Fig. 4. Dielectric constant anomalies of (100) plates of Ca$_2$Ba(C$_2$H$_5$COO)$_6$ at high pressure transitions, (a) around the I-II transition, (b) the II-III transition, (c) the V-VI transition, (d) the IV-VII transition. The transition points are indicated by vertical arrows. Frequency: 1kHz.

transition is of the first order. The III-IV-V triple point exists at around $T = -95°C$, $p = 1.8$ kbar. Above about 5 kbar, slight break instead of maximum in the dielectric constant vs temperature curve is seen around the production of the IV-V phase boundary as shown in Fig. 4(d). Since the anomaly is quite different from the dielectric constant maximum shown in Fig. 2, we consider that phase IV transforms to a new high pressure phase other than phase V above 5 kbar. We will denote the high

pressure phase as phase VII. The IV-VII transition is probably of the second order, because no thermal hysteresis is found for the dielectric constant anomaly. The phase boundaries between phases V, VI, and VII were not determined in the present work. We have speculated possible phase boundaries as indicated by the slashed lines in Fig. 5. The resultant phase diagram is shown in Fig. 5.

§ 4. Discussion and Conclusive Remark

According to Seki *et al.*[2] the volume change Δv in Ca$_2$Ba(C$_2$H$_5$COO)$_6$ at the I-II transition at 1 atm is considerably large; it is about 2.0 %. On the other hand, the transition heat ΔH at the I-II transition is about 1740 cal mol^{-1}.[2] Then, the Clausius-Clapeyron relation $(dT_c/dp)_{p=0} = T_c \Delta v/Q_L$ yields an estimation of the pressure coefficient of the I-II transition as 33.2 deg kbar^{-1} if the transition heat ΔH is put in the place of the latent heat Q_L. The estimated value is about the same as the observed one. This means that most of the transition heat comes from the latent heat at the transition corresponding to a marked first order nature of the I-II transition.

Seki *et al.*[1,2] observed that at the I-II transition the heat capacity peak splits into double peaks. In the present experiment, such a double step nature of the I-II transition was not observed. Since the high pressure phase IV exists in rather low pressure range especially at the temperatures around the I-II transition point, the structure of phase IV can be
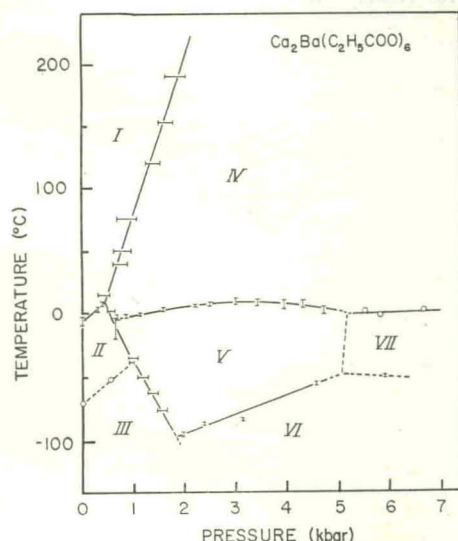

Fig. 5. Pressure-temperature phase diagram of Ca$_2$Ba(C$_2$H$_5$COO)$_6$. Thermal or pressure hysteresis of first order transitions is shown by short bars.

realized as a metastable state at 1 atm through lattice strains introduced by passing the first order I-II transition. The situation is similar to the case of KNO_3 in which a high pressure phase III can be found at 1 atm as metastable phase.[9] Then, the appearance of the metastable IV would make the I-II transition at 1 atm take place in the two steps.

The pressure-temperature phase diagram of $Ca_2Ba(C_2H_5COO)_6$ shown in Fig. 5 is quite different from those of $Ca_2Sr(C_2H_5COO)_6$ and $Ca_2Pb(C_2H_5COO)_6$. The phase diagrams up to 10 kbar for the latter two propionates are rather simple; the two transition points monotonically increase with increasing pressure, and no high pressure phases are found.[10] Therefore, although all of these propionates have three modifications at 1 atm, the nature of the phase transitions in the barium salt should be different from those of Sr- and Pb-salts. In fact, the dielectric anomalies around the I-II and the II-III transitions in Ba-salt at 1 atm are insignificant. However, as shown in Fig. 2, the transition between pressure-induced phases of IV and V is accompanied with a pronounced peak of dielectric constant just alike to the dielectric anomaly at the ferroelectric Curie temperature of Sr-salt.[11] In order to examine whether phase V of Ba-salt is ferroelectric, ferroelectric D-E hysteresis loop was tried to observe with the maximum amplitude of $2\,kV\,cm^{-1}$ at 50 Hz by changing

temperature at $p=0.9\,kbar$. We, however, have not found any ferroelectric hysteresis loops.

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