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The Behaviour of $(NH_4)_2Cd_2(SO_4)_3$ under Pressure

By

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The effect of hydrostatic pressure up to 1400 bar on $(NH_4)_2Cd_2(SO_4)_3$ from 300 to 20 °K was studied. For pressures up to 824 bar the shift of the ferroelectric phase transition temperature, T_{tr}, was found to $\partial T_{tr}/\partial p = +3.35 \times 10^{-3}$ deg/bar. The permittivity, ε, above T_{tr} fulfilled $\partial \varepsilon/\partial p < 0$. 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 $\partial T_{tr}/\partial p = -0.62 \times 10^{-3}$ deg/bar and for the other transition $\partial T_{tr}/\partial p = +10.3 \times 10^{-3}$ deg/bar. At a pressure of 824 bar a triple point exists.

Der Einfluß eines hydrostatischen Druckes bis zu 1400 bar auf $(NH_4)_2Cd_2(SO_4)_3$ wurde zwischen 300 und 20 °K untersucht. Bei Drücken bis 824 bar wurde die Verschiebung der ferroelektrischen Phasenübergangstemperatur T_{tr} zu $\partial T_{tr}/\partial p = +3.35 \times 10^{-3}$ grd/bar gefunden. Die Dielektrizitätskonstante ε erfüllt oberhalb T_{tr} $\partial \varepsilon/\partial p < 0$. 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 $\partial T_{tr}/\partial p = -0.62 \times 10^{-3}$ grd/bar und für den anderen Übergang $\partial T_{tr}/\partial p = +10.3 \times 10^{-3}$ grd/bar beträgt. Bei einem Druck von 824 bar existiert ein Tripelpunkt.

1. Introduction

The dielectric and elastic behaviour of $(NH_4)_2Cd_2(SO_4)_3$, (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 ε 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 ferroeletric 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.

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 mm² 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^{-3} 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, ε was measured at a pressure $p = 0$ and temperatures running from T_{room} to $(T_{tr} - 5 \deg)$ and then up to $(T_{tr} + 10 \deg)$. At this temperature, the hydrostatic pressure was applied and ε 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 ε 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 ε 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. $(\partial \varepsilon / \partial p)_{T > T_{tr}} < 0$; at T_{tr}, ε rises together with the dielectric losses. In the ferroelectric phase, ε behaves differently for various samples; sometimes it goes through several maxima at T_{tr} to $(T_{tr} - 1 \deg)$. The non-monotonous dependence $\varepsilon(T)$ below T_{tr} can be caused — especially at higher measuring fields — by the domain wall contribution to ε [1, 8]. At still lower temperatures, ε slowly decreases, but it usually exceeds its paraelectric value.
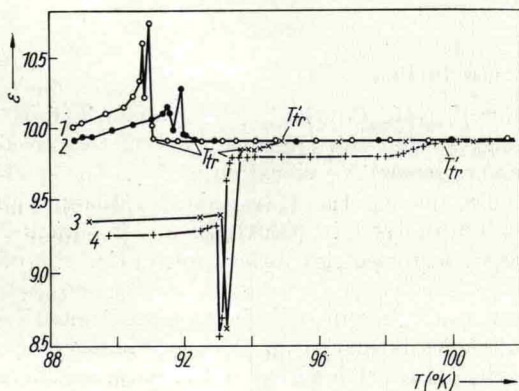

Fig. 1. Temperature dependences of permittivity at decreasing temperature. The curves 1, 2, 3, and 4 correspond to 0, 640, 880, and 1400 bar, respectively
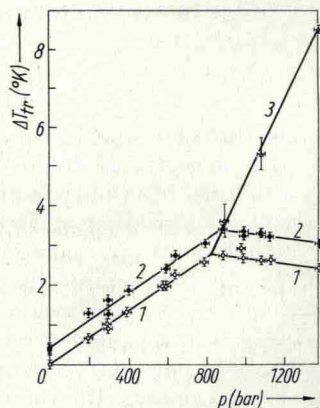
Fig. 2. Variations of the phase transition temperatures with pressure.

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

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

curve 3: $\Delta T'_{tr} = T'_{tr}(p) - T_{tr}^{PF}(0)$