\ T > T_0}} = -\frac{8 \pi Q}{\alpha_0^2 (T - T_0)^2}, \quad (1)$$

$$\left(\frac{\partial T_{\text{tr}}}{\partial p}\right)_{p=0} = -\frac{2 Q}{\alpha_0}, \quad (2)$$

where Q is a combination of components of the electrostrictive tensor and $\alpha_0 (T - T_0)$ is the coefficient before P^2 in the potential; T_{tr} is the ideal temperature of the phase transition.

Using our experimental data equation (1) yields $Q > 0$. Then, from equation (2) it follows that $\partial T_{\text{tr}}/\partial p < 0$, but in the experiment, on the contrary, both $T_{\text{tr}}^{\text{PF}}$ and $T_{\text{tr}}^{\text{FP}}$ shift towards higher temperatures with increasing pressure.

Thus the pressure effects in CAS confirm that the polarization is not a parameter of the phase transition in this substance.

In fact, the phase transition should be described by the thermodynamic potential which is written as a function of mean values of amplitudes of temperature-dependent non-homogeneous modes, acting here as the transition parameters [3, 10]. The potentials of this type have been constructed for GMO [10], boracites [3], and recently for CAS [11]. For boracites, using this potential, the physical parameters which can be affected by the hydrostatic pressure have been calculated [5]:

$$\left(\frac{\partial \varepsilon}{\partial p}\right)_{\substack{p=0 \\ T > T_0}} = -\frac{8 \pi Q}{k_{11}^2}, \quad (3)$$

$$\left(\frac{\partial T_{\text{tr}}}{\partial p}\right)_{p=0} = -\frac{2}{\alpha_0} (\varphi + A Q), \quad (4)$$

where k_{11} is the coefficient before P^2 in the thermodynamic potential and $\alpha_0 (T - T_0)$ stands the combination $(\xi_1^2 + \xi_2^2)$ of the transition parameters. φ represents the interaction of the hydrostatic pressure with the transition parameters and $A > 0$ is the combination of coefficients in the thermodynamic potential (cf. reference [5]).

These results may be used for discussing our experimental data, even though the calculated pressure dependences for CAS will differ in details from those for boracites; but the structure of the formulae will be retained.

Equation (3) together with the experimental data determine the sign of Q : $Q > 0$. Then according to (4), the electrostriction contributes to the lowering of T_{tr} . The observed shift of the phase transition to higher temperatures must be due to the negative value of the interaction coefficient φ , and the inequality

$|\varphi| > A Q$ must be fulfilled. This means that the interaction of the hydrostatic pressure with the non-homogeneous modes is the prevailing factor responsible for the shift of T_{tr} .

3.2 Hydrostatic pressures above 820 bar

Under pressure higher than about 820 bar, the permittivity usually decreases sharply just below T_{tr} (Fig. 1, curves 3 and 4); the origin of this negative peak remains unexplained. Below $(T_{\text{tr}} - 1 \text{ deg})$ ϵ is nearly temperature-independent and decreases with pressure. The transition point now shifts towards lower temperatures (Fig. 2) with $\partial T_{\text{tr}}^{\text{PF}}/\partial p = \partial T_{\text{tr}}^{\text{FP}}/\partial p = -0.62 \times 10^{-3} \text{ deg/bar}$. The temperature hysteresis is 0.6 deg.

Beginning from about 820 bar a slight decrease of ϵ at a certain temperature in the paraelectric phase takes place. We suggest that it is a manifestation of a new phase transition. Its temperature T'_{tr} depends on pressure as $\partial T'_{\text{tr}}/\partial p = +10.3 \times 10^{-3} \text{ deg/bar}$. The line $\Delta T'_{\text{tr}}(p)$ in the phase diagram (curve 3 in Fig. 2) begins at the break of the $\Delta T_{\text{tr}}^{\text{PF}}(p)$ dependence at 824 bar, which becomes a triple point.

There exist no experimental data on the symmetry of the new phase. Obviously, it should be described by some subgroups of the point group 23, which is the symmetry of the paraelectric phase, i.e. either 1, 2, 3 or 222. From these, the group 2 describes the symmetry of the well-known ferroelectric phase below $T_{\text{tr}}^{\text{PF}}$.

No further suspicious points in the $\epsilon(T)$ dependence at $p = 0$ were observed down to 20 °K.

4. Conclusions

The shift of the phase transition together with the changes of ϵ in the paraelectric phase under low hydrostatic pressure ascertain that the polarization cannot be the parameter of the phase transition in CAS, i.e., CAS is an improper ferroelectric. This fact follows also from its dielectric and elastic behaviour [1]. The same conclusion comes from the group-theoretical analysis developed recently for CAS [11], which shows that all possible ferroelectric phase transitions in CAS have to be caused by non-homogeneous modes.

For pressures higher than 824 bar, two phase transitions occurred. At 824 bar there exists a triple point.

References

- [1] M. GLOGAROVÁ, J. FOUSEK, and B. BŘEZINA, Proc. 2nd European Meeting on Ferroelectricity, Dijon 1971 (to appear as Suppl. of J. Physique).
- [2] V. DVOŘÁK, phys. stat. sol. (b) **45**, 147 (1971).
- [3] V. DVOŘÁK, Czech. J. Phys. **B21**, 1250 (1971).
- [4] V. DVOŘÁK and J. PETZELT, Czech. J. Phys. **B21**, 1141 (1971).
- [5] J. FOUSEK, C. FRENZEL, F. SMUNTÝ, and E. HEGENBARTH, Ferroelectrics **4**, 23 (1972).
- [6] A. M. SHIROKOV, V. P. MILOV, A. I. BARANOV, and T. M. PROCHORTSEVA, Fiz. tverd. Tela **13**, 3108 (1971).
- [7] E. HEGENBARTH and C. FRENZEL, Cryogenics **7**, 331 (1967).
- [8] M. GLOGAROVÁ and J. FOUSEK, to be published.
- [9] G. A. SAMARA, Advances in High Pressure Research, Vol. 3, Academic Press, London 1969 (p. 155).
- [10] V. DVOŘÁK, phys. stat. sol. (b) **46**, 763 (1971).
- [11] V. DVOŘÁK, phys. stat. sol. (b) **52**, 93 (1972).

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