0.5 deg kbar^{-1}, respectively. The pressure coefficient of the II–III transition temperature gradually decreases as pressure approaches the critical pressure. The critical point at which the first order II–III phase line terminates exists at $p_{crit} = 1.78 \pm 0.05$ kbar and $T_{crit} = -40.5 \pm 0.5°$C. Above the critical pressure the temperature at which the dielectric constant shows the maximum increases with increasing pressure with a rate of 18.1 ± 0.5 degkbar^{-1}. Thebehavior is shown in Fig. 4 by closed circles.

§4. Discussion and Conclusion

The pressure-temperature phase diagrams of $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$ shown in Figs. 1 and 4 quite resemble each other. The fact suggests that the phase transition mechanisms of the two salts are close to each other. This is the reason why we intended to reexamine the polarity in Phase II of $Ca_2Pb(C_2H_5COO)_6$.[8] The discovery of the ferroelectric activity in Phase II of the Pb-salt[9] and the results of the optical rotatory power[10] also supported the above expectation.

Recently, Kobayashi et al.[15] interpreted the ferroelectric transition in $Ca_2Sr(C_2H_5COO)_6$ in terms of improper ferroelectricity. A simple phenomenological treatment of improper ferroelectrics[16] shows that the pressure coefficient of an improper ferroelectric Curie temperature is expressed as

$$dT_c/dp = -CQ_h/(2\pi),\qquad(1)$$

where C is the Curie constant, and $Q_h = 2Q_{13} + Q_{33}$ is the volume electrostrictive coefficient which is defined as $Q_h = \Delta v_s/P_s^2$, where Δv_s and P_s are respectively the spontaneous change in volume and the spontaneous polarization. Kobayashi et al.[15] showed that the ratio $\Delta v_s/P_s^2$ in Phase II of $Ca_2Sr(C_2H_5COO)_6$ is considered to be a constant only in a limited temperature region below the Curie temperature. At $-13°$C, where the proportionality between Δv_s and P_s^2 is held, the spontaneous strains along the a- and c-axis are estimated to be $(x_1)_s = 0.16 \times 10^{-3}$ and $(x_3)_s = -1.0 \times 10^{-3}$, respectively.[15] At the same temperature, the spontaneous polarization is $0.32 \ \mu$C cm^{-2}.[15] Then, one gets the volume electrostrictive coefficient as $Q_h = \{2(x_1)_s + (x_3)_s\}/P_s^2 = -7.8 \times 10^{-10}$ cgs esu. The value is almost 10^2 as large as that observed for proper ferroelectrics such as triglycine sulfate. The above value of Q_h together with the Curie constant $C = 156$ K[17] yields $dT_c/dp = 20$ deg kbar^{-1}.

The estimation is in very good agreement with the observed value of 19.7 deg kbar^{-1}. On the other hand, the electrostrictive coefficients Q_{i3}^d which are deduced from the piezoelectric coefficients d_{3i} and the dielectric susceptibility along the c-axis χ_{33} by the relation $Q_{i3}^d = d_{3i}/(2\chi_{33}P_s)$ show strong temperature dependence especially in the vicinity of the Curie temperature.[18,25] The anomalous behavior of Q_{i3}^d can be interpreted by assuming the material being improper ferroelectric.[15,16] A simple phenomenological treatment of an improper ferroelectric[16] shows that a relation between Q_{i3} and Q_{i3}^d,

$$Q_{i3}^d = Q_{i3} + (\zeta/\chi_{33})\qquad(2)$$

is held, where ζ is a parameter which measures the strength of the coupling between the polarization and the transition parameter. If one assumes the parameter ζ being temperature independent, $Q_{i3}^d = Q_{i3}$ when $1/\chi_{33}$ goes to zero. According to Hamano's results,[18] Q_{13}^d and Q_{33}^d just below the Curie temperature where $1/\chi_{33}$ is considerably small are given as 0.26×10^{-9} cgs esu and -2.1×10^{-9} cgs esu, respectively. Putting these values into eq. (1) one gets $dT_c/dp = 40$ deg kbar^{-1}. The value is about twice as large as the observed one but gives the correct order of magnitude.

Recently, Takashige et al.[9] showed that as grown crystals of $Ca_2Pb(C_2H_5COO)_6$ are strongly biased, and that the bias field can be removed by annealing at 250°C. The rather broad dielectric constant peak[1] and very small anomaly in specific heat reported in earlier works are due to the bias field. Our preliminary measurements on the dielectric constant of $Ca_2Pb(C_2H_5COO)_6$ which was annealed at 250°C for 48 hr showed that there is a very sharp λ-type peak of dielectric constant at the I–II transition, and at the same time the temperature at which the dielectric constant shows maximum is lowered by about 5°C. The value of the Curie constant of the annealed $Ca_2Pb(C_2H_5COO)_6$ is estimated as $C = 40$ K. Influence of the bias field on the pressure coefficient of the I–II transition temperature would not be so serious, since the shape of the dielectric constant peak does not change appreciably with pressure. Then, the volume electrostrictive coefficient Q_h of $Ca_2Pb(C_2H_5COO)_6$ is given from eq. (1) as -3.7×10^{-9} cgs esu by using the Curie constant and observed pressure coefficient. The value of Q_h is about five times as large as the one obtained for the Sr-salt.

The volume change at the II-III transitions in $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$ at 1 atm can be evaluated from the specific heat data[1] and the initial pressure coefficient of the transition temperature by using the Clausius-Clapeyron relation $\Delta v = Q_L \cdot (d \ln \Theta_{II-III}/dp)_{p=0}$. If one puts the measured transition heats of 255 cal mol^{-1} for the Sr-salt and 1160 cal mol^{-1} for the Pb-salt into the place of the latent heat Q_L, one gets $\Delta v = 1.1\%$ for the Sr-salt and $\Delta v = 1.9\%$ for the Pb-salt. The relatively large volume change at the II-III transition at 1 atm would cause crashing of a single crystal by passing the transition.

The results shown in Figs. 1, 3, and 4 indicate the first order II-III transition lines in $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$ terminate at the critical points. Generally saying, a first order phase boundary curve can terminate in the pressure-temperature plane (a) at a triple point where three phase boundaries meet together, (b) at a critical point through which the first order nature of the transition passes into the second order one; such a critical point may be called as the Curie critical point according to the terminology of Ginzburg,[20] and (c) at a liquid-vapor type critical point where the transition terminates, and above the critical point no phase transition exists.[19] The case (c) can occur only if the crystal symmetry does not change through the transition.[19] Such a transition which may be called as an isomorphous transition is unquestionablly seldom among the solid state transitions. So far the liquid-vapor type critical points have been observed only for the $\gamma-\alpha$ transition in Ce[21] and for the Mott transition in Cr-doped V_2O_3.[22] So far as the dielectric property was concerned, no evidence for existence of a triple point was obtained for the II-III transitions in the present materials. On the other hand, the pressure and temperature dependence of the low frequency dielectric constant above the critical point shows a resemblance to that of the temperature coefficient of the electrical conductance and the volume thermal expansion coefficient around the liquid-vapor type critical point of the $\gamma-\alpha$ transition in Ce.[21,23] Up to date, no detailed structure analysis has been published for Phase III of $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$. However, at least Phases II and III of the both salts are polar, and unpublished x-ray data[1] showed that Phase III of the Pb-salt is isomorphous

with Phase II of the Sr-salt. Recent experimental results[8-10] seem to suggest that Phase II of the Pb-salt is isomorphous with Phase II of the Sr-salt. Then, it is possible that Phases II and III of $Ca_2Pb(C_2H_5COO)_6$ are isomorphous with each other. Although the final conclusion should be postponded until the structure analysis of Phase III of the two propionates is completed, it is tempting to speculate that the II-III transitions in $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$ are isomorphous transitions, and the II-III phase boundaries terminate at the liquid-vapor type critical points just alike the $\gamma-\alpha$ transition in Ce. Such an isomorphous transition can take place in a ferroelectric through a displacement of ions between general positions which belong same site symmetry of the crystal space group. A simple phenomenological theory[24] based upon the above assumption gives a semi-quantitative agreement with the pressure and temperature dependence of low frequency dielectric constant of $Ca_2Pb(C_2H_5COO)_6$ in the critical region and in the supercritical region.

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