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An X-ray Study on the Phase Transition of Phenanthrene Crystal

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The presence of a higher-order phase transition at around 60—70°C in phenanthrene crystal, previously suggested by the anomalies in electrical conductivity and in thermal expansion, and by the endothermic phenomenon, has been confirmed through an X-ray powder diffraction study. The results disclose the following facts: (1) the phenomena of the transition begin about 45°C and gradually become remarkable with a rise in the temperature, until the phenomena practically cease to occur at 68—69°C; (2) the lattice constants for the monoclinic cell increase conspicuously in the temperature range from about 50°C to 68°C, while both the crystal system, which is monoclinic, and the space group, $P2_1$, remain unaltered on passing through the transition temperature, and (3) the unit cell dimensions of the high-temperature modification determined at 80°C are: $a=8.54$, $b=6.25$, $c=9.55$ Å and $\beta=99.0°$.

In previous papers,[1,2] the present authors have reported that anomalies in electrical conductivity and in thermal expansion, and an endothermic phenomenon were shown by phenanthrene in the temperature range from about 60°C to 70°C. Namely, the resistivity starts to increase abruptly with the rise in the temperature around 64°C; the anomalous phenomenon continues to exist until the temperature reaches near 71°C, at which point the resistivity becomes 6—7 times greater than that at 64°C. The mean coefficient of the linear thermal expansion definitely undergoes a conspicuous change at 68.7°C; the value of 1.67×10^{-4} abruptly changes to 1.05×10^{-4} at this point. There appears in the DTA thermogram an endothermic peak with a vertex-temperature of about 71°C, accompanied by the enthalpy change of 0.26 kcal/mol associated with the endothermic behavior.

The authors also suggested in those papers that the above-mentioned anomalous properties reveal the presence of a phase transition at around 60—70°C in the phenanthrene crystal, and that the phase transition may be of what is called a higher-order transition.

It seemed that it would be of interest to make an X-ray investigation in order to see what will occur in the course of transformation from a low-temperature modification to a high-temperature

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[1] S. Matsumoto and T. Tsukada, This Bulletin, **38**, 2023 (1965).
[2] S. Matsumoto, *ibid.*, **39**, 1811 (1966).

one. This paper will present the results of detailed studies, by the X-ray powder method, of the phase transition in phenanthrene crystal.

Experimental

The material used in this experiment was finely-ground phenanthrene (Eastman Kodak), purified by a combination of recrystallization and zone-melting. The specimen was in the form of a pellet, with a thickness of 2 mm and a diameter of 13 mm, compressed at 13 ton/cm^2.

X-Ray diffraction measurements were performed by means of a diffractometer (Toshiba ADX-103) equipped with a high-temperature specimen holder (Toshiba SUR-021), using CuK_α-radiation. In order to see what difference exists between a low-temperature modification and a high-temperature one, the diffraction patterns in the $8° < 2\theta < 57°$ region were recorded both at room temperature and at 80°C. Scanning was made at 0.5° per minute. Furthermore, a series of diffraction patterns in the limited region of $18° < 2\theta < 26°$[*1] were obtained at various temperatures, from room temperature up to about 85°C, for the purpose of observing the variation in the diffraction patterns with the rise in the temperature. In this case, the patterns were recorded at a scanning speed of 0.5° per minute and at a heating rate of about 0.2°C per minute.

Results and Discussion

The X-ray diffractometer record at 80°C is shown in Fig. 1, along with the record at room temperature (20°C). All the reflections appearing

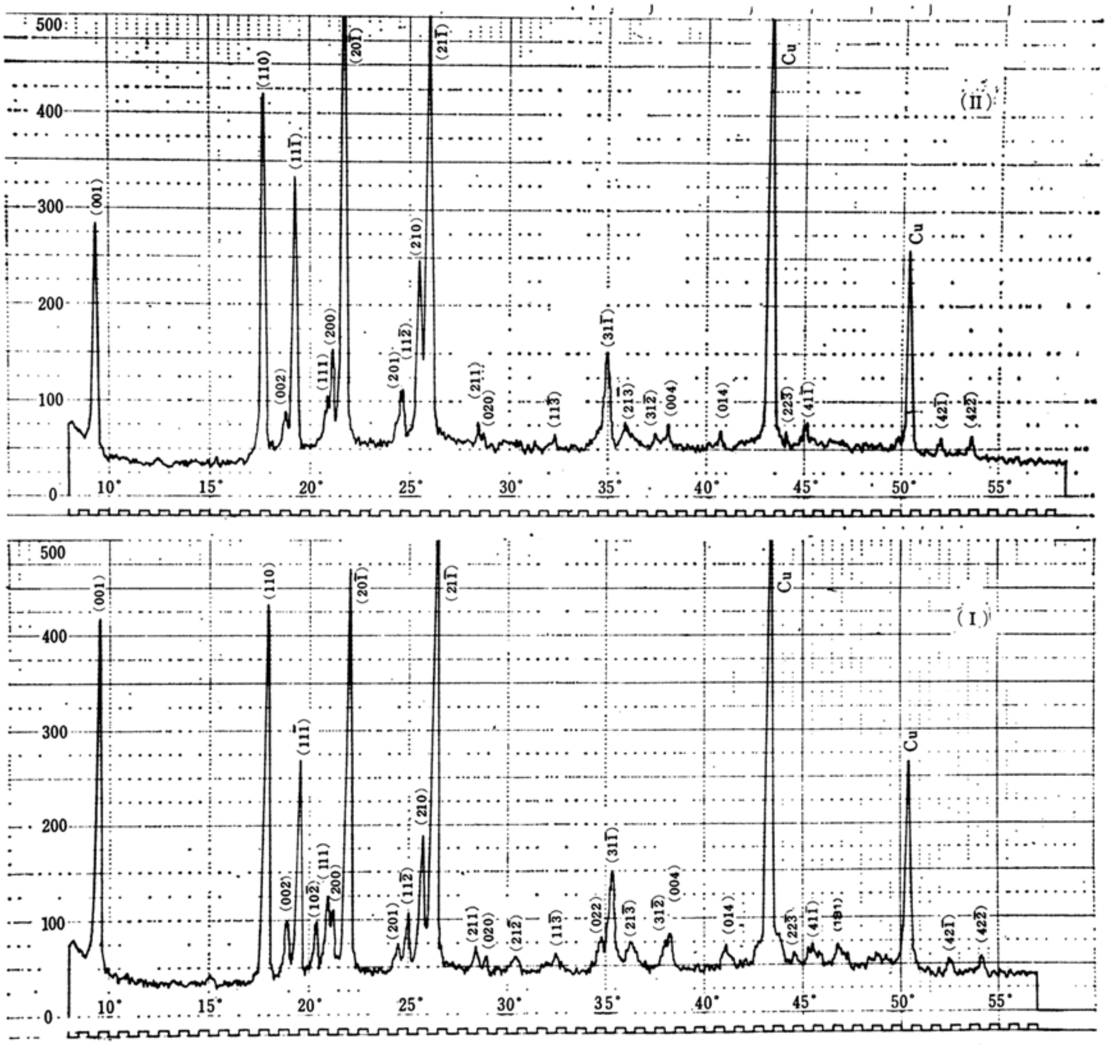

Fig. 1. The X-ray diffractometer records of phenanthrene at 20°C (I) and 80°C (II).

[*1] This limited region involves, as is shown in Fig. 1, the (002), (11$\bar{1}$), (10$\bar{2}$), (111), (200), (20$\bar{1}$), (201), (11$\bar{2}$) and (210) reflections, which were used to observe the variation in the intensity of reflection and in the lattice constants with the rising temperature.

on a diffraction pattern at room temperature were satisfactorily indexed without any ambiguity on the basis of the lattice constants for the monoclinic cell with the space group, $P2_1$, of phenanthrene, $a=8.46$, $b=6.16$, $c=9.47$ Å and $\beta=97.7°$, as given by Trotter.³⁾ The diffraction pattern at 80°C was, as a whole, nearly the same as that at room temperature, although some reflections showed distinct differences in their relative intensities and their fine structures. The most noticeable changes are as follows. The $(10\bar{2})$, $(21\bar{2})$ and (131) reflections almost diasppear at 80°C. Each pair of reflections, (111) and (200), (201) and $(11\bar{2})$ and (022) and $(31\bar{1})$, which are neighbors, become degenerated into nearly a single one at 80°C. Intensities of a pair of the reflections, (111) and (200), mentioned above become reversed at 80°C. We were lead to the assumption that these phenomena appearing in the diffraction pattern at 80°C might be connected with a phase transition of a higher-order at around 60—70°C, the presence of which had been suggested in our previous papers.¹,²⁾

The similarity of the diffraction pattern at 80°C to that at room temperature might suggest that there were no changes in either the crystal system or the space group in this phase transition. No changes in them were practically verified through indexing or by applying the extinction rule for reflections. There was no crystal system other than a monoclinic one which was successful in indexing the reflections on a diffraction pattern at 80°C, although all the possible crystal systems were tried. Moreover, the possible space group was either $P2_1$ or $P2_1/m$ from the extinction rule, but the $P2_1$ space group is more reasonable in this case because the $P2_1/m$ space group is excluded from Basak's steric considerations.⁴⁾

A series of diffraction patterns were taken at various temperatures in the $18°<2\theta<26°$ region, the region which was the most convenient for the following investigations.

The Intensity-Variation of the Reflection with the Temperature. Among those reflections which changed their intensities, the $(10\bar{2})$ reflection showed the remarkable change; it almost disappeared at 80°C. Therefore, it was chosen as the representative reflection in order to observe the intensity-variation with the temperature. The results are shown in Fig. 2, where the height of the reflection peak is conveniently adopted as the intensity of reflection.

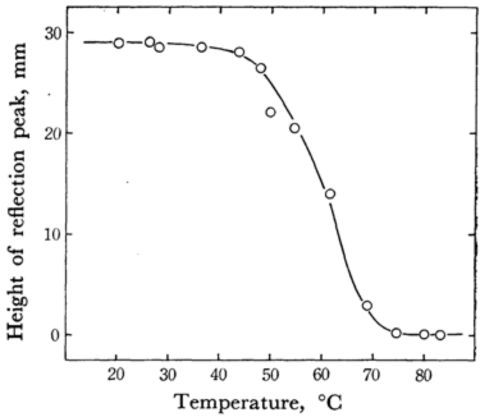

Fig. 2. The intensity-variation of the reflection $(10\bar{2})$ with temperature.

The intensity gradually decreases from about 45°C and almost disappears at 75°C; there is also an abrupt decrease in the range from about 50°C to 70°C. The intensity variation is not observed practically below 45°C or above 75°C. This relation between the intensity of reflection and the temperature may characterize a higher-order phase transition.

The Variation of the Axial Angle with the Temperature. The variation of the axial angle, β, with the temperature was determined from the lattice spacings of the (002), $(11\bar{1})$, (111) and (200) planes observed at various temperatures. Namely, the equation, (2), used to evaluate the axial angle, β, is derived from the well-known relation, (1), of the lattice parameters of a monoclinic system:

$$1/d^2 = h^2/a^2\sin^2\beta + k^2/b^2 + l^2/c^2\sin^2\beta - 2hl\cos\beta/ac\sin^2\beta \qquad (1)$$

$$\cos\beta = d_{200}d_{002}(1/d^2_{11\bar{1}} - 1/d^2_{111}) \qquad (2)$$

As is shown in Fig. 3, the axial angle, β, increases linearly between room temperature and about 45°C, and above about 70°C; however, in the temperature range from about 50°C to 68°C, the angle shows a continuous but sharp increase. These results are in accordance with the intensity-variation of the $(10\bar{2})$ reflection with the temperature described in the preceding paragraph.

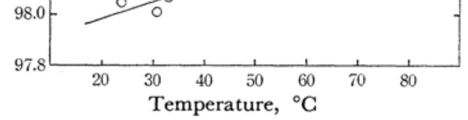

Fig. 3. The variation of the axial angle β with temperature.

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3) J. Trotter, *Acta Cryst.*, **16**, 605 (1963).

4) B. S. Basak, *ibid.*, **1**, 224 (1948); *Indian J. Phys.*, **24**, 309 (1950).

The Variation of the Lattice Constant with the Temperature. Figure 4 gives the variation of the lattice constant, a, with the temperature. The value of a at various temperatures was evaluated from the following relation:

$$a = 2d_{200}/\sin\beta$$

where d_{200} is the lattice spacing of the (200) plane observed at various temperatures, and where β is the axial angle at each temperature obtained from the relation between the axial angle and the temperature shown in Fig. 3.

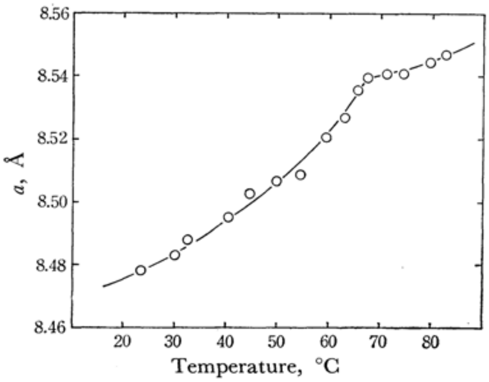

Fig. 4. The variation of the lattice constant a with temperature.

As is shown in Fig. 4, the shape of a graphical representation of the variation of the lattice constant with the temperature is characteristic of a higher-order transition. These results are consistent with those obtained regarding the variation in reflection-intensity and axial angle with the temperature, the results described in the preceding paragraphs.

The temperature variations in the reflection-intensity, the axial angle and the lattice constant were found to be quite reproducible and reversible. Diffraction patterns obtained after cooling were practically the same as those obtained before heating.

The results of the X-ray study mentioned above disclose the following facts: (1) the phase transition of phenanthrene is of a higher-order; both the crystal system, which is monoclinic, and the space group, $P2_1$, may remain unaltered on passing through the transition temperature, (2) the transition temperature range is as wide as about 25°C; the low-temperature modification starts to change into a high-temperature one from about 45°C, with the change almost fully completed at 68—69°C, and (3) the lattice constants and the axial angle show anomalous increases, the increases much larger than their ordinary increases associated with a thermal expansion, in the temperature range from about 50°C to 68°C. These facts are quite consistent with the results obtained in investigations by dilatometry and by differential thermal analysis.2)

The Unit Cell Dimensions of the High-temperature Modification. The unit cell dimensions of the high-temperature modification determined at 80°C are given in Table 1, together with those of the low-temperature modification determined from our data at 20°C. The unit cell dimensions at 20°C in Table 1 agree very well with those at room temperature given by Trotter.3)

TABLE 1. THE UNIT CELL DIMENSIONS OF THE HIGH- AND LOW-TEMPERATURE MODIFICATIONS

	80°C	20°C
a	8.54 Å	8.46 Å
b	6.25	6.18
c	9.55	9.48
β	99.0°	97.8°

In the course of the transformation from the low-temperature modification to the high-temperature one, the π-orbital overlap of molecules in phenanthrene crystal is expected, from the anomalous increment of the lattice constants on passing the transition temperature, to be considerably decreased. This decrease in the π-orbital overlap must be connected with the anomaly in electrical conductivity observed around 64—71°C.1)

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