

## Phase Transitions in Crystalline Divalent Metal Dicalcium Propionates. II. Proton Magnetic Resonance Investigation\*<sup>1</sup>

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(Received September 6, 1967)

The motions of the propionate anions in strontium-, lead-, and barium-dicalcium propionates were examined with the proton magnetic resonance method at low temperatures. It was found that the methyl groups rotate about the  $C_3$ -axes even at 20°K in the Sr-, and the Ba-salts. In the Sr-salt the gradual decrease of the second moment below the ferroelectric transition point was observed and this phenomenon was related to the large angle torsional oscillations of the ethyl groups about the  $C_3'$ -axes as introduced in Part I: Near the ferroelectric transition point the observed second moment shows the possibility of excitation of the  $C_3'$ -rotation which would make the crystal to be paraelectric above the transition point. It was expected that the  $C_3'$ -torsion is to some extent excited in the Pb-salt at liquid nitrogen temperature, a slight discrete change being observed at the lower transition point. A sharp line width transition was also observed in the Ba-salt and this fact resulted in the finding of a new  $\lambda$ -type phase transition with the peak at about 204°K by the differential thermal analysis. A slight decrease of the second moment was observed at the upper transition point and the  $C_3'$ -rotation was assumed to be fully excited above that point.

In 1955 calorimetric and dilatometric studies were carried out on  $BaCa_2(C_2H_5CO_2)_6$  in the authors' laboratory, and a phase transition was found to occur at  $-8.5^\circ C$ .<sup>1)</sup> Calorimetric study was also performed on the mixed crystals between the Ba-salt and  $PbCa_2(C_2H_5CO_2)_6$  and it was suggested that ordering effect of the orientations of the methyl groups in the propionate anions is responsible to the phase transition of the Ba-salt.

On the other hand, Matthias and Remeika have found in 1957 that  $SrCa_2(C_2H_5CO_2)_6$  undergoes a ferroelectric phase transition at  $8.5^\circ C$ .<sup>2)</sup>

In the previous paper<sup>3)</sup> the present authors reported the results of the calorimetric study on the Sr-salt and suggested, on the basis of the crystal symmetry consideration and of the fact that the anomaly in the heat capacity is of typical  $\lambda$ -type, that the ferroelectric phase transition is closely related to an orientational ordering of the methyl groups in the propionate anions. An attempt was made to correlate the torsional oscillation of the ethyl group around the  $C_{\text{carboxyl}}-C_\alpha$  axis to the temperature dependence of the spon-

aneous polarization near the Curie point. The X-ray analysis was performed later by Tomiie and others on the room temperature phase of this substance.<sup>4)</sup> There was shown the possibility of the rotational motion of the ethyl groups about the  $C_{\text{carboxyl}}-C_\alpha$  axes from extremely large temperature factors of  $C_\alpha$ -carbons and also from the undeterminable positions of the methyl-carbon atoms. In addition, it was found a new phase transition takes place at  $104.2^\circ K$  by the calorimetric study and the features of this transition were already described in Part I.

In the case of  $PbCa_2(C_2H_5CO_2)_6$  two phase transitions were found at  $191.5^\circ K$  and  $333^\circ K$ , respectively, and no existence of the ferroelectric phase was confirmed by a hysteresis bridge method as reported in Part I.

It has been suggested there that the proton magnetic resonance is a powerful method of obtaining further informations about the motions of the propionate anions in the Ba-, Sr-, and Pb-salts. In this paper, the results of the second moment measurement are reported. It will be shown that for the Sr-salt, the result of NMR experiment supports the assumptions on the motions of the propionate anions proposed in Part I: In the Pb-salt, the full account of the nature of the phase transitions remains still in difficulty even applying the NMR method. The line width transition observed in the proton resonance study of the

\*<sup>1</sup> This paper was read before the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964. (See abstract of the Meeting, p. 461)

1) S. Seki, M. Momotani, K. Nakatsu and T. Ôshima, *J. Chem. Phys.*, **19**, 1061 (1951); This Bulletin, **28**, 411 (1955).

2) B. T. Matthias and J. P. Remeika, *Phys. Rev.*, **107**, 1727 (1957).

3) N. Nakamura, H. Suga, H. Chihara and S. Seki, This Bulletin, **38**, 1779 (1965), afterwards referred to as Part I.

4) Y. Tomiie, private communication.

Ba-salt will be discussed based on the new transition phenomenon at 204°K found by the differential thermal analysis.

### Experimental

The procedure of the sample preparation was already described in the previous papers.<sup>1,3)</sup> Proton second moments were measured on the powdered specimens by a Robinson-type spectrometer at 20 MHz; the absence of the saturation effect was confirmed by changing the rf-levels especially at low temperatures; the correction of the modulation width was made after Andrew.<sup>5)</sup> The temperature was left to increase very slowly and the resonance signals were recorded with measuring the temperatures by a chromel-constantan thermocouple; the temperature increase in each sweep is within 1°C above the liquid nitrogen temperature and at most 1.5°C near liquid hydrogen temperature.

### Experimental Results and Discussion

Figures 1, 2 and 3 show the results of the second moment measurements on the Sr-, Pb- and Ba-salts, respectively, the heat capacity curves being illustrated for reference.

**Calculation of the Second Moment.** For a propionate anion the intra-ionic contribution to the

second moment was calculated by the usual method<sup>6)</sup> by using the values,  $r_{CC}=1.54 \text{ \AA}$ ,  $r_{CH}=1.10 \text{ \AA}$ ,  $\angle HCH=\angle HCC=\angle CCC=109^\circ 28'$ . The second moments were calculated for the typical four cases: 1) the rigid lattice (the *trans*-conformation was assumed); 2) the lattice in which only the rotation of the methyl group about the axis connecting  $\alpha$ - and  $\beta$ -carbon atoms is excited ( $C_3$ -rotation); 3) both the  $C_3$ -rotation and the torsional oscillation of the methyl and ethyl groups about the  $C_{\text{carboxyl}}-C_\alpha$  axis ( $C'$ -torsion) are excited; 4) both the  $C_3$ -rotation and the rotation of the methyl and ethyl groups about the  $C_{\text{carboxyl}}-C_\alpha$  axis are

TABLE I. CALCULATED VALUE OF THE SECOND MOMENT FOR THE PROPIONATE ANION

	Second moment (gauss <sup>2</sup> )
Intra-ionic contribution	
Rigid lattice	20.02
$C_3$ -rotation	11.62
$C_3$ -rotation + $C_3'$ -torsion	$2.38 + 1.10 \cdot J_0^2(\theta_1) + 8.14 \cdot J_0^2(2\theta_1)$
$C_3$ -rotation + $C_3'$ -rotation	2.38
Inter-ionic contribution	
$C_3$ -rotation + $C_3'$ -rotation (for the Ba-salt)	~1.8

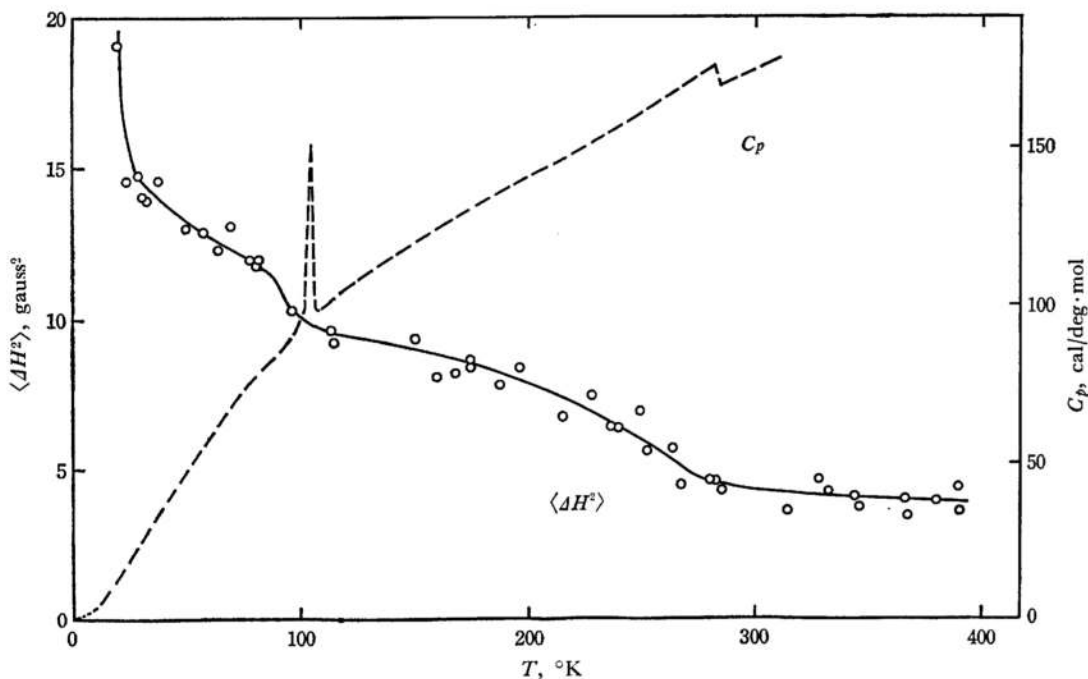


Fig. 1. Temperature dependence of the second moment (—○—) and of the heat capacity (—) of  $\text{SrCa}_2(\text{C}_2\text{H}_3\text{CO}_2)_6$ .

5) E. R. Andrew, *Phys. Rev.*, **91**, 425 (1953).

6) J. H. Van Vleck, *ibid.*, **74**, 1168 (1948); J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1704

(1953); E. R. Andrew and R. A. Newing, *Proc. Phys. Soc.*, **72**, 959 (1958).

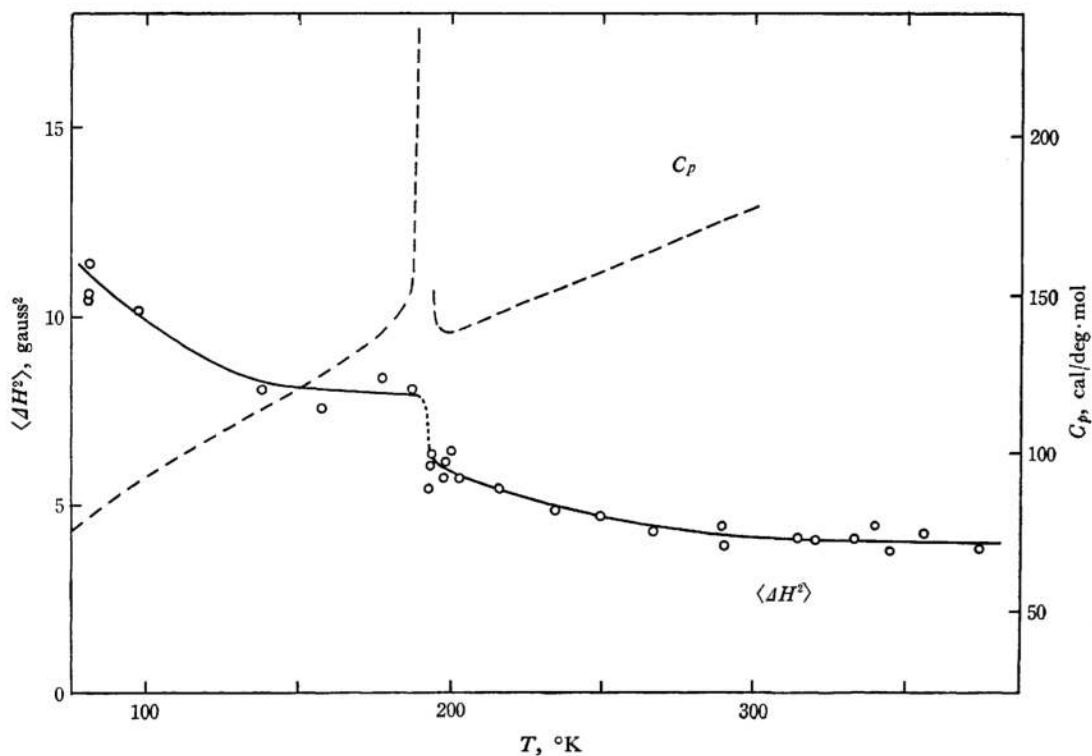


Fig. 2. Temperature dependence of the second moment ( $-\circ-$ ) and of the heat capacity ( $---$ ) of  $\text{PbCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$ .

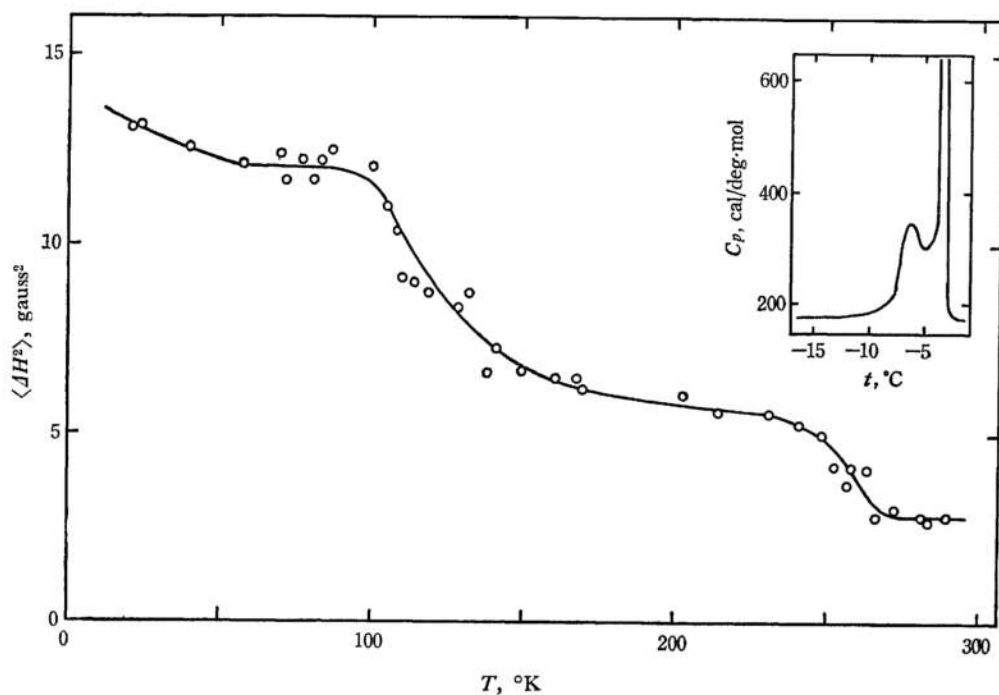


Fig. 3. Temperature dependence of the second moment of  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$ . The inset figure shows the heat capacity near the upper transition point.

excited ( $C_3'$ -rotation). The results of the calculation are given in Table 1, where  $J_0$ 's are the Bessel's functions of zeroth order, and  $\theta_1$  the mean amplitude of the  $C_3'$ -torsional oscillation.

The inter-ionic contribution was only estimated for the Ba-salt, by using the crystal structure data for the room temperature phase, and by assuming both the  $C_3$ - and the  $C_3'$ -rotations. The result of the calculation is also given in Table 1. In the case of the lower temperature phase of the Ba-salt, as well as of each phase of the Sr- and Pb-salts, no crystallographic data is available for the calculation of the inter-ionic contribution. In the following we proceed to the discussion of the temperature variation of the molecular motion in each salt, separately.

**SrCa<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>6</sub>.** The second moment at the liquid hydrogen temperature, *i. e.*, 19.1 gauss<sup>2</sup>, as shown in Fig. 1, is smaller than the rigid lattice value which should somewhat be larger than 20.02 gauss<sup>2</sup> (See Table 1) if we add the inter-ionic contribution to this value. The  $C_3$ -rotation, therefore, may be excited to some extent already at this temperature. Above the liquid hydrogen temperature the second moment decreases down rapidly to the value 11.9 gauss<sup>2</sup> at 85°K. This value is only 0.3 gauss<sup>2</sup> larger than the value for the  $C_3$ -rotation. Accordingly it is reasonable to consider that the  $C_3$ -rotation is completely excited at 85°K. For the calculation of the contribution from the  $C_3$ -rotation, the following equation presented by Powles and Gutowsky may be applied:<sup>7)</sup>

$$\ln\{(\langle\Delta H^2\rangle_r/\langle\Delta H^2\rangle)^{1/2}\tan(\pi/6\cdot\langle\Delta H^2\rangle/\langle\Delta H^2\rangle_r-1)\} = E_a/RT + C,$$

$$C = \ln\{4\pi\mu\tau_0(\langle\Delta H^2\rangle_r)^{1/2}/h\},$$

where  $\langle\Delta H^2\rangle$  is the second moment at temperature  $T$  and  $\langle\Delta H^2\rangle_r$  corresponding to the complete free rotation,  $E_a$  the activation energy for the  $C_3$ -rotation, and  $\tau_0$  the mean life-time at one of the three possible equilibrium positions for the methyl group. The experimental data were analysed with the aid of this equation, and the plot of  $\ln\{\dots\}$  against  $1/T$  is shown in Fig. 4, where  $\langle\Delta H^2\rangle_r$  was set to be 11.9 gauss<sup>2</sup> (at 85°K): From the slope of this straight line,  $E_a=1.5$  kcal/mol and  $\tau_0=9.4\cdot 10^{-8}$ s were obtained, respectively.

A small but significant decrease in the second moment was found between 90°K and 100°K. This abrupt change of the second moment may be due to the change in the crystal structure accompanied with the phase transition found in Part I.

A gradual decrease of the value from 10.0 gauss<sup>2</sup> at 100°K to 7.8 gauss<sup>2</sup> at about 200°K may be attributed to the partial averaging out of the

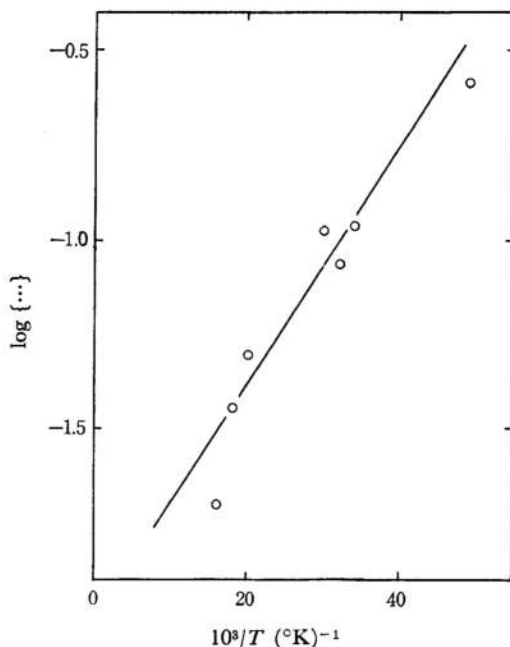


Fig. 4. The term  $\ln\{\dots\}$  plotted against  $1/T$  for the experimental second moment of SrCa<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>6</sub> between 20°K and 85°K.

dipolar interactions caused by the gradual excitation of the large angle torsional oscillation of each ethyl group about the  $C_3'$ -axis: Such an assumption on the motion of the ethyl group was already introduced in Part I in order to explain the temperature dependence of the spontaneous polarization in the ferroelectric phase. In the case of the  $C_3'$ -torsion which is simultaneously accompanied with the  $C_3$ -rotation the following expression for the intra-ionic contribution to the second moment may be written by making a small modification of the Andrew's theory;<sup>8)</sup>  $\langle\Delta H^2\rangle = 2.38 + 1.10 \cdot J_0^2(\theta_1) + 8.14 \cdot J_0^2(2\theta_1)$ , (in gauss<sup>2</sup>), where  $\theta_1$  is the mean amplitude of the  $C_3'$ -torsion and  $J_0(x)$  the Bessel function of zeroth order. If one assumes that the inter-ionic contributions to the second moment remain constant from 100°K to above the ferroelectric transition point, one can estimate the force constant for the  $C_3'$ -torsion by using the classical relationship:  $\kappa\theta_1^2 = kT$ , and by fitting the experimental data to the above relation. The analysis gives  $\kappa = 5 \cdot 10^{-3}$  mdyn/Å and this value corresponds to the mean amplitude of torsional oscillation of  $\pi/5$  at 150°K. This result does not agree exactly with the value of  $\kappa = 1.1 - 1.6 \cdot 10^{-3}$  mdyn/Å obtained in Part I from the  $P_s$  vs.  $T$  curve, but it seems to be reasonable to consider that the ethyl groups in the propionate anions librate with considerably large amplitudes below the ferroelectric transition point.

7) J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **23**, 1692 (1955).

8) E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950).

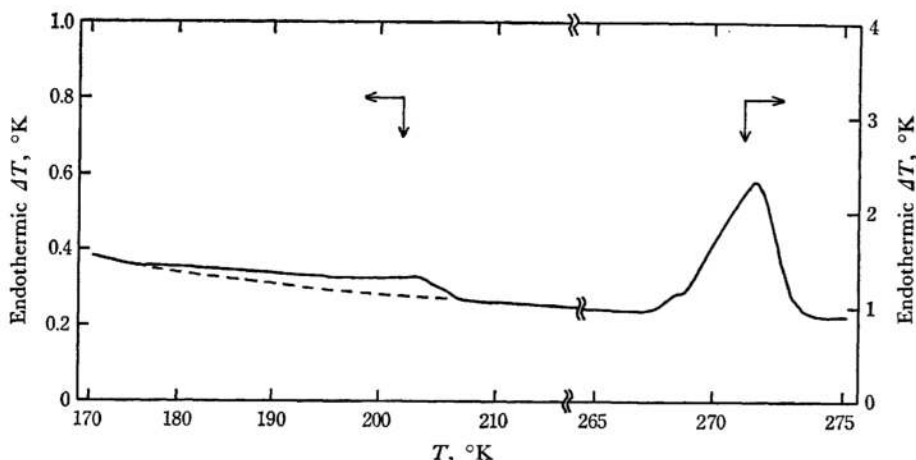


Fig. 5. Differential thermal analysis curve of  $\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$ . The plausible base line for the lower transition region is indicated by the broken line.

Further decrease of the second moment near the ferroelectric transition point may reflect the onset of the  $\text{C}_3'$ -rotation. In this case, some modification of Powles and Gutowsky's equation<sup>7</sup> gives the following expression:

$$\ln\left\{\frac{\langle\Delta H^2\rangle_r}{\langle\Delta H^2\rangle} \cdot \tan 0.128\pi \cdot \frac{\langle\Delta H^2\rangle}{\langle\Delta H^2\rangle_r - 1}\right\} = \frac{E_a}{RT} + C,$$

$$C = \ln 4\pi\mu\tau_0\langle\Delta H^2\rangle^{1/2}/h$$

The meaning of the notations in this equation is the same as before. The analysis of the experimental data gives  $E_a = 630$  cal/mol and  $\tau_0 = 1.2 \cdot 10^{-6}$ s, and the latter seems to be somewhat unreasonable. Anyhow, it is possible to consider that the  $\text{C}_3'$ -rotation removes the polarization due to propionate anions which were originally aligned parallel to the crystalline  $c$ -axis and as the result the paraelectric phase appears. The continuous change from  $\text{C}_3'$ -torsion to  $\text{C}_3'$ -rotation may explain that the transition is of order-disorder type as assumed in Part I.

Above the transition point no distinct change was observed in the second moment, and 4.3 gauss<sup>2</sup> at room temperature may be the sum of the intramolecular contributions of 2.38 gauss<sup>2</sup> and inter-ionic contribution of about 1.9 gauss<sup>2</sup>.

**$\text{PbCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$ .** The second moment of 10.9 gauss<sup>2</sup> at liquid nitrogen temperature may be explained by the partial excitation of the  $\text{C}_3'$ -torsion in addition to the  $\text{C}_3$ -rotation. Near the transition temperature, 191.5°K, a slight discrete change was observed as shown in Fig. 2. This discontinuity in the second moment as well as the discontinuity in the dielectric constant described in Part I may be due to the change in the crystal structure accompanied with the phase transition.

Above the transition temperature the second moment decreases gradually and settled down to

4.0 gauss<sup>2</sup> above room temperature. The value of 4.0 gauss<sup>2</sup> is comparable to 4.3 gauss<sup>2</sup> for the room temperature phase of the Sr-salt. Therefore, it may be concluded that the  $\text{C}_3$ - and  $\text{C}_3'$ -rotations are completely excited in the Pb-salt above the room temperature.

No remarkable change in the second moment was observed through the transition at 333°K where the dielectric constant shows a large anomaly.

**$\text{BaCa}_2(\text{C}_2\text{H}_5\text{CO}_2)_6$ .** The second moment decreases slightly from the liquid hydrogen temperature to about 100°K, and 12.0 gauss<sup>2</sup> at this temperature suggests the complete excitation of the  $\text{C}_3$ -rotation. The second moment falls further remarkably from 12.0 gauss<sup>2</sup> to about 6 gauss<sup>2</sup> at 160°K. This line width transition can be treated by the following theoretical expressions developed by Gutowsky and Pake;<sup>9</sup>

$$(\delta\nu)^2 = B^2 + C^2(2/\pi)\tan^{-1}(\alpha \cdot \delta\nu/\nu_c) \text{ and}$$

$$\nu_c = \nu_0 \cdot \exp(-E_a/RT),$$

where  $A = (B^2 + C^2)^{1/2}$  is the line width in the rigid lattice,  $B$  the narrowed line width characteristic to a motion,  $\nu_c$  the correlation frequency,  $\nu_0$  the frequency factor and  $\alpha$  a numerical factor characterized by the line shape. From the activation plot the activation energy,  $E_a = 1.5$  kcal/mol, and the frequency factor  $\nu_0 = 1.5 \cdot 10^7$  s<sup>-1</sup> were obtained by assuming  $\alpha = 1$ . Such a decrease of the second moment may be explained by assuming the  $\text{C}_3'$ -rotation of only four among six propionate anions in the unit cell, if we want to fit the magnitude of the second moment at 160°K (6.2 gauss<sup>2</sup>) with the crystal model. The preliminary differential thermal analysis study shows the existence of a small  $\lambda$ -type anomaly with the

9) H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

peak at about 204°K which is the evidence of a kind of phase transition (See Fig. 5). It is, therefore, considered that the phase transition may be related to some anisotropic motion of the propionate anions mentioned above.

Further remarkable decrease of the second moment occurs at 267°K which corresponds to the first order phase transition reported previously.<sup>13</sup>

#### Note Added in Proof

After the completion of this work, we noticed that the second moment of  $\text{BaCa}_2(\text{C}_2\text{H}_3\text{CO}_2)_6$  has been measured by Chezeau, Dufourcq and Lemanceau in the temperature region from 100 to *ca.* 320°K:<sup>10</sup> Their second moment values are slightly larger than ours just below the upper transition point, but their model assumed for the motion of the ethyl group is essentially the same as that proposed by us.

10) Jean-Michel Chezeau, J. Dufourcq and B. Lemanceau, *J. Chim. Phys.*, **64**, 412 (1967).

As to the second moment of  $\text{SrCa}_2(\text{C}_2\text{H}_3\text{CO}_2)_6$  Nakamura, Hikichi and Furuichi have reported also their data obtained between -190°C and +100°C;<sup>11</sup> their experimental second moments are quite consistent with our results.

Although we referred to the structural data on  $\text{SrCa}_2(\text{C}_2\text{H}_3\text{CO}_2)_6$  as a private communication from Tomiie (Ref. 4), the short communications on the crystal structures of the para- and ferroelectric phases of  $\text{SrCa}_2(\text{C}_2\text{H}_3\text{CO}_2)_6$  were published after this paper was submitted.<sup>12</sup>

The authors would like to express their thanks to Mr. Takuji Nakamura for his help in the measurements.

11) E. Nakamura, K. Hikichi and J. Furuichi, *J. Phys. Soc. Japan*, **23**, 471 (1967).

12) H. Maruyama, Y. Tomiie, I. Mizutani, Y. Yamazaki, Y. Uesu, N. Yamada and J. Kobayashi, *ibid.*, **23**, 899 (1967); I. Mizutani, Y. Yamazaki, Y. Uesu, N. Yamada, J. Kobayashi, H. Maruyama and Y. Tomiie, *ibid.*, **23**, 900 (1967).