Polymorphic Phase Transition of Barium-dicalcium Propionate $BaCa_2(C_2H_5CO_2)_6$*

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(Received February 9, 1955)

Introduction

The crystal structure of barium-dicalcium propionate has been completely determined independently by Nitta and Watanabé[1a] and by Harris and Biefeld[1b] in 1935. According to their results, this crystal at room temperature belongs to the cubic modification and in order to satisfy the requirement of the symmetry properties of its space group, O^4-F4_13, it was found necessary to assume that the methyl group of the propionate ion should lie on the digonal axis including C–C bond of the α- and carboxyl carbons. Considering the tetrahedral bond angle of the α-carbon atom, this fact should be interpreted by assuming either the dynamical model in which the methyl group is making rotational motion, partial or free about the C_α–C_{carboxyl} bond, or the statical model which assumes that the crystal as a whole is a mixture of an equal number of ethane-carboxyl groups bent rightwards, as it were, and of those bent leftwards, each form being distributed in such a disordered way as to satisfy the digonal character mentioned above.

Now, it seems plausible to suppose that the methyl group would settle down in a definite orientation and as a result the crystal symmetry would become lower by forming an ordered lattice, if the crystal is cooled down below a certain critical temperature. We undertook this investigation to ascertain such a possibility and to elucidate the mechanism of the phase transition if it would really occur, in view of the recently recognized fact that the thermal motion as well as mutual interaction of molecules having methyl groups at their peripheries exhibit some interesting behaviour in the solid state; for example in the cases of $C(SCH_3)_4$,[2] $Pb(C_5H_5)_4$,[3] $Sn(C_2H_5)_4$,[3] $C_2(CH_3)_6$[4], etc.*

Experimental

1) Sample

a) Pure sample of barium dicalcium propionate (in the following referred to Ba-salt for brevity).—Into aqueous solution of propionic acid, calcium carbonate and barium hydroxide were dissolved, each of which are in the molar ratio corresponding to the chemical formula, and then the Ba-salt was precipitated by slow evaporation of this solution in the thermostat at about 45°C. This sample was then recrystallized twice from water. Under the poralized microscope it was confirmed that they were homogeneous cubic crystals. The chemical composition was also checked by the chemical analysis of the content of Ba^{++}.

b) Mixed crystal of the Ba-salt and $PbCa_2(C_2H_5CO_2)_6$ (Pb-salt for brevity).—It is known[5] that the Ba-salt can form mixed crystal of cubic modification with the Pb-salt up to the concentration of 14.5 molar % of the latter. The region between 14.5–44.4 mole % of the concentration of Pb-salt is known as the miscibility gap, but beyond 44.4 mole % these two components form again a mixed crystal, although they now belong to the tetragonal system.

In order to clarify the mechanism of the phase transition, we have prepared the mixed crystal of various concentrations of the Pb-salt according to the method by Grenall[6]. The specimens of the molar ratios of Ba^{++} and Pb^{++} ions corresponding to (100: 2), (100: 5), (100: 8) and (100: 100) were used. The concentration of Pb^{++} ion was determined by the chemical analysis and the real formation of the mixed crystal was ascertained by taking Debye photographs. To make the crystal as homogeneous as possible, the crystallized specimens were ground up to very fine powders and then they were again put into the mother liquors and left for a long time. These processes were repeated two or three times.

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* A part of this investigation has been already published in *J. Chem. Phys.*, 19, 1061 (1951).

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1a) I. Nitta and T. Watanabé, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) 26, 164 (1935).

1b) L.P. Harris and P.M. Biefeld, *J. Am. Chem. Soc.*, 57, 396 (1935).

2) H. J. Backer and W. G. Pedrock, *Rec. trav. chim.*, 61, 553 (1943).

3) L.A.K. Staveley et al., *J. Chem. Soc.*, 2290 (1950).

4) F. Seyer, R. B. Bennett and F. C. Wiliams, *J. Am. Chem. Soc.*, 71, 3447 (1949).

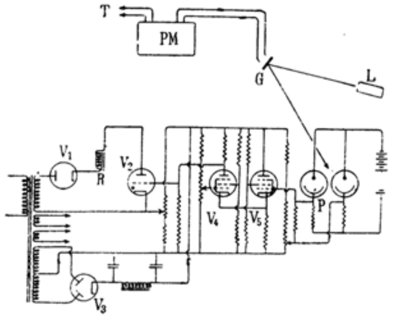
* As one part of a series of our investigation on the rotational transition, we have studied the phase transitions of $Be_4O(CH_3CO_2)_6$ and $C_6(CH_3)_6$. These results will be published shortly.

5) P. Groth, Chemische Krystallographie III, 203.

6) A. Grenall, *J. Chem. Phys.*, 17, 1036 (1949).

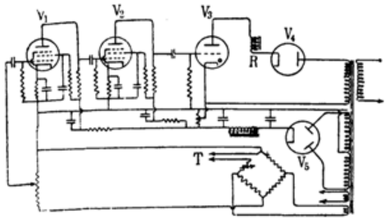
2) Apparatus and Procedures

a) Specific heat measurements.—For the preliminary study to ascertain the occurrence of the phase transition we carried out the differential thermal analysis using the Ba-salt and found in fact the existence of the phase change at about −6°C. To investigate further in detail we then measured the specific heats in the vicinity of this temperature in heating as well as in cooling directions by the conduction calorimeter, the description of which was already given precisely in the previous paper⁷⁾. In the present investigation, we have improved the apparatus in the control of the temperature difference between the calorimeter heater and the cell containing the sample and also deviced an automatic regulator of the thermostat surrounding the calorimeter. The electric circuit used for the maintenance of the temperature head mentioned above is shown in Fig. 1. By use of this, we can regulate automatically the temperature difference at a constant value (we usually maintained it between 1°–5°C.) within the fluctuation of ±0.01°C. Special precaution was taken to prevent the effect on the photoelectric tube caused by the variation of the brightness of the room. The relay circuit employed for the thermostat is shown in Fig. 2.



L	Lamp
PM	Potentiometer
T	to Thermocouple
G	Galvanometer
R	Magnetic Relay
V_1	KX–12F
V_2	66G–GT
V_3	5Y3–GT
V_4, V_5	6AC7–GT
P	Photoelctric Tube

Fig. 1. Electric circuit for the maintenance of the temperature head of calorimeter.



V_1, V_2	6SJ7–GT
V_3	66G–GT
V_4	KX–12F
V_5	5Y3–GT
T	to Thermister
R	Magnetic Relay

Fig. 2. Relay circuit for the thermostat.

Thermister prepard from the mixture of cobalt- and nickel-oxides was used*. The temperature fluctuation was minimized within 0.1–0.01°C.

b) Dilatometric measurements.—By using a simple glass-made dilatometer with mercury as a dilometomer liquid⁷⁾ the thermal expansions below and above the said transition temperature were measured with the rate of 0.1°C/min. both in heating and cooling directions.

Results and Discussion

The data of specific heats of the Ba-salt as well as of the mixed crystals of the Ba-

TABLE I

SPECIFIC HEATS OF $BaCa_2(C_2H_5COO)_6$

Heating direction				Cooling direction			
t°C	$C_p \frac{cal}{mole}$	t°C	$C_p \frac{cal}{mole}$	t°C	$C_p \frac{cal}{mole}$	t°C	$C_p \frac{cal}{male}$
−17.60	179.96	−5.05	298.86	−16.25	182.4	−6.00	399.4
−16.25	176.96	−4.49	301.72	−14.85	184.8	−5.34	848.9
−14.84	177.28	−4.00	332.60	−13.50	190.2	−4.67	1432.3
−13.50	179.83	−3.60	924.44	−12.10	192.7	−4.66	998.6
−12.10	179.99	−3.08	730.61	−10.76	205.8	−4.52	634.7
−10.96	182.53	−2.92	485.38	−10.09	257.3	−4.39	322.3
−9.38	190.33	−2.78	211.50	−9.38	339.6	−4.00	172.8
−8.04	203.22	−2.66	196.06	−9.12	344.7	−2.66	175.2
−7.34	252.23	−1.50	175.37	−8.71	327.0	0.00	175.2
−6.69	334.67	−0.00	175.37	−8.04	293.5		
−6.30	345.02			−7.36	285.7		
−5.34	301.41			−6.69	298.0		

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7) I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**, (9) 25 (1950).

* We are very much indebted to Mr. Saito of the physics department of this faculty who kindly prepared the present thermister for us.

and Pb-salts (Ba: Pb=100:100 (mole)) are shown in Tables I and II and the specific heat curves of all kinds of mixed crystals investigated are illustrated in Figs. 3-7.

TABLE II
SPECIFIC HEATS OF (Ba, Pb) $Ca_2(C_2H_5COO)_6$; Ba: Pb=100: 100 (mole)
Heating direction

t°C	$C_p \frac{cal}{mole}$	t°C	$C_p \frac{cal}{mole}$
107.45	181.55	162.38	221.11
109.66	182.03	164.45	220.14
111.85	182.28	166.45	217.95
114.05	182.28	168.41	215.77
118.35	182.76	170.43	212.61
122.74	182.76	172.43	208.73
127.04	183.00	174.44	205.09
131.26	183.97	176.46	200.24
135.47	184.46	178.45	197.32
137.56	184.70	180.46	194.41
141.72	197.32	182.45	190.04
143.79	200.24	184.41	188.10
145.85	208.00	186.39	187.13
147,90	211.40	188.36	187.37
149.96	213.83	190.30	187.61
152.03	216.74	192.00	186.89
154.60	218.20	194.20	185.92
156.18	222.57	196.20	186.16
158.25	223.54	198.20	183.97
160.33	221.84	200.00	184.22

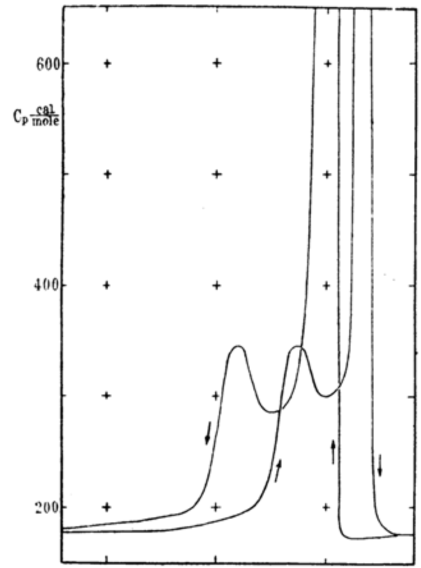

Fig. 3. Heat capacity vs. temperature curve (pure Ba-salt).

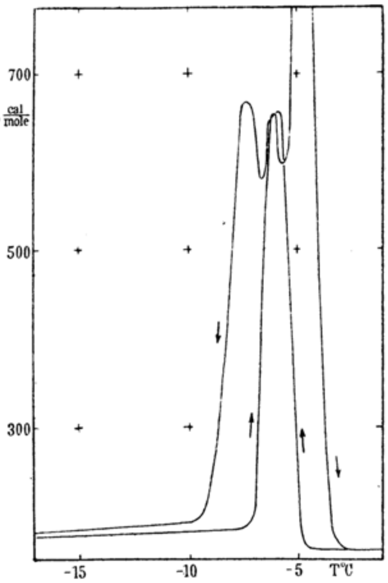

Fig. 4. Heat capacity vs. temperature curve (Ba-salt: Pb-salt=100: 2).

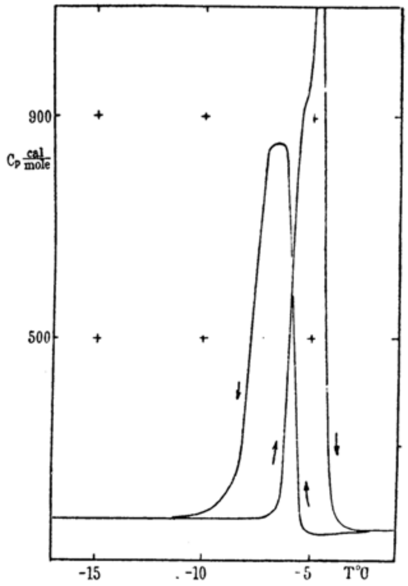

Fig. 5. Heat capacity vs. temperature curve (Ba-salt: Pb-salt=100: 5).

The tramsition temperatures, the heats and entropy changes at these transition temperatures of these salts are all summarized in Table III.

In this table and the figures given above, we can find that both the heat and entropy changes become smaller as the Pb^{++} content increases and the general trends of the specific heat curves are not always the same in heating and cooling directions.

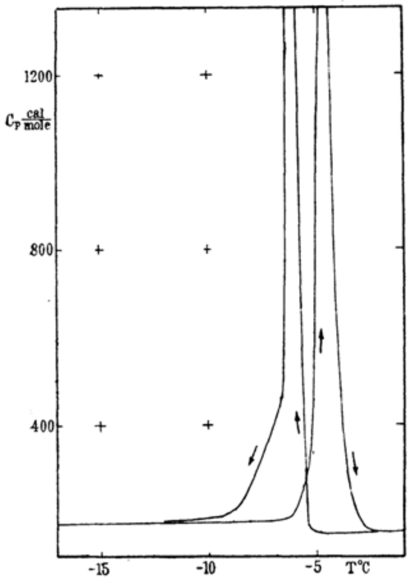

Fig. 6. Heat capacity vs. temperature curve (Ba-salt: Pb-salt = 100: 8).

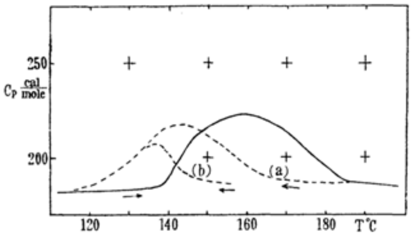

Fig. 7. Heat capacity vs. temperature curve (Ba-salt: Pb-salt = 100: 100).

Now, let us consider the mechanism of the phase transition a little more in detail. For this purpose we should like to consider first the simpler case of the phase transition of the pure Ba-salt and thereafter to proceed to the effect of the substitution of the Pb^{++} ion. It will be convenient for the following discussion, however, that we give a brief account of the relative molecular arrange-

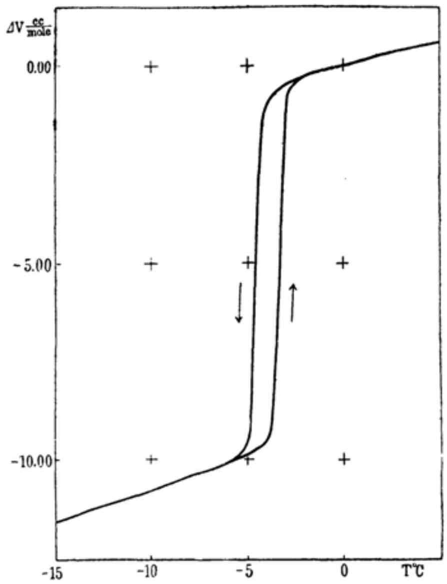

Fig. 8. Volume vs. temperature curve of pure Ba-salt.

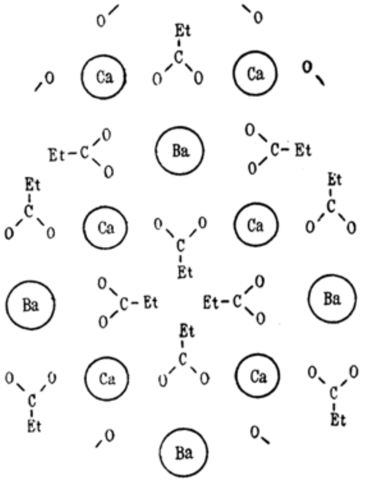

Fig. 9. Two dimensional schematic representation of relative arrangement of carboxyl radicals around metallic ions.

TABLE III

TRANSITION TEMPERATURE, HEATS AND ENTROPIES OF TRANSITION, AND VOLUME CHANGE AT TRANSITION OF Ba- AND MIXED SALTS

			Ba-Salt	$(Ba, Pb)Ca_2(C_2H_5CO_2)_6$		
				100: 2	100: 5	100: 8
Transition Temperature t°C	Heating	LTS	−6.30	−6.02	−4.80	−4.50
		HTS	−3.23	−4.38	—	—
	Cooling	LTS	−9.10	−7.34	−6.20	−6.20
		HTS	−4.67	−5.80	—	—
Heat of Transition cal./mol.	Heating		1741	1464	1355	1260
	Cooling		1745	1470	1356	
Entropy of Transition e.u.	Heating		6.502	5.45	5.05	4.54
	Cooling		7.00	5.50	5.08	
Volume Change	V_{cc}/mol.		9.07	—	—	—

ment in this crystal. As shown schematically in Fig. 9, a barium atom is surrounded by twelve oxygen atoms of the six carboxyl radicals at the corners of an octahedron and a calcium atom is surrounded by six oxygen atoms at the corners of a nearly regular octahedron. Each oxygen atom of the carboxyl group is facing to barium on one side and to calcium on the other, and, while the behavior of the two oxygen atoms in a carboxyl group is the same towards the central barium atom, it is only one of these oxygen atoms that comes into contact with the same calcium atom. However this latter oxygen atom is taking an important part of mediator between the two kinds of metallic cations, as it were, and the whole crystal is joined together by them.

As is evident from the constitution of this crystal, we may point out two main contributions to the cohesive energy; viz, the electrostatic interaction between the positive metallic ion and the negative carboxyl radical and the van der Waals forces common in organic molecular crystals.

Taking these circumstances into consideration, we may put forward a tentative explanation of the mechanism of this transition phenomenon which seems to be not quite unreasonable. As already mentioned this transition is supposed to be intimately connected with the enhancement of the thermal motion of the methyl groups of the propionate ion. Although the complete crystal structure of the low temperature modification is not yet determined, it may be supposed that the six methyl groups which belong respectively to six different Ba^{++} ions confront each other, so to say, nearly hexahedrally in this modification as in the cubic one. Below the transition point, these methyl radicals may be more or less fixed in definite orientations and as shown schematically in Fig. 10, the distance of the oppositely situated methyl groups, for instance, A–A, will be a little larger than those of the other two pairs, B–B, for the reason given above that the crystal system will become tetragonal or orthorhombic*. As the temperature rises, the rotational vibration of these methyl groups about the C_α–C_{carboxyl} bond will become more and more violent. In this case, if the distance between methyl groups are small enough to come in contact with each other, then we must assume that their mutual location should vary in phase just like meshing-gear-wheels and in such a case it will be realized that only the four of the six methyl groups can come into coupling as shown in Fig. 10. This situation may be said to be similar in a way to the rotational motion in long chain hydrocarbon crystals considered by Andrew[8]. We must recall here the fact that the LTS (low temperature side) hump in the spesific heat curve is more sensibly affected by the substitution of Ba^{++} ion by Pb^{++} ion. Such replacement of the metallic ion will probably cause a more remarkable effect on the electrostatic interaction than the Van der Waals forces. The movement of carboxyl radical attached to the substituted Pb^{++} ion will be more limited, since the ionic radius of Pb^{++} ion is smaller than Ba^{++} ion. Indeed, we confirmed by taking Debye photographs of the two sorts of mixed crystals containing Pb^{++} ion in molar ratios of (100 : 2) and (100 : 5), that the decrease of the lattice constant of the former amounts to 0.3% and that of the latter to 0.4%. Thus, the LTS phase transition will be more or less directly connected with the change of the thermal motion of the carboxyl radicals, this change influencing at the same time the rotational vibration of the methyl groups. When the temperature rises further, the rotational vibration will go over into a hindered rotational motion in which the six methyl groups will become equivalent and the crystal will be converted into the cubic modification. Thus, we may suppose that the HTS (high temperature side) large specific heat peak will be due to the equal participation in the rotational motion of all the six methyl groups which will be accompanied by a considerable volume change. Such explanation of the present two-step transition will be not unreasonable from the experimental fact that, while the LTS specific heat hump

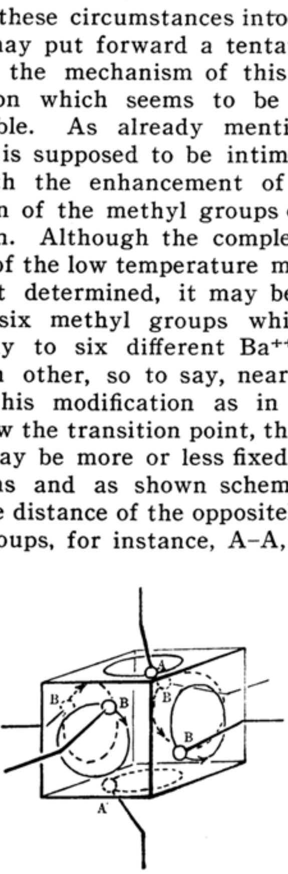

Fig. 10. Schematic illustration of the correlated molecular motion of six methyl groups.

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* We confirmed by the observation of the appearence of the birefringence below the transition point that the low temperature one has no longer any cubic structure. According to the private communication of Professor Oda of Osaka University of Liberal Arts and Education, it is also confirmed by Debye-photograph that this low temperature phase has lower symmetry than the cubic modification.

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

shows no appreciable volume change, the HTS one goes along with a considerable volume change (see Fig. 8).

Although the correlation between the thermal motions of the two different parts in one propionate ion is not clear in detail, it is rather remarkable that such a small content of Pb^{++} ion causes a considerable effect. Probably the neighbouring lattice region surrounding the substituted Pb^{++} ion would undergo a sort of lattice distortion, the effect of which will be propagated through the whole crystal by the action of carboxyl radical which plays the role of an mediator in the crystal structure as mentioned above. Anyhow, our discussion hitherto given may be only of qualitative nature and for the more quantitative discussion of such a complex phenomenon, crystal structure determination below as well as in the transition temperature region, study of nuclear magnetic reasonance absorption in respect to the movement of the methyl group, spectroscopic study of the part of the carboxyl radical, etc. are highly desirable.

Finally a few remarks may be added for the phase transition which occurs in the tetragonal mixed crystal having the composition of (100 : 100) molar ratio of Ba^{++} and Pb^{++} ions. As shown in Fig. 7, this phase transition takes place at around 160°C. In comparison with the cubic modification of the mixed crystal containing a small amount of Pb^{++} ion, the transition temperature is displaced to much higher temperature and this phase transition occurs very gradually, the shape of its anomalous region being similar to that of $BaTiO_3$[9] at 393°K or of $C_6(CH_3)_6$ at 135–136°K[10]. The dotted line (a) is for cooling direction and the curve (b) corresponds also to the specific heat in the same direction starting from about 155°C where the phase transition is not completed yet in heating process. Hysteresis phenomenon is also very remarkable. It was ascertained by the microscopic observation that the high temperature form belongs to the cubic modification. In this respect, the above-mentioned phase transition, which occures at about -6°C, seems to be displaced to this higher temperature region by virtue of the large amount of the Pb^{++} ion. However, for the detailed discussion on the relation between them, the crystal structure as well as other physicochemical properties should be studied further.

In conclusion, the authors wish to express their hearty thanks to Professor Nitta for his helpful suggestions and gracious encouragement throughout this work. A part of the cost of this research was defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Expenditure Grant from the Ministry of Education to which the thanks of the present authors are due.

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[9] H. Blattner and W. Merz, *Helv. Phys. Acta*, **21**, 210 (1948).

[10] Huffman, Parks and Daniels, *J. Am. Chem. Soc.*, **52**, 1547 (1930).