Phase Transitions in Crystalline Divalent Metal Dicalcium Propionates. I. Calorimetric and Dielectric Investigations of Strontium- and Lead Dicalcium Propionates

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There are three substances known as the double propionates of divalent metals: barium-, strontium- and lead-dicalcium propionates. The room temperature modification of the barium salt is known to be cubic.[1] The X-ray crystal structure analysis of this phase was made in 1935 by Nitta and Watanabé,[2] and also, independently, by Harris and Biefeld,[3] and its space group was found to be O^4–$F4_13$. In 1951, it was found in our laboratory by the use of the calorimetric method, that this material undergoes a phase transition at −8.5°C.[4] Taking account of the crystal symmetry and molecular shape, this phase transition was supposed to be a kind of order-disorder type with regard to the motion of the propionate anions in the crystal lattice.

In the case of strontium salt, the spontaneous polarization was measured by Matthias and Remeika in 1957; it was thus revealed that this salt becomes ferroelectric below 8.5°C.[5] The crystal symmetry of this compound at room temperature is tetragonal,[1] and the ferroelectric axis is the c-axis. Orioli and Pieroni applied the X-ray method to this salt in 1959 and proposed a probable space group, D_4^4–$P4_12_12$ or D_4^8–$P4_32_12$; they also determined the positions of the heavy atoms.[6] The crystal symmetry and the space group of the lower temperature phase was determined by Kobayashi and Yamada in 1962, the modification being found to be tetragonal, while the space group is either C_4^4–$P4_3$ or C_4^3–$P4_2$.[7]

The lead salt at room temperature is of tetragonal symmetry and is isomorphous to the strontium salt.[1] Using the differential thermal analysis method, the authors have found a new phase transition at about −80°C. The crystal structure analysis of its room temperature phase was made by Ferroni and Orioli in 1959; they obtained a structure similar to that for the room temperature phase of the strontium.[8] Yamada analyzed the lower temperature phase of the compound and found that it to be of tetragonal symmetry, the space group being either C_4^4 or C_4^3.[9]

It seems highly desirable to obtain further information about the mechanism of the phase transitions of these three compounds. For this purpose, the present authors have studied the thermal properties of the strontium- and the lead salts and the dielectric properties of the lead salt. In the present paper, such experimental data will be presented, and the mechanisms of the phase transitions in these two salts will be discussed.

Experimental Procedures

Materials. — *a)* $SrCa_2(CH_3CH_2CO_2)_6$.—An aqueous solution of sodium carbonate (extra pure grade, manufd. by Wako Chem. Ind., Ltd.) was added to an aqueous solution of strontium chloride (Merck). The strontium carbonate precipitates were then washed with water and dried at 40°C. Powdered strontium carbonate and calcium carbonate were mixed together in the molar ratio of 1 : 2, and the mixture was dissolved in an aqueous solution of propionic acid, which, by evaporation at 40°C, yielded colorless crystals. The crystals obtained were, then, recrystallized from an aqueous solution, fed into the calorimeter vessel, and then dried in a vacuum of 10^{-4} mmHg at room temperature for about 30 hr.

b) $PbCa_2(CH_3CH_2CO_2)_6$. — The sample for the calorimetric study was prepared by a method similar to that used for strontium salt. Lead carbonate was prepared from lead dichloride (extra pure grade, manufd. by Wako Chem. Ind., Ltd.) and sodium carbonate (see in a)). For the measurement of the dielectric constant, the sample for calorimetry was dissolved again in water and kept at 25°C in a thermostated bath for about 20 days, in order to grow a single crystal about 15 mm. across. Disk specimens were then cut out with the

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1) A. Fitz and F. Sansoni, *Z. Krist.*, **6**, 68 (1882); P. Groth, "Chemische Krystallographie," Vol. III, Verlag von Wilhelm Engelmann, Leipzig (1910), p. 203.

2) I. Nitta and T. Watanabé, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **26**, 164 (1935).

3) L. P. Harris and P. M. Biefeld, *J. Am. Chem. Soc.*, **57**, 396 (1935).

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

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

6) P. Orioli and M. Pieroni, *La Ricerca Sci.*, **29**, 295 (1959).

7) J. Kobayashi and N. Yamada, *Bull. Science and Engineering Research Lab., Waseda Univ.*, **18**, 63 (1962).

8) E. Ferroni and P. Orioli, *Z. Krist.*, **111**, 362 (1959).

9) Y. Yamada, Private communication.

parallel planes corresponding to the crystallographic (110) and (001) planes. The directions of the axes were identified by taking Laue photographs. For the dielectric measurements, the specimen was sandwiched between the electrodes and dried in situ under 10^{-5} mmHg pressure for 5 hr. at room temperature.

Calorimetry. — The calorimetric measurements were made on single loadings of 25.97 g. (0.04287 mol.) and 29.53 g. (0.04071 mol.) for the strontium and the lead salts respectively. The measurements were carried out with an adiabatic calorimeter in the temperature region from 15 to 300°K. The details of the apparatus and the methods of operation have already been described.[10]

Dielectric Measurements. — The dielectric constants of the lead salt were measured for the planes (100) and (001) with a Cole-type mutual-inductance bridge (Ando Elec. Co., Ltd.) in the frequency range between 100 c.p.s. and 1 Mc.p.s., covering the temperature region from the liquid nitrogen temperature to 90°C. Temperatures were measured with two copper-constantan thermocouples attached to the electrodes; the errors are estimated to be within 0.5°. The details of the apparatus and the method. of operation have been described elsewhere.[11]

Dilatometry.—By using a simple glass-tube dilatometer, with mercury as the confining liquid, a preliminary dilatometric study was carried out with a powdered specimen of the lead salt in the temperature region from room temperature to 70°C.

Experimental Results

The Thermodynamic Properties of $SrCa_2(CH_3CH_2CO_2)_6$ and $PbCa_2(CH_3CH_2CO_2)_6$.— The heat capacity curves for the strontium and the lead salts obtained are shown in Figs. 1 and 2 respectively. The smoothed values of the heat capacities, enthalpies, entropies and Gibbs energy functions are tabulated in Tables I and II for the strontium and lead salts respectively. These values are expressed in terms of the defined thermochemical calorie, equal to 4.1840 absolute joules. The ice point is taken to be 273.15°K. The experimental errors in the heat capacity were estimated to be within 1% and 0.3% in the liquid hydrogen and the liquid nitrogen temperature regions respectively. The thermodynamic functions at the standard state are shown in Table III.

As a result of this experiment on the strontium salt, we found a new phase transition at 104°K. At an ordinary cooling rate, the temperature of the calorimeter went down to the liquid hydrogen temperature with no indication of any transition. When the calorimeter was then heated, an exothermic effect appeared at around 83°K, and the crystal was

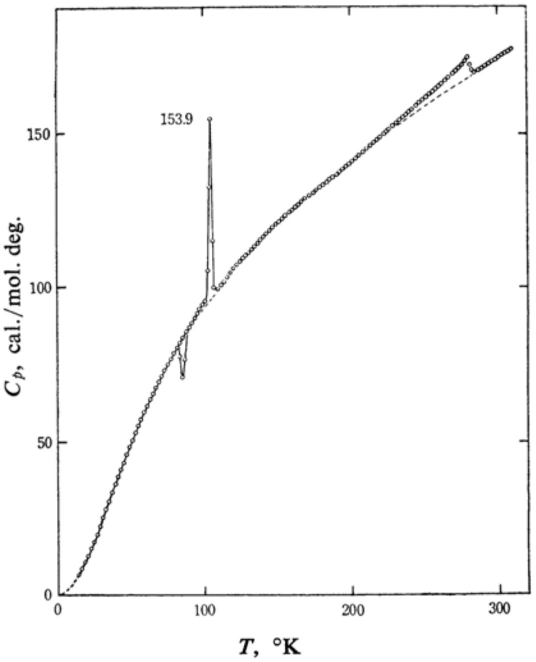

Fig. 1. Heat capacity of $SrCa_2(CH_3CH_2CO_2)_6$. Dashed curve shows the estimated normal heat capacity. Three points around 83°K below the normal curve correspond to the exothermic effect described in the text.

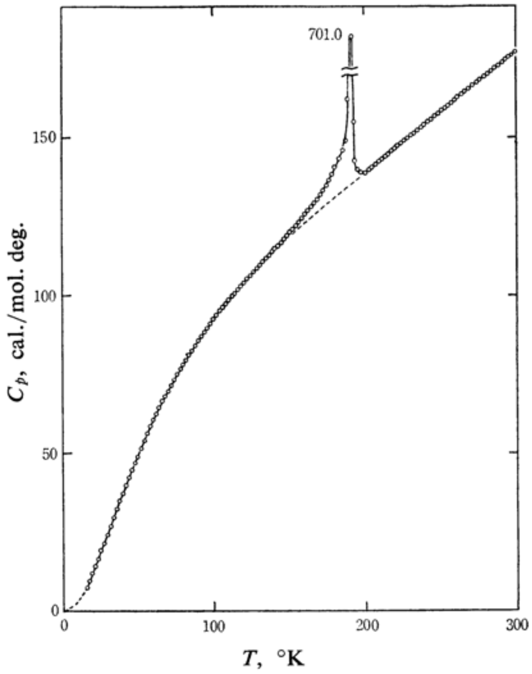

Fig. 2. Heat capacity of $PbCa_2(CH_3CH_2CO_2)_6$. Dashed curve shows the estimated normal heat capacity.

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[10] H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

[11] H. Chihara, S. Okawa and S. Seki, This Bulletin, **37**, 1373 (1964).

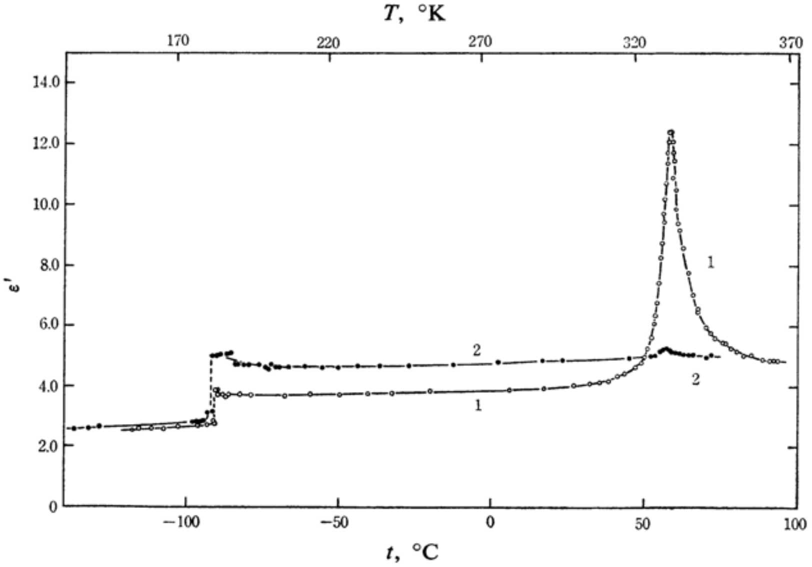

Fig. 3. Dielectric constants of $PbCa_2(CH_3CH_2CO_2)_6$ at 10 kc.p.s.
Curve 1: Parallel to c-axis, (001). Curve 2: Perpendicular to c-axis, (110)

Table I. Thermodynamic properties of $SrCa_2(CH_3CH_2CO_2)_6$

T °K	$C_p°$ cal./mol./deg.	$S°$ cal./mol./deg.	$(H°-H_0°)/T$ cal./mol./deg.	$-(G°-H_0°)/T$ cal./mol./deg.
5	(0.28)	(0.10)	(0.07)	(0.02)
10	(1.96)	(0.69)	(0.50)	(0.19)
20	11.97	4.88	3.61	1.31
30	23.61	11.88	8.27	3.61
40	35.78	20.39	13.67	6.72
50	46.44	29.57	19.22	10.37
60	58.10	39.10	24.76	14.36
70	68.81	48.88	30.31	18.59
80	78.23	58.70	35.71	22.99
90	85.90	68.40	40.89	27.49
100	94.36	77.82	45.75	32.05
100.5	95.25	78.28	45.99	32.29
104.2±0.5		Lower transition		
106.0	97.04	88.19	53.39	34.80
110	99.38	92.11	56.48	35.64
130	110.71	109.68	64.01	45.70
150	120.05	126.20	70.87	55.33
170	128.61	141.76	77.18	64.60
190	136.38	156.50	82.98	73.50
210	144.43	170.53	88.46	82.08
230	152.56	184.04	93.69	90.37
250	161.02	197.11	98.74	98.38
270	169.76	209.83	104.28	105.55
280	174.88	216.09	106.72	109.37
282.6±0.1		Upper transition		
285	170.27	219.17	107.89	111.28
290	171.73	222.14	108.99	113.17
310	177.77	233.78	113.22	120.58

TABLE II. THERMODYNAMIC PROPERTIES OF $PbCa_2(CH_3CH_2CO_2)_6$

T °K	$C_p°$ cal./mol./deg.	$S°$ cal./mol./deg.	$(H°-H_0°)/T$ cal./mol./deg.	$-(G°-H_0°)/T$ cal./mol./deg.
5	(0.24)	(0.10)	(0.07)	(0.02)
10	(2.29)	(0.72)	(0.55)	(0.17)
20	13.96	5.64	4.16	1.48
30	26.82	13.74	9.58	3.20
40	39.46	23.18	15.46	7.72
50	50.77	33.22	21.42	11.81
60	61.09	43.40	27.18	16.23
70	70.51	53.56	29.30	24.26
80	78.83	63.53	37.95	25.55
90	86.43	73.26	43.88	29.37
100	92.69	82.70	48.47	34.23
120	104.26	100.62	56.81	43.81
140	114.89	117.50	64.34	53.16
160	126.08	133.56	71.34	62.19
170	132.70	141.40	74.76	66.64
180	140.56	149.19	78.18	71.01
185	146.35	153.11	79.95	73.16
186.5	148.95	154.30	80.47	73.81
187.5	151.70	155.09	80.86	74.24
191.5±0.5		Lower transition		
194.5	140.54	168.60	92.16	76.44
196.0	137.17	169.65	92.35	77.30
197.5	138.39	170.72	91.71	79.02
200	138.77	172.45	92.31	80.16
220	146.66	186.05	96.87	89.17
240	154.33	199.12	101.34	97.80
260	162.07	211.79	105.71	106.07
280	169.89	224.07	110.02	114.08
300	177.66	236.07	114.27	121.80

TABLE III. THERMODYNAMIC FUNCTIONS AT STANDARD STATE

Substance	$C_p°_{298.15}$ cal./mol./deg.	$(H°_{298.15}-H_0°)/T$ cal./mol./deg.	$S°_{298.15}$ cal./mol./deg.	$(G°_{298.15}-H_0°)/T$ cal./mol./deg.
$SrCa_2(C_2H_5CO_2)_6$	174.1±0.7	110.7±0.4	226.9±0.9	−116.2±0.5
$PbCa_2(C_2H_5CO_2)_6$	177.0±0.7	113.9±0.5	235.0±0.9	−121.1±0.5

TABLE IV. TRANSITION TEMPERATURES, ENTHALPIES AND ENTROPIES OF TRANSITIONS

Substance	T_t, °K	ΔH_t, cal./mol.	ΔS_t, e.u.
$SrCa_2(C_2H_5CO_2)_6$	104.2±0.5 282.6±0.1	255±5 159.6±0.5	3.2±0.1 0.61±0.02
$PbCa_2(C_2H_5CO_2)_6$	191.5±0.5	1160.0±5.0	5.82±0.03
$BaCa_2(C_2H_5CO_2)_6$	266.9	1741	6.50

transformed into the stable lower temperature phase, as is shown in Fig. 1. The heat capacities of the stable and the metastable phases below the transition point are nearly equal within the range of experimental error and, therefore, the exothermic effect does not modify the interpretation of the results given in the following section.

For the lead salt, we also found two phase transition phenomena, as will be mentioned later. The upper transition, however, was not studied by the calorimetric method because of the limited capability of the apparatus. Table IV lists the transition temperatures and the heats and the entropies of transition obtained for the strontium and lead salt, together with those previously obtained for the barium salt for the sake of comparison.

The Dielectric Properties of $PbCa_2(CH_3CH_2CO_2)_6$.—As is shown in Fig. 3, the dielectric constants in each crystallographic plane, measured only in the cooling direction, jump abruptly at about 183°K; this temperature corresponds to the transition temperature observed by the

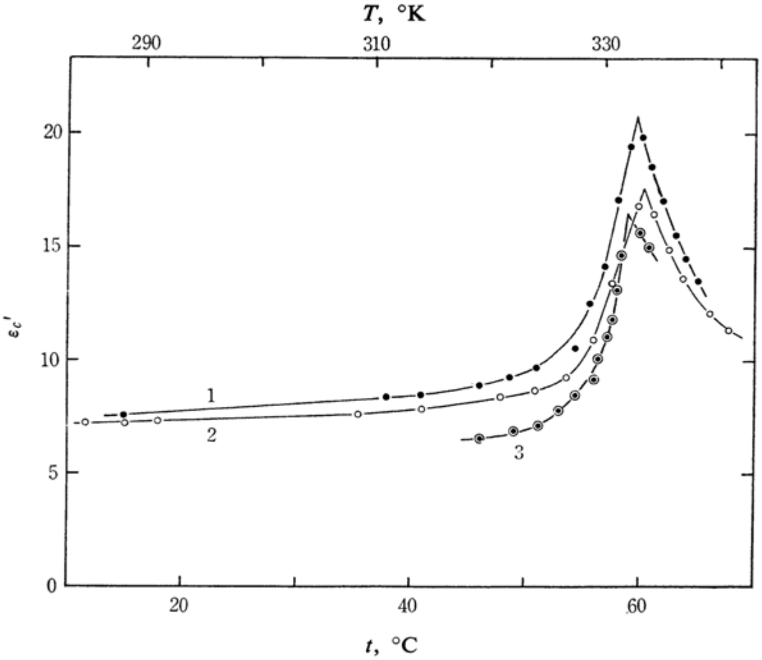

Fig. 4. Frequency dependence of dielectric constant of $PbCa_2(CH_3CH_2CO_2)_6$ (parallel to c-axis).
Curve 1 : 300 c.p.s. Curve 2 : 1 kc.p.s. Curve 3 : 10 kc.p.s.

calorimetry, as has been mentioned above. The discrepancy in the transition temperatures found by these two methods may be due to thermal hysteresis, accompanied by a phase transition. The crystals were shattered below this temperature, and measurements in the heating direction were not possible.

No anomalous dispersion was observed in the temperature region from that of liquid nitrogen to room temperature. On further heating, we found another anomaly, around 60°C, in both directions; it is more prominent when the electric field is perpendicular to the (001) plane. The maximum temperature of the ε' seems to be independent of the frequency, as is shown in Fig. 4.

With regard to this dielectric anomaly, further study was made by use of a dielectric hysteresis bridge,[12] but no hysteresis phenomenon characteristic of ferroelectricity and/or antiferroelectricity was detected either above or below this transition point. For the lower transition (183°K), no such experiment was attempted, because it has already been shown by Remeika that the crystal is not ferroelectic below room temperature.[13]

The Thermal Expansion of $PbCa_2(CH_3CH_2CO_2)_6$.—The results of the dilatometry of the lead salt are shown in Fig. 5. A conspicuous change in the expansion coefficient was detected at about 58°C, a change which corresponds to the anomaly found by the dielectric method. The shape of the change is indicative of what is called a higher-order transition.

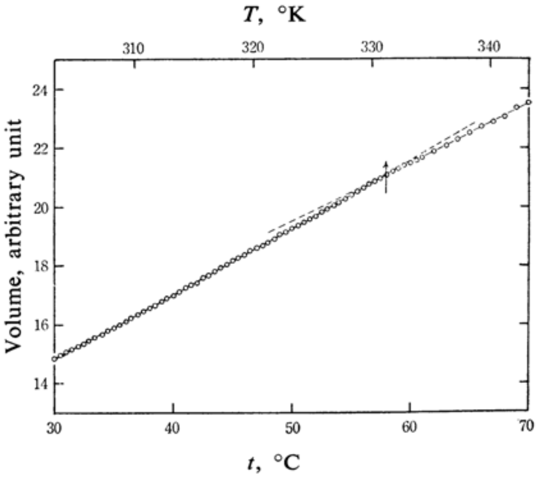

Fig. 5. Volume expansion of $PbCa_2(CH_3CH_2CO_2)_6$.

Discussion

$SrCa_2(CH_3CH_2CO_2)_6$.—As the crystal structure is not precisely known, it seems difficult to propose a detailed molecular mechanism of

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[12] H. Diamant, K. Drenck and R. Pepinsky, *Rev. Sci. Instr.*, **28**, 30 (1957).

[13] F. Jona and G. Shirane, "Ferroelectric Crystals," Pergamon Press, Oxford (1962), p. 357.

TABLE V. TRANSITION TEMPERATURES AND CRYSTALLINE DATA

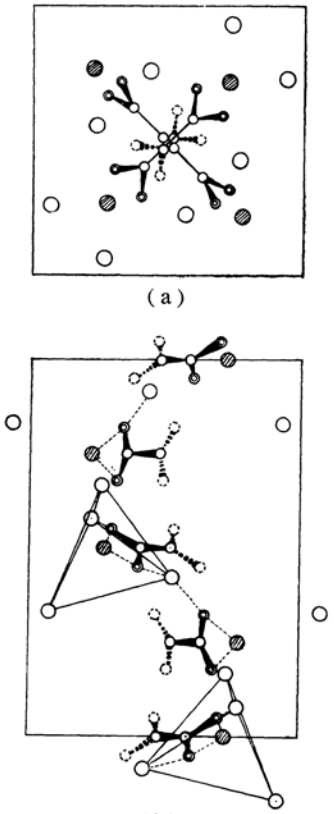
Substance	T_t, °K	Phase	Symmetry	Space group
$SrCa_2(C_2H_5CO_2)_6$		III	tetragonal	D_4^4–$P4_12_1$ or D_4^8–$P4_32_12$
	282.6			
		II	tetragonal	C_4^4–$P4_3$ or C_4^3–$P4_2$
	104.2			
		I	—	—
$PbCa_2(C_2H_5CO_2)_6$		III	—	—
	333			
		II	tetragonal	D_4^4–$P4_12_12$ or D_4^8–$P4_32_12$
	191.5			
		I	tetragonal	C_4^4–$P4_3$ or C_4^3–$P4_2$
$BaCa_2(C_2H_5CO_2)_6$		II	cubic	O^4–$F4_13$
	266.9			
		I	—	—

the ferroelectric phase transition. However, by a comparison of the crystalline data given in Table V with those for the barium salt, of which a much more precise X-ray analysis has been carried out, and also from the behavior of the heat capacity curve, it would be reasonable to assume for the strontium salt a kind of orientational order-disorder transition with respect to the methyl groups in the propionate anions.

In the room temperature phase, each methyl group must be found at two equivalent positions with an equal probability in order to satisfy the required two-fold symmetry about the axis connecting the carboxyl- and the α carbon atoms. Figure 6 illustrates one of the possible models assumed for this modification, the orientational disorder of the methyl groups being indicated by broken lines.

For the lower temperature phase, only the space group has been determined by Kobayashi and Yamada.[7] However, it would be plausible to consider that such disorder would gradually disappear as the absolute zero of temperature is approached. Thus, in the ordered state, each methyl group will be located in only one of the crystallographically equivalent sites of the two possible orientations (broken lines) depicted in Fig. 6(b).

If these two different structures are assumed for the higher and the lower temperature phases, the phase transition between them may be treated, as a first approximation, by the Bragg-Williams theory. According to this theory, with $T_t=282.6$°K determined by calorimetry, the potential difference between the two possible sites of a methyl group becomes 560 cal. mol^{-1}. As both the upper and the lower temperature phases have a tetragonal symmetry, it may be anticipated that, among the six propionate anions in the unit cell, only four, those in which the $C_{carboxyl}$–C_α axes are in the c-plane of the crystal, contribute to the phase transition. The height of the jump in heat capacity and the entropy change associated with the transition can be obtained theoretically, the values being calculated to be 11.9 cal. mol^{-1} deg^{-1} and 5.5 e.u. respectively. The experimental values are, on the other hand, 5.7 cal. mol^{-1} deg^{-1} and 0.6 e.u. for the heat capacity jump and the entropy of transition. The agreement beween the theoretical and the experimental values is thus not very good; this suggests that the short range or other correlations, including the heavy atoms, should be taken into consideration in a more detailed discussion.


(a)

(b)

Fig. 6. Crystal structure of $SrCa_2(C_2H_5CO_2)_6$. (a) (001) projection, (b) (100) projection

▨ Sr ○ Ca ○ C ◎ O

In the next place, we should like to proceed to the problem of the temperature dependence of the spontaneous polarization, P_s. The greater part of the P_s value may arise from the displacement of the metallic cations relative to the negative propionate anions, and by the electronic polarization of the large oxygen atoms. However, it seems reasonable to assume as the 1st approximation, that, each propionate anion having a small dipole moment, the change in the direction of this dipole moment, accompanied by some kind of motion in the methyl group, reflects the change in the macroscopic P_s value. The motions responsible for the effective change in this quantity may be assumed to consist of the torsional oscillation of the methyl group about the C_{carboxyl}–C_α axis, and also of the population difference between the two possible sites of the methyl groups mentioned above. Here we may assume that the magnitude of a dipole moment of one propionate anion, μ_0, at absolute zero will decrease to $\mu_0 \cos\theta$ when the methyl group of the anion rotates about the C_{carboxyl}–C_α axis through an angle, θ, around its equilibrium position at elevated temperatures. In the simple harmonic approximation, the potential function, U, is represented by $U=1/2\,\kappa\theta^2$; where κ is the effective force constant for the torsional oscillation of the methyl group. According to classical statistical mechanics, the mean value of the dipole moment at a given temperature, T, $\overline{\mu_{\text{vib}}(T)}$, is given by:

$$\overline{\mu_{\text{vib}}(T)} = \frac{\int \mu_0 \cos\theta \exp(-U/\boldsymbol{k}T)\,\mathrm{d}\theta}{\int \exp(-U/\boldsymbol{k}T)\,\mathrm{d}\theta} = \frac{\int \mu_0 \cos\theta \exp(-\kappa\theta^2/\boldsymbol{k}T)\,\mathrm{d}\theta}{\int \exp(-\kappa\theta^2/\boldsymbol{k}T)\,\mathrm{d}\theta} = \mu_0 \exp(-\boldsymbol{k}T/2\kappa) \qquad (1)$$

where $\boldsymbol{k}$ is the Boltzmann constant; the kinetic part of the partition function was not considered because it is not relevant to the present discussion.

Another contribution which decreases the mean value of the dipole moment comes from the inversion of the moment due to the order-disorder transition. In the Bragg-Williams approximation, an order parameter x is introduced which varies from unity at completely ordered, to zero at completely disordered, states. Therefore, the probability of the moment being in one of the positions is given by $(1/2)(1+x)$, and that of its being in the other, inverse, position, by $(1/2)(1-x)$.

If the contributions from the torsional oscillation, as well as from the order-disorder transition, are taken into account, the effective dipole moment at T°K is represented by:

$$\overline{\mu(T)} = \mu_0 \exp(-\boldsymbol{k}T/2\kappa)\{1/2(1+x) - 1/2(1-x)\} = \mu_0 x \exp(-\boldsymbol{k}T/2\kappa) \qquad (2)$$

where the force constant for the torsional oscillation is assumed to be the same for the two sites of the methyl group. The macroscopic spontaneous polarization, $P_s(T)$, at T°K becomes:

$$P_s(T) = N\mu_0\, x \exp(-\boldsymbol{k}T/2\kappa) = P_s(0)\, x \exp(-\boldsymbol{k}T/2\kappa) \qquad (3)$$

by the use of Eq. 2, where N is the number of those propionate anions per unit volume that have their C_{carboxyl}–C_α axes in the c-plane, and where $P_s(0)$ is the spontaneous polarization at absolute zero.

The value of κ was evaluated semi-quantitatively from Eq. 3, using the $P_s(0)=0.6$ coulomb cm^{-2} value obtained by the extrapolation of the experimental P_s vs. T curve[5,7] to absolute zero, and fitting the theoretical $P_s(T)$ to the experimental data at 188°K or at 262°K. The values obtained are 1.1 and $1.6\cdot 10^{-3}$ md. Å^{-1} respectively. Figure 7 shows the experimental[5,7] and the theoretical P_s curves calculated for these two κ values (curves 1, 2 and 3). The agreement of the experimental and the theoretical curves is fairly good if the difficulties in the accurate measurement of the spontaneous polarization are taken into account.

Now that the force constant, κ, and $\overline{\mu_{\text{vib}}(T)}$ have been obtained, we may discuss the mean maximum amplitude of the torsional oscillation of the methyl groups at each temperature on the basis of classical statistical mechanics. If the mean maximum amplitude of oscillation is represented by θ_1, the mean value of the dipole moment, $\overline{\mu_{\text{vib}}(\theta_1)}$, can be given as follows:

$$\overline{\mu_{\text{vib}}(\theta_1)} = \int_{-\theta_1}^{+\theta_1} \mu_0 \cos\theta \cdot p(\theta)\,\mathrm{d}\theta \Big/ \int_{-\theta_1}^{+\theta_1} p(\theta)\,\mathrm{d}\theta = \mu_0 \cdot J_0(\theta_1) \qquad (4)$$

where $p(\theta)$ is the probability of the dipole being rotated by an angle, θ, and $J_0(\theta_1)$ the Bessel function of zeroth order. It may easily be shown that $p(\theta)$ is proportional to $(\theta_1{}^2 - \theta^2)^{-1/2}$. By setting $\overline{\mu_{\text{vib}}(\theta_1)}$ to be equal to $\overline{\mu_{\text{vib}}(T)}$ in Eq. 1, θ_1 can be calculated for each temperature. The results of the calculation for the two κ values are shown in Fig. 7 (curves 4 and 5). The force onstant, κ, and the mean amplitude, θ_1 will be discussed in a following paper.

The features of the newly-found phase transition of this crystal at 104°K were described

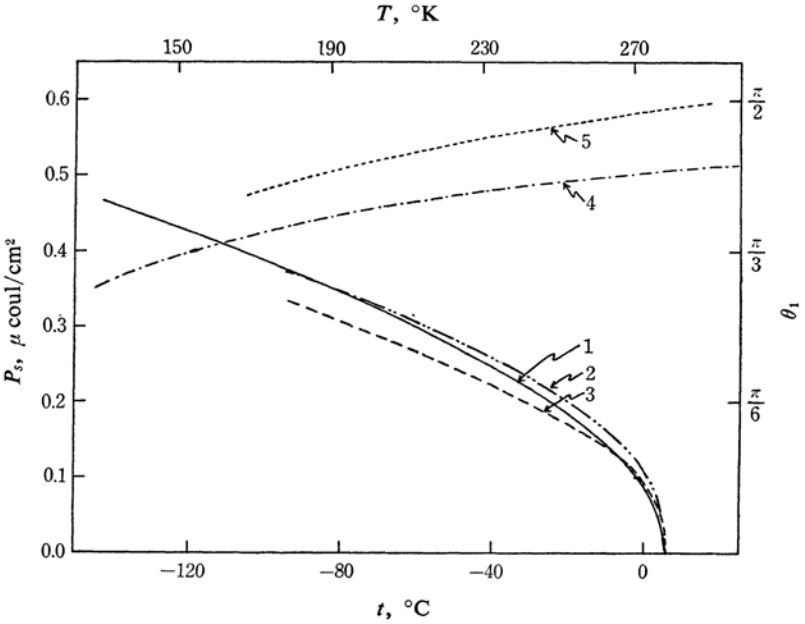


Fig. 7. Spontaneous polarization and maximum amplitude of torsional oscillation of the methyl groups in $SrCa_2(CH_3CH_2CO_2)_6$.

Curve 1 : P_s, experimental (See refs. 5 and 7)
Curve 2 : P_s, theoretical, fitted at 188°K
Curve 3 : P_s, theoretical, fitted at 262°K
Curve 4 : θ_1, calculated from curve 2
Curve 5 : θ_1. calculated from curve 3

in the previous section. Recently, Kobayashi informed us that there is a slight, discontinuous change in P_s values at about −177°C.[14] However, more detailed analyses for this transition phenomenon will require other experimental data, especially on the crystal structure of the lowest temperature phase.

$PbCa_2(CH_3CH_2CO_2)_6$. — In this salt, the enthalpy and entropy changes for the phase transition at 191.5°K are larger than those of the strontium salt, and it is noticeable that the value of $\Delta S_t = 5.8$ e.u. is rather close to that for the barium salt[4] (see Table IV).

If the mechanism assumed for the strontium and barium salts also applies to this salt, the calculated value of the entropy of transition, 5.5 e.u., agrees fortuitously well with the experimental value of 5.8 e.u.

The phase transition at about 60°C found by dielectric and dilatometric measurements may be due to some displacement of the metallic ions,* but no detailed discussion can be made at present.

No possibility of the appearence of ferroelectricity in the lead- and barium salts has been confirmed by Remeika below room temperature,[13] or by the present work for the phase above 60°C. The considerable difference between the dielectric properties of the strontium salt and those of the lead salt as well as of the barium salt is difficult to interpret from only the standpoint of the motions of the propionate anions assumed in the present paper.

A detailed discussion of the difference in the behavior of the propionate anions in these salts will be made in the following paper.

Summary

Heat capacities have been measured for strontium and lead dicalcium propionates from 15 to 300°K with an adiabatic-type calorimeter in connection with the ferroelectric phase transition of strontium salt. The heat capacities, enthalpies, entropies and Gibbs energy functions in the standard state have been determined. For the strontium salt, the transition temperature, the heat of transition, and the entropy of transition for the ferroelectric phase transition are 282.6°K, 159.6 cal. mol^{-1}, and 0.6 e.u. respectively. Another phase transition was discovered at 104°K; the heat and entropy of this transition amount to 255 cal. mol^{-1} and 3.2 e.u. respectively.

For the lead salt, a phase transition was found at 191.5°K, and the heat and the entropy of the transition are 1160.0 cal. mol^{-1} and 5.8 e.u.

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[14] J. Kobayashi, Private communication.

* A preliminary X-ray analysis was undertaken for a powdered specimen of the lead salt, above 60°C; it was thus found that the symmetry of the phase is lower than cubic.

respectively. Low frequency dielectric constants have been measured for the lead salt from the liquid nitrogen temperature to 90°C. A discontinuous change in the dielectric constants at 183°K and another dielectric anomaly at 60°C have been observed. The absence of evidence of ferroelectricity above room temperature has also been confirmed.

The ferroelectric phase transition of the strontium salt has been treated by the Bragg-Williams theory. The temperature dependence of the spontaneous polarization has tentatively been interpreted with torsional oscillations of the methyl groups of the propionate anions.

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