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Effect of Hydrostatic Pressure on the Antiferroelectric Phase Transition Point of $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$

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Cupric formate tetrahydrate $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ has antiferroelectric activity below -39°C .^{1,2)} The crystal belongs to the monoclinic system, and the space group of the room temperature phase is $P2_1/a$.³⁾ The present note reports the effect of hydrostatic pressure on the antiferroelectric phase transition point of $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ studied by dielectric constant measurements. The experimental procedure used was described elsewhere.⁴⁾

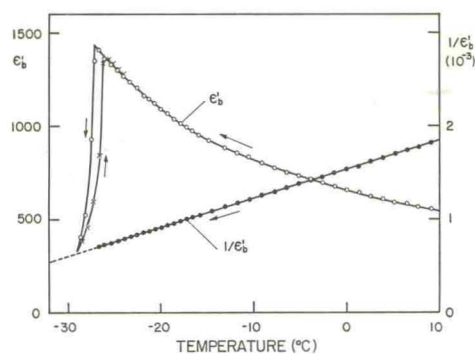


Fig. 1. Temperature dependence of the real part of dielectric constant ϵ'_b and its reciprocal $1/\epsilon'_b$ along the b -axis of $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ at a hydrostatic pressure of $p=2.89$ kbar. Frequency: 1 kHz. \circ : on cooling, \times : on heating.

Figure 1 shows a temperature dependence of the real part of dielectric constant along the b -axis ϵ'_b and its reciprocal $1/\epsilon'_b$ at a hydrostatic pressure of $p=2.89$ kbar. A pronounced peak of dielectric constant existed at the antiferroelectric transition point. A thermal hysteresis of the transition of about 1 degree was observed between cooling and heating runs. The relation between $1/\epsilon'_b$ and temperature was linear in a wide temperature region above the transition point. However, the pressure dependence of the Curie-Weiss temperature and the Curie constant was not definitely determined because of gradual dehydration of the specimen in the pressure transmitting fluid.

Figure 2 indicates the pressure dependence of the transition point. In the figure the vertical bars on the points show the thermal hysteresis. We assumed that the transition in thermal equilibrium would take place at the midpoint of the thermal hysteresis. A linear relation between the transition point T_c and hydro-

static pressure p , $T_c = T_c^0 + Kp$ with $T_c^0 = -39.40 \pm 0.06^\circ\text{C}$ and $K = 4.36 \pm 0.02$ deg kbar⁻¹, was found over the pressure range studied (up to about 6 kbar).

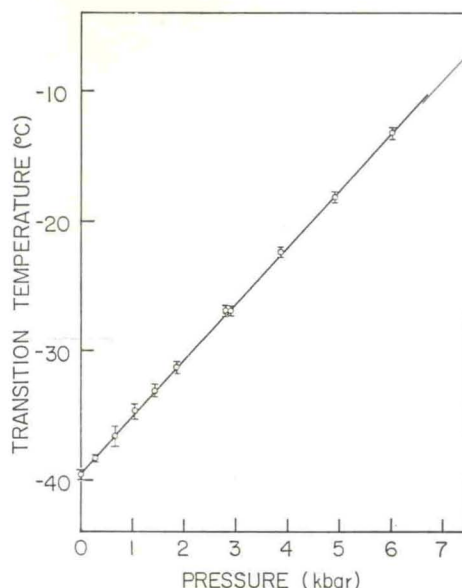


Fig. 2. Hydrostatic pressure dependence of the antiferroelectric transition point of $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$. The vertical bars measure the thermal hysteresis between heating and cooling runs.

Seo *et al.*⁵⁾ have observed a discontinuous volume change $\Delta v = 0.15$ cm³ mol⁻¹ at the transition point. If we use the observed values of the transition heat of 185 cal mol⁻¹ by Okada⁶⁾ and 200 cal mol⁻¹ by Seki and Suga⁷⁾ in place of the latent heat Q_L in the Clausius-Clapeyron relation $K = T_c \Delta v / Q_L$, we get $K = 4.5$ deg kbar⁻¹ and $K = 4.1$ deg kbar⁻¹, respectively. These estimations of the coefficient of transition point are in good agreement with the present experimental value. The agreement indicates that the transition heat is mostly attributed to the latent heat at the transition point reflecting the marked first-order character of the transition.

References

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