

temperature measurements. Descriptions of the pressure bombs and the pressure system used were published elsewhere.^{13,14)}

The dielectric constant of the specimen was measured with an LCR-meter or a three terminal capacitance bridge as a function of temperature at various pressures up to about 8.5 kbar. Pressure was measured with a manganin gauge, and temperature was measured with an alumel-chromel thermocouple or a copper-constantan thermocouple set closely around the specimen. The transitions at high pressures were detected by anomalies in dielectric constant.

§ 3. Results

(a) $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$

The dielectric constant along the *c*-axis of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ shows a λ -type maximum at the I-II transition temperature (the ferroelectric Curie point). The I-II transition temperature shifts towards higher temperatures as pressure

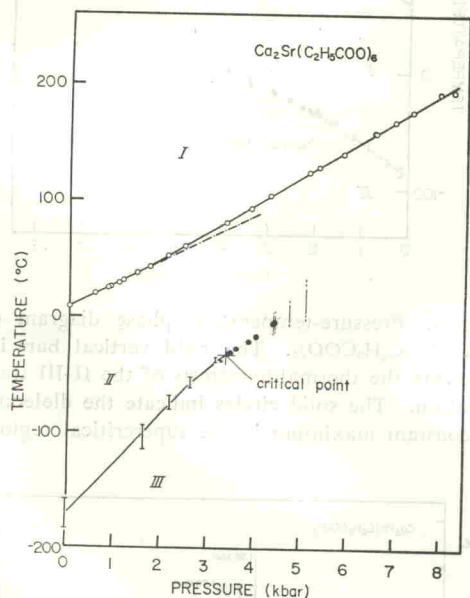


Fig. 1. Pressure-temperature phase diagram of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$. The bold vertical bars indicate the thermal hysteresis of the II-III transition. The solid circles indicate the maximum of the dielectric constant in the supercritical region. The slash-and-dot line shows the initial slope of the I-II phase boundary.

increases. The maximum value of the dielectric constant gradually decreases with increasing pressure. This is partially due to crashing of the specimen at high pressures.¹¹⁾ The pressure

dependence of the I-II transition temperature is shown in Fig. 1 by open circles. The I-II transition temperature at 1 atm and the initial pressure coefficient $(d\theta_{I-II}/dp)_{p=0}$ are $8.7 \pm 0.2^\circ\text{C}$ and $19.7 \pm 0.2 \text{ deg kbar}^{-1}$, respectively. The slope of the I-II transition temperature vs pressure curve increases with increasing pressure as seen in Fig. 1; above about 6 kbar, the pressure derivative of the transition temperature is estimated to be 24 deg kbar^{-1} .

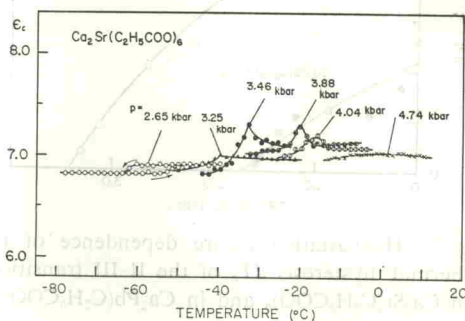


Fig. 2. Temperature dependence of the dielectric constant along the *c*-axis of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ at various hydrostatic pressures in the vicinity of the critical point. Frequency: 1 kHz.

At the II-III transition temperature, a discontinuous change in the dielectric constant and a thermal hysteresis of about 25°C was observed at 1 atm; they correspond to the marked first order nature of the transition and usually the crystal was crashed by passing the II-III transition at 1 atm. Figure 2 indicates the temperature dependence of the dielectric constant along the *c*-axis at various pressures. The thermal hysteresis of the II-III transition temperature ΔT_c gradually decreases with increasing pressure, and finally disappears at about 3.35 kbar as shown in Fig. 3. As shown in Fig. 2, the dielectric constant shows a small but distinct λ -type maximum around the critical pressure at which the first order nature of the transition disappears. As pressure increases exceeding the critical pressure the sharpness of the dielectric constant maximum is rounded off, and above about 4.5 kbar the peak of dielectric constant becomes so diffuse that one can hardly recognize the maximum position. The above behavior of the temperature dependence of dielectric constant is reversible unless the crystal is experienced the first order transition below the critical pressure. The pressure dependence of the II-III transition temperature is also shown in Fig. 1.

The II-III transition temperature at 1 atm and the initial pressure coefficient are estimated as $-173 \pm 2^\circ\text{C}$ and $43.5 \pm 0.5 \text{ deg kbar}^{-1}$, respectively. Here we assumed that the equilibrium transition temperature is at the middle point

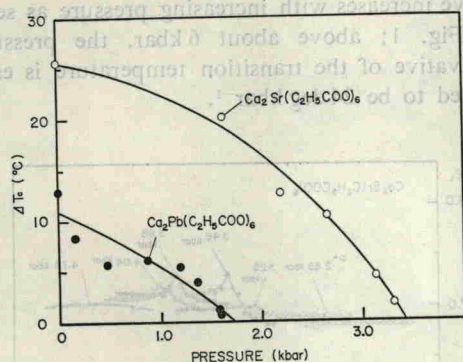


Fig. 3. Hydrostatic-pressure dependence of the thermal hysteresis ΔT_c of the II-III transitions in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{COO})_6$ and in $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$.

of the thermal hysteresis observed. The observed II-III transition temperature at 1 atm is comparable to -169°C reported by Nakamura *et al.*¹⁾ As seen in Fig. 1, the II-III phase boundary gradually deviates from the linear relation, and the pressure coefficient becomes smaller as pressure approaches to the critical pressure. The critical point exists at $p_{\text{crit}} = 3.35 \pm 0.05 \text{ kbar}$ and $T_{\text{crit}} = -35.0 \pm 0.5^\circ\text{C}$. Above the critical pressure, the temperature at which the dielectric constant shows the maximum increases with increasing pressure with a rate of $28.5 \pm 0.2 \text{ deg kbar}^{-1}$ as shown by closed circles in Fig. 1.

(b) $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$

The pressure dependence of the I-II transition of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ is shown in Fig. 4. The relation between the transition temperature and pressure can be expressed by a linear function over the pressure range studied. The observed I-II transition temperature at 1 atm and the pressure coefficient are $60.4 \pm 0.3^\circ\text{C}$ and $23.4 \pm 0.2 \text{ deg kbar}^{-1}$, respectively. The former value is in good agreement with 59.8°C obtained by Nakamura *et al.*¹⁾ for as grown crystal.

At the II-III transition temperature, the dielectric constant along the *c*-axis shows a discontinuous change and thermal hysteresis of about 13°C at 1 atm. As pressure increases the thermal hysteresis ΔT_c decreases, and completely vanishes at a critical pressure of 1.73 kbar as shown in Fig. 3. Figure 5 indicates the tem-

perature dependence of the dielectric constant along the *c*-axis at various pressures. At around the critical pressure a sharp λ -type maximum of the dielectric constant is seen. Above the critical pressure, the sharpness of the peak decreases with increasing pressure, and above about 4 kbar the maximum becomes very obscure. The pressure dependence of the II-III transition temperature is shown in Fig. 4 by bold vertical bars. The II-III transition temperature at 1 atm and the initial pressure coefficient are estimated as $-88.3 \pm 0.5^\circ\text{C}$ and $28.4 \pm$

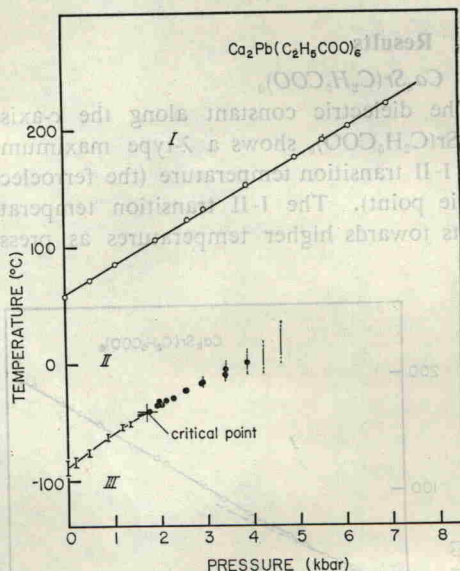


Fig. 4. Pressure-temperature phase diagram of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$. The bold vertical bars indicate the thermal hysteresis of the II-III transition. The solid circles indicate the dielectric constant maximum in the supercritical region.

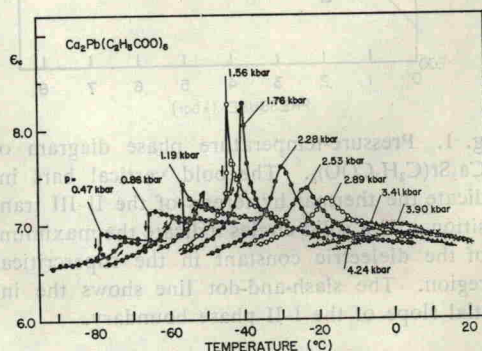


Fig. 5. Temperature dependence of the dielectric constant along the *c*-axis of $\text{Ca}_2\text{Pb}(\text{C}_2\text{H}_5\text{COO})_6$ at various hydrostatic pressures in the vicinity of the critical point. Frequency: 1 kHz.