Polymorphic Phase Transition of Beryllium Oxyacetate $Be_4O(CH_3CO_2)_6$*

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Introduction

In 1943, by Preston and Trotter1) as well as by Beevers2) it was found that the symmetry of Laue photograph of the cubic modification of this crystal changes from T_h-m3 to O_h-m3m in the temperature interval of 30°∼50°C. Beevers explained this phase transition as due to the change in the parameter values of the carboxyl oxygen atom from (−0.17, −0.06, −0.04) to (−0.17, −0.05, −0.05) when the temperature rises and passes the transition range, thus bringing all the oxygen atoms exactly onto (110) planes. On the other hand, in 1947, Jaffray3) measured the specific heat of this crystal below and above the transition region and found that at 40.5±0.5°C there is an anomaly of typical λ-type in the heat capacity curve.

In 1949, Watanabé and Saito4) observed that this crystal became waxy when it was heated above 160°C, though it melted very sharply at about 285°C. They studied the crystal structure of this high temperature modification as well as the above-mentioned phase transition at about 40°C by the X-ray method and in order to explain the results they put forward a mechanism of the order-disorder type. They also investigated the so-called γ-form of this crystal which was obtained by sublimation at ordinary pressure.

We have undertaken to study these phase transitions as a part of our thermochemical investigation on the nature of the so-called plastic crystals.

Experimental

a) Sample.—Beryllium oxide was dissolved in acetic acid and by evaporating the excess acid in the evaporating dish we obtained the crude specimen. This was then recrystallized three times from chloroform and finally subjected to fractional sublimation under high vacuum (10^{-5} mmHg), m.p. 286.7°C.

b) Apparatas and Procedures.—The apparata used for the differential thermal analysis,5) dilatometry6), vapor pressure measurement7) and the conduction calorimetry8) were all the same as those that have been used hitherto in our laboratory, so that their description may be omitted here.

Experimental Results

i) Differential thermal analysis.—As mentioned above, by the observation of the change of appearance of the crystal above 160°C by Watanabé and Saito, it was strongly inferred that this crystal would undergo a phase transition around this temperature. To determine the accurate temperatures of transition and melting, we carried out the differential thermal analysis. One of the typical curves is given in Fig. 1. From this curve, it was found that the magnitude of the heat effects accompanying these two phase changes are comparable with each other. To examine the nature of the polymorphic phase transition further in detail, we then performed a series of thermal analyses under various conditions. All the experimental curves of the deflection of the galvanometer for measuring the temperature head are shown in Fig. 2.* We may enumerate some features of these curves as follows:

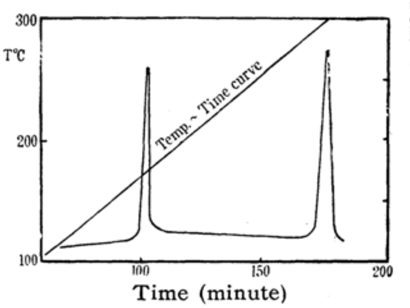

Fig. 1. Curves of differential thermal analysis of $Be_4O(CH_3CO_2)_6$.

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* A part of this research was already published in *Nature*, **163**, 226 (1949).

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1) G. D. Preston and T. Trotter, *Nature*, **151** 166 (1943).

2) C.A. Beevers, *Nature*, **152**, 447 (1943).

3) J. Jaffray, *Compt. rend.*, **225**, 106 (1947).

4) T. Watanabé and Y. Saito, *Nature*, **163**, 225 (1949), T. Watanabé, Y. Saito and H. Koyama, ibid., **164**, 1056 (1949).

5) H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).

6) I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**, (10) 11, (1950).

7) I. Nitta, S. Seki, M. Momotani and K. Sato, *J. Chem. Soc. Japan*, **71**, 378 (1950).

8) S. Seki, M. Momotani, K. Nakatsu and T. Oshima, This Bulletin, (in press).

* The figure attached at the highest temperature side of each curve means the temperature at which the heating was stopped.

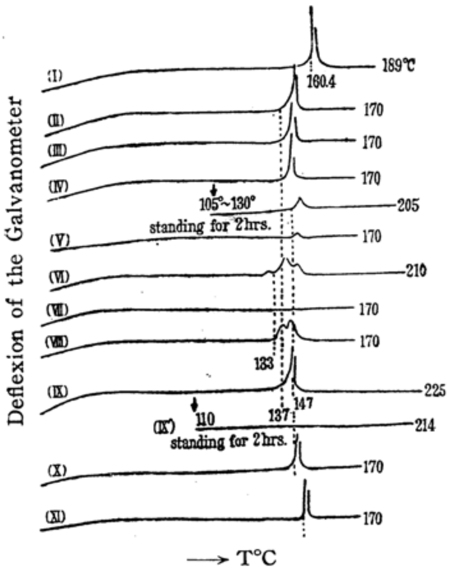

Fig. 2. Curves of differential thermal analyses of $Be_4O(CH_3CO_2)_6$ at various conditions.

(a) Curve (i) represents the result of the sample which has been stored for about half a year in a desiccator over calcium chloride. As shown in the figure this sample shows the highest transition point of 160.4°C (heating velocity is about 2∼2.5°C/min.).

(b) When the sample was not heated above around 210°C, it always shows the transition point at about 140°∼147°C (curves (ii), (iii), (iv)).

(c) If the sample was cooled down below 110°C, standing it at this temperature for about two hours and then heated again, it showed a small hump at about 147°C. However, if it was not cooled down below 110°C, no transition phenomenon could be observed.

(d) If the sample was heated above 210°C and then left to natural cooling down to the room temperature, there appeared no transition phenomenon in the heating curve which was measured again, even on the following day (two sets of curves (vi) and (vii), and (ix) and (ix)'). However, if the supercooled sample which showed no phase change was ground in an agate mortar at room temperature, it exhibited phase change of a rather complex nature (curves (vi) and (viii)).

(e) Freshly prepared sample by sublimation shows normal phase change at about 147°C (see Fig. 1 and curve (x)). But, when such sample was thoroughly ground to very fine powders, it showed a little higher temperature of phase change (curve (xi)).

A possible explanation of the somewhat complex characteristics of these curves may be given after the following description on the dilatometric investigation.

ii) Dilatometric investigation.—Since the method of differential thermal analysis was not sensitive enough to detect a phase change with small heat effect, we then measured the volume change very carefully using the freshly prepared specimen in order to find out some clues to explain the complex nature just mentioned above. As the results, we could find out that the expansion coefficient changes at four temperatures, namely, 32±0.5°C, 42±0.4°C, 77±0.4°C, and 124.5±0.5°C, and further that the volume itself increases abruptly at 148°C by a great amount which corresponds to about 5.6% of the volume at 25°C. Of these temperatures, the secound one, 42±0.4°C, coincides with that determined by Jaffray, while the third and the fourth were discovered first by the present experiment. Moreover, it was revealed that the transition at 148°C shows a hysteresis phenomenon covering over a wide range of temperatures, the volume change in the cooling curve taking place at 110±2°C, far below the transition point observed in heating direction. Among these changes of expansion coefficient at four temperatures only the first one has the plus sign. It is to be added that after these results were published,** Jaffray⁹⁾ recently confirmed our experimental results.

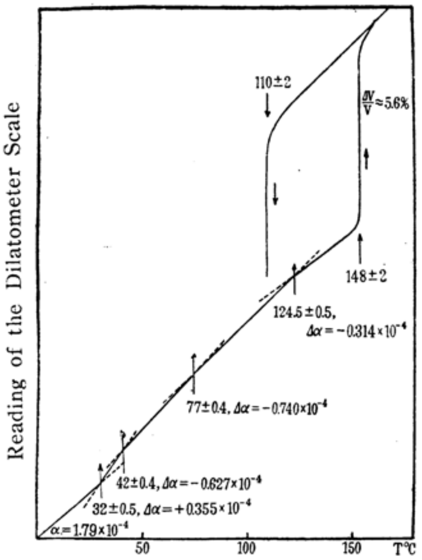

Fig. 3. Volume vs. temperature curve of $Be_4O(CH_3CO_2)_6$.

iii) Heat capacity measurement.—As mentioned above, the transition at about 42°C seems to be of particular interest, since the crystal structures on each side of the transition temperature have been already known. Although Jaffray has measured the heat capacities at these temperatures, the temperature range was not wide enough to determine the heat of transition, so we measured anew the heat capacities extending our measurements over a much wider temperature range both in heating and cooling directions. Our

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** See footnote (*) in page 325.

9) J. Jaffray, Compt. rend. de la deuxième Réunion Annuelle tenue en Commun avec la Commission de Thermodynamique de l'Union Internationale de Physique Changements de Phases. p. 267. (1952).

data are given in Table I and the heat capacity curves are shown in Fig. 4. In the figure, we can realize that the heating curve almost completely coincides with the cooling one, showing no hysteresis. By this measurement, it was made clear that the temperature (32°C) where the expansion coefficient increases sharply, corresponds to the temperature where the heat capacity curve begins to increase.

TABLE I

HEAT CAPACITY OF $Be_4O(CH_3CO_2)_6$

Heating direction		Cooling direction	
t°C	$C_p\frac{\text{cal.}}{\text{mole}}$	t°C	$C_p\frac{\text{cal.}}{\text{mole}}$
0.00	116.5	85.22	138.1
13.02	118.7	79.60	136.0
19.4	120.93	76.84	135.5
25.7	123.0	75.20	138.7
31.48	127.9	73.81	131.9
38.15	133.7	73.15	130.7
41.78	136.3	71.78	138.4
43.05	129.6	70.58	132.4
44.20	126.6	69.20	131.5
50.21	126.9	62.20	129.0
62.20	129.0	56.25	126.8
66.87	129.9	50.21	124.7
69.20	130.9	47.82	124.1
71.52	134.1	45.41	124.7
72.68	131.8	43.05	127.7
73.81	132.1	40.60	135.0
74.99	132.9	40.08	134.4
76.13	135.9	38.15	132.2
76.84	134.9	35.66	130.8
78.46	134.8	30.72	126.1
80.73	135.9	25.70	122.8
83.00	136.6		
85.22	137.8		
97.48	139.1		

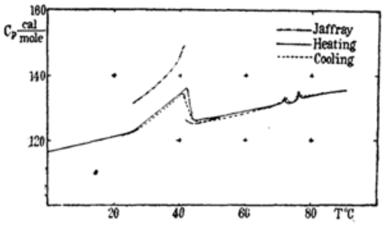

Fig. 4. Heat capacity vs. temperature curves of $Be_4O(CH_3CO_2)_6$.

iv) Vapor pressure measurement.—This material sublimes slowly even at room temperatures, so we attempted to measure the sublimation pressures below and above the transition point to determine the heat of sublimation as well as the heat of transition. The results are all given in Table II. The heat and entropy of fusion were estimated to be 6.5 kcal./mole and 11.6 e.u., respectively by comparison of the corresponding areas of the two peaks obtained by the thermal analysis (see Fig. 1).

TABLE II

VAPOR PRESSURES OF $Be_4O(CH_3CO_2)_6$

t°C	P mm Hg×10^3	t°C	P mm Hg×10^3
120.7	2.828	152.6	52.22
124.9	4.081	156.3	65.33
126.5	4.539	160.0	92.92
134.4	9.508	164.6	124.8
135.1	11.30	168.3	164.1
139.9	15.93	172.8	213.6
145.6	29.60		
145.7	30.43		
148.6	39.98		

$$\log P = 15.029_9 - 6934.8/T$$
(below the transition point)
$$\log P = 12.626_6 - 5922.8/T$$
(above the transition point)

	$\Delta H\frac{\text{kcal.}}{\text{mole}}$	$\Delta F\frac{\text{cal.}}{\text{mole}}$	ΔS e.u.
Sublimation (low-temp. phase)	31.7	31734–60.170T	60.2
Sublimation (high-temp. phase)	27.1	27102–44.598T	44.6
Transition	4.6	—	15.6

Discussion of Results

As pointed out by Watanabé and Saito, the fact that the melting point of this material is abnormally higher than those of other compounds of homologous series and also that the soft waxy appearance above the transition temperature of 148°C suggests that the high-temperature modification will belong to the so-called plastic crystal. By our measurements of the entropy changes at the transition and melting points, we can confirm the fact that their prediction is correct. They further investigated the X-ray diffraction effects of the high temperature modification at various temperatures of 160°, 170°, 220°, 270° and 280°C. According to them, the crystal structure gradually changes with the rise of temperature and approaches the final structure which belongs to a rhombohedral lattice with the cell dimensions of $a = 9.72$ kX and $\alpha_r = 54°20'$, containing one molecule in it.[10] They noticed, however, that the crystal structure just above the transition temperature may be of a little lower symmetry than the final rhombohedral lattice structure which is reached gradually between 220° and 280°C. In our thermal analysis study, we have noticed the curious fact that the sample which was

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[10] Y. Saito, *X-rays*, 7, 1 (1952).

previously heated above about 210°C did not exhibit the transition phenomenon in the repeated heating experiments carried out on the following day. This phenomenon and the above-mentioned results of the X-ray investigation seem to imply that the crystal structure in the temperature region between the transition point and about 210°～220°C will retain some characteristic feature of the structure below the transition point rather than that of the high temperature form above 220°C.

The transition at 148°C is of a typical 1-st order type, judging from the discontinuities of vapor pressure curves and of volume change. This transition point is, however, sensitive to the history of the crystal lattice and is displaced to higher temperatures when the crystal was stored for a long time after the preparation (see curve (i) in Fig. 2) or ground mechanically (curve (xi) in Fig. 2). The curves of the differerential thermal analysis sometimes show more or less complex structures which are observed in the temperature region about 130°～147°C (see curve (vi) and (viii) in Fig. 2). This process may also be explained as due to the relative degree of metastability of the phases which exist between 124°C and 148°C and of the high temperature phase above the transition point.[11] This result also reminds us of the fact that $Pb(C_2H_5)_4$ and Sn $(C_2H_5)_4$[12] show several melting points depending on the heating or cooling rate as well as on the previous histories. These phenomena suggest that for the molecular crystals composed of molecules which have methyl groups at their periphery, it is rather difficult to establish the real equilibrium state on account of the meshing-gear-like interaction between methyl groups belonging to one and the same molecule as well as to the neighbouring other molecules.

Now, we proceed to the discussion of the phase transition at about 40°C. As shown in Fig. 4, the heat capacity curve is of typical λ-type and the heat of transition is very small compared with that at 147°C. Nonexistence of the hysteresis phenomenon is in agreement with the prediction by Staveley from the stand point that the lattice strain energy is very small in the case of higher-order phase transition[13]. Thus, these facts reasonably indicate the higher order type of this transition.

As already mentioned, the crystal structures above and below this transition point are already investigated in detail by several authors. According to their results, it may be said that there may exist two kinds of molecules of *d*- and *l*- types, so to speak, below the transition temperature in reference to the two equivalent potential minima for the orientation of the oxygen pair of the carboxyl group.* Confining our study to the intramolecular interaction, no difference can exist between these two kinds of molecules. However, if we consider the intermolecular interaction, the interaction energy between two different types of molecule will be different from that between two of the same type of molecule and the former is probably larger than the latter. As a result, it may be assumed that the *d*- (or *l*-) type molecule is the more stable the larger the number of the neighbouring *l*- (or *d*-) type molecules. As the temperature rises, the rotational vibration of the carboxyl group about C–C axis becomes more and more violent and the distinction between these two types of molecule will disappear when two oxygen atoms of the carboxyl group surmount the potential barrier between the two potential minima. The difference of intermolecular energies between a pair of the same kind of molecules and a pair of different kinds just mentioned above also disappears at the same time. In such a way, we may understand this phase transition as a kind of order-disorder type. In the case of the ordinary order-disorder transition of an alloy system, the interchange of the atomic position between different kinds of atoms takes place, while in the present case only the transition of atoms from unequivalent potential minima to equivalent ones occurs within one and the same molecule. Thus, it may be said that this case is somewhat similar to the so-called Ising model designed for the ferromagnetic transition, etc.

Finally, we should like to propose a tentative theory on the rotational transition of the molecular crystal of this sort, although it may be of qualitative nature.

Following the theory of Fowler on the rotational phase transition[14], we assume all the libration and rotation to be classical. Then the total energy in Hamiltonian form is

$$H=T+V, \qquad \text{with } V=\frac{W}{2}\cos\theta,$$

where T is the kinetic energy of rotation of the rigid rotator with axial symmetry, V

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[11] A.R. Ubbelohde, *Nature*, **169**, 832 (1952).

[12] D.G. Thomas and L.A.K. Staveley, *J. Chem. Soc.*, (1951) 2572.

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

* As to the possibility of two forms of this molecule, see reference 11).

[14] Fowler: *Statistical Mechanics* (1936), p. 810.

the potential energy due to the surrounding field of force, W the height of the hindering potential of the rotator, and θ the displacement of the axis of figure from a single preferred direction of equilibrium. The probability $P(\theta)d\theta$ of finding the rotator between θ and $\theta+d\theta$, is

$$P(\theta)d\theta=\int_0^{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}e^{-H/kT}dP_\theta dP_\varphi d\varphi d\theta$$

The partition function f is then given by

$$f=\frac{2\pi IkT}{h^2}\cdot 2\pi\cdot\int_0^{\pi}e^{-V/kT}\sin\theta d\theta$$

$$=\frac{8\pi^2 IkT}{h^2}\cdot\frac{kT}{W}\sin hW/kT \qquad (3)$$

where I is the moment of inertia of the rotationg group of the molecule. As is well known, Fowler defined the degree of nonrotation S by the next equation:

$$S=f_0/f$$

where

$$f_0=\int\int_{H<\beta V}e^{-H/kT}dP_\theta d\theta \qquad (4)$$

Here, the parameter β is the measure of nonrotation in the sense that the molecule having less energy than βV can not rotate anyhow. However, the physical meaning of β is not very obvious, and this ambiguity may be removed in a slightly improved way by defining the order parameter by the following quantity,

$$S=\int_0^{\pi}P(\theta)(-\cos\theta)d\theta/f$$

$$=\int_0^{\pi}e^{-W/2kT\cos\theta}(-\cos\theta)\sin\theta d\theta$$

$$=\coth W/2kT-2kT/W \qquad (5)$$

At 0°K, $S=1$ and as temperature rises S decreases gradually from 1. According to the Bragg-Williams approximation, we then assume

$$W=W_0S+W_0^\circ\,. \qquad (6)$$

In this equation, W_0° is the part of W which does not depend on S. In other words, this means that even above the transition temperature the molecules are not necessarily to be looked upon as free rotators. W_0° is, therefore, a measure of hindering potential which is not affected by the long range cooperation. Thus, if the ratio of W_0°/W is not zero, the straight line representing the above equation does not start from the origin in the plot of S against α $(=W/2kT)$ (see Fig. 5).

Now, on the assumption, in the case of the present substance, that for the potential energy V for the rotation of carboxyl radical,

$$V=\frac{W}{2}\cos 2\theta,$$

the order parameter S mentioned above becomes

$$S=I_1/I_0,$$

where I_1 and I_0 are the 1-st and 0-th order modified Bessel functions, respectively. The relation between S and α is shown in Fig. 5, and that between S and T/T_c is given in Fig. 6. In these figures two cases of W_0°/W_0 $=0$ and $=0.1$ are represented. By the ordinary method we can then calculate the energy as a function of temperature as illustrated in Fig. 7. By differentiation we can finally find the heat capacity curve as shown in Fig. 8.

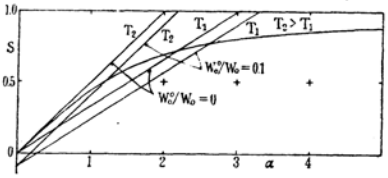

Fig. 5. Dependence of order parameter S upon α.

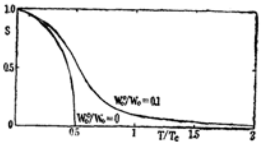

Fig. 6. Relation between order parameter S and T/T_c.

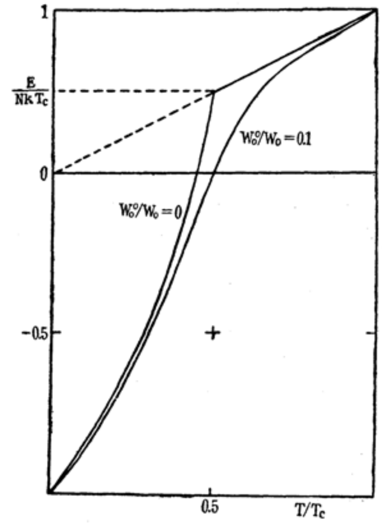

Fig. 7. Curves of E/NkT_c vs. T/T_c.

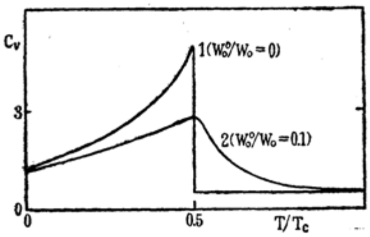

Fig. 8. Curves of C_v (calculated) vs. T/T_c.

From the results of these curves, we can find out that when the ratio $W_0°/W_0$ is not zero, there occurs no phenomenon of the latent heat. The heat capacity curve (1) in Fig. 8 is similar in shape to the actual behavior found in this material at about 40°C. In this case the value of W_0 is calculated to be about 2.5 kcal./mole which seems to be not so unreasonable an order of magnitude for a molecular crystal like the present material.

Although these results are only of qualitative nature, it may be of some significance to understand the rotational phase transition in such a simple way.

In conclusion, the authors should like to express their hearty appreciation to Professor Nitta for his gracious interest during this work and to Dr. Y. Saito of Osaka City University and Dr. K. Motojima of Kyoto Ritsumeikan University for kindly giving the samples used. 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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Note added in Proof: K. N. Semenenko, Yu. P. Simanov and A. V. Novoselova have recently raised an objection about the reality of the transition at 148°C. (Vestnik Moskov Univ., 9, No. 2, Ser. Fiz-Mat. i Est. Nauk No. 1, 61 (1954)). They, however, dealt only with the monoclinic γ-modification, even though prepared by three different methods, and did nothing with the cubic modification. Because they carried out neither the thermal analysis nor the dilatometric investigations of the cubic modification, it is quite natural that they did not observe the transition at 148°C. The determination as to which of the monoclinic or the rhombohedral modification is more stable at high temperatures requires measurements of the vapor pressures of the monoclinic form in addition to those of the rhombohedral form described in the present paper.