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## The Behaviour of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ under Pressure

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The effect of hydrostatic pressure up to 1400 bar on  $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$  from 300 to 20 °K was studied. For pressures up to 824 bar the shift of the ferroelectric phase transition temperature,  $T_{\text{tr}}$ , was found to  $\partial T_{\text{tr}}/\partial p = +3.35 \times 10^{-3}$  deg/bar. The permittivity,  $\epsilon$ , above  $T_{\text{tr}}$  fulfilled  $\partial\epsilon/\partial p < 0$ . These experimental results cannot be explained by the electrostrictive interaction only. This can be done, however, using the thermodynamic potential taking into account that the phase transition is caused by the instability in non-homogeneous lattice vibration modes. For pressures higher than 824 bar two phase transitions occurred. It was found that  $\partial T_{\text{tr}}/\partial p = -0.62 \times 10^{-3}$  deg/bar and for the other transition  $\partial T_{\text{tr}}/\partial p = +10.3 \times 10^{-3}$  deg/bar. At a pressure of 824 bar a triple point exists.

Der Einfluß eines hydrostatischen Druckes bis zu 1400 bar auf  $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$  wurde zwischen 300 und 20 °K untersucht. Bei Drücken bis 824 bar wurde die Verschiebung der ferroelektrischen Phasenübergangstemperatur  $T_{\text{tr}}$  zu  $\partial T_{\text{tr}}/\partial p = +3,35 \times 10^{-3}$  grad/bar gefunden. Die Dielektrizitätskonstante  $\epsilon$  erfüllt oberhalb  $T_{\text{tr}}$   $\partial\epsilon/\partial p < 0$ . Diese experimentellen Ergebnisse lassen sich durch die elektrostriktive Wechselwirkung allein nicht erklären, jedoch mit dem thermodynamischen Potential, wenn man berücksichtigt, daß der Phasenübergang durch die Instabilität der nichthomogenen Gitterschwingungsmoden verursacht wird. Für Drücke höher als 824 bar treten zwei Phasenübergänge auf. Es wurde gefunden, daß  $\partial T_{\text{tr}}/\partial p = -0,62 \times 10^{-3}$  grad/bar und für den anderen Übergang  $\partial T_{\text{tr}}/\partial p = +10,3 \times 10^{-3}$  grad/bar beträgt. Bei einem Druck von 824 bar existiert ein Tripelpunkt.

### 1. Introduction

The dielectric and elastic behaviour of  $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ , (CAS), above its ferroelectric phase transition at 92 °K suggest that this transition should be caused by a thermal instability in non-homogeneous lattice vibration modes. The spontaneous polarization, therefore, could not be the transition parameter [1]. A similar situation occurs in gadolinium molybdate, (GMO), [2] and in boracites [3, 4]. In this aspect these improper ferroelectrics differ substantially from other proper ferroelectrics.

In the first approximation the hydrostatic pressure affects the phase transition in the improper ferroelectrics through its influence on the non-homogeneous modes and changes the value of  $\epsilon$  in the paraelectric phase by the electrostrictive interaction [5], while in the proper ferroelectrics only the electrostriction can play a role in the hydrostatic pressure effects.

The well-known improper ferroelectric Co-I-boracite [5] and GMO [6] have been already studied under hydrostatic pressure. The aim of the present paper is a study of the effects of hydrostatic pressure on CAS.

DEC 16 1974

## 2. Experimental

CAS single crystals were grown from a saturated water solution at 80 °C by evaporating. The (100) plates, 0.4 mm thick and 20 to 30 mm<sup>2</sup> in area, were provided with evaporated gold electrodes.

Dielectric measurements at pressure 0 to 1400 bar were performed in a high-pressure cryostat using helium as a pressure transmitting medium [7]. The capacity was measured at 1 kHz and 100 V/cm with the sensitivity of 10<sup>-3</sup> pF. A relatively high measuring electric field could be used as there are no dielectric non-linearities above the phase transition temperature,  $T_{tr}$  [1].

For all samples,  $\epsilon$  was measured at a pressure  $p = 0$  and temperatures running from  $T_{room}$  to  $(T_{tr} - 5 \text{ deg})$  and then up to  $(T_{tr} + 10 \text{ deg})$ . At this temperature, the hydrostatic pressure was applied and  $\epsilon$  measured again at temperatures running down and up at a rate of 0.2 deg/min through  $T_{tr}$ . After the pressure measurements were finished, a control measurement at  $p = 0$  was performed in order to ascertain whether the sample has not been pressure-damaged. The values of  $T_{tr}$  at  $p = 0$  were reproducible within 0.1 deg.

For one sample  $\epsilon$  was measured at  $p = 0$  down to 20 °K.

## 3. Results and Discussion

### 3.1 Hydrostatic pressures from 0 to about 820 bar

Typical temperature dependences of  $\epsilon$  are shown in Fig. 1 (curves 1 and 2): In the paraelectric phase the permittivity is temperature-independent, but its value decreases with increasing pressure, i.e.  $(\partial\epsilon/\partial p)_{T > T_{tr}} < 0$ ; at  $T_{tr}$ ,  $\epsilon$  rises together with the dielectric losses. In the ferroelectric phase,  $\epsilon$  behaves differently for various samples; sometimes it goes through several maxima at  $T_{tr}$  to  $(T_{tr} - 1 \text{ deg})$ . The non-monotonous dependence  $\epsilon(T)$  below  $T_{tr}$  can be caused — especially at higher measuring fields — by the domain wall contribution to  $\epsilon$  [1, 8]. At still lower temperatures,  $\epsilon$  slowly decreases, but it usually exceeds its paraelectric value.

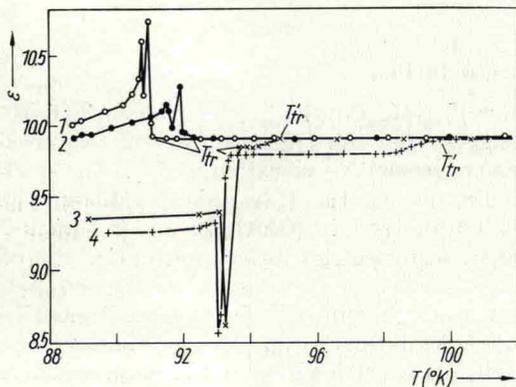


Fig. 1. Temperature dependences of permittivity at decreasing temperature. The curves 1, 2, 3, and 4 correspond to 0, 640, 880, and 1400 bar, respectively

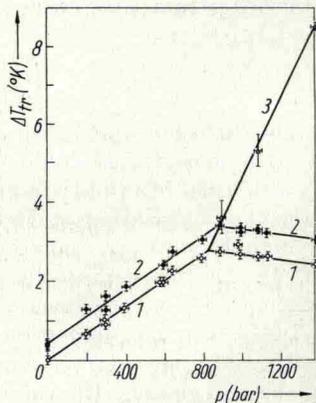


Fig. 2. Variations of the phase transition temperatures with pressure.

Curve 1:  $\Delta T_{tr}^{PF} = T_{tr}^{PF}(p) - T_{tr}^{PF}(0)$ ;

curve 2:  $\Delta T_{tr}^{FP} = T_{tr}^{FP}(p) - T_{tr}^{FP}(0)$ ;

curve 3:  $\Delta T_{tr}' = T_{tr}'(p) - T_{tr}'(0)$

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,  $\Delta T_{\text{tr}}$ , 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;  $T_{\text{tr}}$  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.  $\varphi$  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  $T_{\text{tr}}$ . The observed shift of the phase transition to higher temperatures must be due to the negative value of the interaction coefficient  $\varphi$ , 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  $T_{\text{tr}}$ .

### 3.2 Hydrostatic pressures above 820 bar

Under pressure higher than about 820 bar, the permittivity usually decreases sharply just below  $T_{\text{tr}}$  (Fig. 1, curves 3 and 4); the origin of this negative peak remains unexplained. Below  $(T_{\text{tr}} - 1 \text{ deg})$   $\epsilon$  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  $\epsilon$  at a certain temperature in the paraelectric phase takes place. We suggest that it is a manifestation of a new phase transition. Its temperature  $T'_{\text{tr}}$  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  $\epsilon$  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.

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