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Studies on the Phase Transition near the Melting Point in Acetylferrocene

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The entitled compound shows an anomalous temperature dependence of the mean-square amplitude of iron atoms derived from the Lamb-Mössbauer factor near the melting point. To clarify the anomaly, the crystal structure of this compound was determined at room temperature by X-ray diffraction. The crystal is monoclinic with space group $P2_1/c$, a=20.595(2), b=5.7909(4), c=18.840(2) Å, β=116.870(7)°, U=2004.4(3) Å^3, and Z=8. Weissenberg and oscillation photographs taken at a high temperature lead us to propose a model in which the acetylferrocene molecules rotate around the central iron atoms.

It is well-known that ferrocene undergoes an apparently second-order transition at 163.9 K from a disordered ($P2_1/a$) phase to an ordered ($F\bar{1}$, Z=16) phase.[1-3] In the low-temperature phase, the crystal consists of an ordered array of molecules, while it takes on a partial degree of rotational disorder structure above the transition point. Rotation of the cyclopentadienyl (C_p) rings has been observed in ^{1}H-NMR spectra, and ascribed to a cooperative jump-rotation, rather than a free rotation.[4]

Formylferrocene was reported by Daniel and Leadbetter to show a plastic crystal phase between 44 °C and the melting point.[5] The structure of the plastic crystal phase was assigned to a simple face-centered cubic lattice with a unit-cell parameter a=9.99 Å accompanied by an orientational disorder based on a diffuse scattering pattern.[5] Recently the structures of both the crystal and plastic phases have been determined to be orthorhombic by using single-crystal X-ray diffraction and the transition from the crystal to plastic phase has been attributed to translational molecular motions along the a axis, in accordance with the temperature dependence of the Mössbauer spectrum.[6]

1,1′,2,2′-Tetrachloroferrocene and 1,1′,2,2′,3,3′,4,4′-octachloroferrocene were also reported to exhibit a mesophase by Hedberg and Rosenberg.[7] The structure and the nature of the mesophase of 1,1′,2,2′-tetrachloroferrocene were studied using X-ray diffraction and Mössbauer spectroscopy.[8] 1,1′-Diethylferrocene was found to have a glassy state by thermal analysis, and the thermal vibration was studied by measuring the temperature dependence of the Lamb-Mössbauer factor for iron atoms.[9]

Although the critical phenomena before melting and phase transitions in ferrocene derivatives are of great interest, little is known concerning the structural features of the mesophases. It was preliminarily reported that some kind of transition occured a little below the melting points in acetyl and carboxylferrocenes.[10] In the present paper, the crystal structure of acetylferrocene was determined at room temperature by X-ray diffraction and the transitional process was investigated, based on the detailed data obtained from oscillation and Weissenberg photographs, Mössbauer spectroscopy and thermal analysis.

Experimental

Mössbauer Spectra. Acetylferrocene was prepared by the method described in Ref. 11, and purified by recrystallization and sublimation. The purity was confirmed by checking the melting point and by elemental analysis. No impurity was detected in IR, NMR, and Mössbauer spectra.

Mössbauer spectra were obtained using an Austine Science Associated Mössbauer spectrometer. Velocity calibration was carried out based on the room-temperature spectra of metallic iron. By fitting the resonance line-shape to a Lorentzian function, the Mössbauer parameters were extracted.

Low-temperature measurements were preformed using a CA thermocouple embedded in a copper sample holder in a cryostat. The precision of the temperature measurement was within approximately ±1° over a period of several hours. A high-temperature apparatus was constructed with a heater in a vaccum furnace. The samples were sealed to prevent sublimation. Temperature was checked by a CA thermocouple with precision of about ±0.1°.

Structure Determination and Refinement. Brown needle crystals of acetylferrocene were grown from a benzene-hexane solution. Although preliminary oscillation and Weissenberg photographs indicated an orthorhombic symmetry, this specimen was concluded to be a twin as described below. A single crystal of 0.30×0.25×0.35 mm was sealed in a Lindemann-glass capillary and the intensities were measured with Mo $K\alpha$ radiation monochromated by a graphite plate.

Crystal data are tabulated in Table 1. The positions of the Fe, C, and O atoms were deduced from the sharpened Patterson maps and successive Fourier syntheses. The posi-

TABLE 1. CRYSTAL DATA AT 24 °C

Acetylferrocene	M.W. 228.1
Monoclinic	
Space group	$P2_1/c$
a/Å	20.595(2)
b/Å	5.7909(4)
c/Å	18.840(2)
β/°	116.870(7)
U/Å^3	2004.4(3)
Z	8
D_c/g cm^{-3}	1.517
μ/cm^{-1}	1.54

tion of all the hydrogen atoms were deduced from difference synthesis. There are two crystallographically independent molecules I and II in a unit cell. After several cycles of refinement it turned out that the methyl groups of the two crystallographically independent molecules take two alternative sets of positions with an equal probability.

The block-diagonal least-squares program HBLS-4[12)] was employed assuming anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. Two reflections, 210 and 102, were excluded in the refinement, since they suffered from secondary extinction. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1974).[13)] Unit weight was adopted for all the reflections. The R values reduced to 0.036 for 3194 independent reflections with $|F_o|>3\sigma(|F_c|)$ up to $2\theta=55°$. Final atomic parameters are given in Table 2.[††]

Acetylferrocene often crystallizes as a twin which pretends to have an orthorhombic unit cell as shown by dotted lines in Fig. 1, because $c^*\sin(90-\beta^*)$ is close to $a^*/2$. There are two equivalent monoclinic components A and B described by solid and broken lines respectively, with a common b* axis; the rotation of the monoclinic component A around the c axis by 180° gives the component B.

TABLE 2. POSITIONAL PARAMETERS
($\times 10^5$ FOR FE AND $\times 10^4$ FOR C AND O)

	x	y	z	$B_{eq}\times 10/\text{Å}^2$
FE(1)	14365(2)	22916(9)	42569(3)	25(1)
C(1)	330(2)	1979(8)	3654(2)	39(1)
C(2)	661(2)	−191(7)	3736(2)	36(1)
C(3)	1126(2)	−77(8)	3367(2)	40(1)
C(4)	1082(3)	2137(9)	3061(2)	48(2)
C(5)	586(3)	3430(8)	3235(2)	48(1)
C(6)	1981(2)	5088(6)	4917(2)	32(1)
C(7)	2455(2)	3724(8)	4738(2)	37(1)
C(8)	2484(2)	1486(7)	5041(2)	35(1)
C(9)	2025(2)	1415(7)	5419(2)	31(1)
C(10)	1710(2)	3658(6)	5347(2)	27(1)
C(11)	1167(2)	4408(7)	5609(2)	35(1)
C(12)	828(3)	2603(9)	5896(3)	54(2)
O(1)	1011(2)	6422(5)	5594(2)	53(1)
FE(1′)	64602(2)	24021(9)	21803(3)	26(1)
C(1′)	6587(2)	−95(7)	1492(2)	36(1)
C(2′)	7197(2)	−61(7)	2251(2)	39(1)
C(3′)	7518(2)	2157(8)	2373(3)	44(1)
C(4′)	7103(2)	3494(7)	1675(3)	45(2)
C(5′)	6528(2)	2080(8)	1134(2)	38(1)
C(6′)	5543(2)	1531(7)	2274(2)	33(1)
C(7′)	6142(2)	1640(8)	3043(2)	38(1)
C(8′)	6434(2)	3903(9)	3159(2)	43(1)
C(9′)	6029(2)	5213(7)	2471(2)	36(1)
C(10′)	5468(2)	3776(6)	1914(2)	28(1)
C(11′)	4953(2)	4446(7)	1105(2)	34(1)
C(12′)	4464(2)	2610(9)	568(3)	51(2)
O(1′)	4920(2)	6423(6)	877(2)	52(1)

Results and Discussion

Anomalous Mean-Square Amplitude of Iron Atom. Figure 2 shows the temperature dependence of the mean-square amplitude of the iron atoms estimated from the areal intensities of Mössbauer spectra of acetylferrocene.[10)] The mean-square amplitude is proportional to the absolute temperature up to room temperature, indicating an harmonic intermolecular vibration. The value of the mean-square amplitude at room temperature by applying the high-temperature approximation[9)] from 78 K to room temperature is 3.0×10^{-2} Å^2 for acetylferrocene, while the value based on the isotropic thermal factor in the X-ray diffraction study is 3.2×10^{-2} Å^2. A remarkable anomaly in the temperature dependence of the mean-square amplitude is found at temperatures a few degrees below the melt-

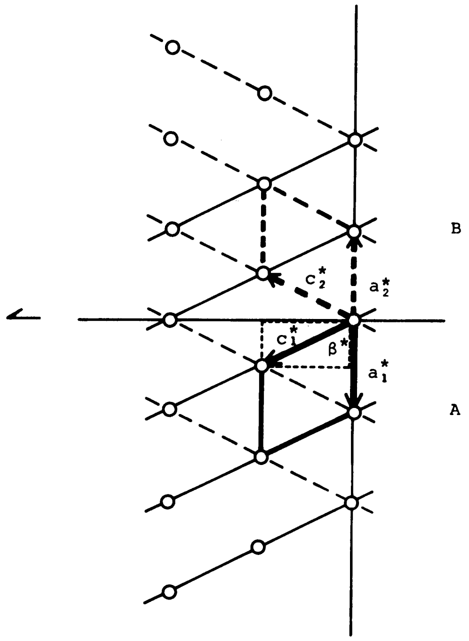

Fig. 1. Unit cell of the twinned crystal consisting of two equivalent monoclinic components looks like an orthorhombic unit cell shown by the dotted lines, because $c^*\sin(90-\beta^*)$ is close to a^*.

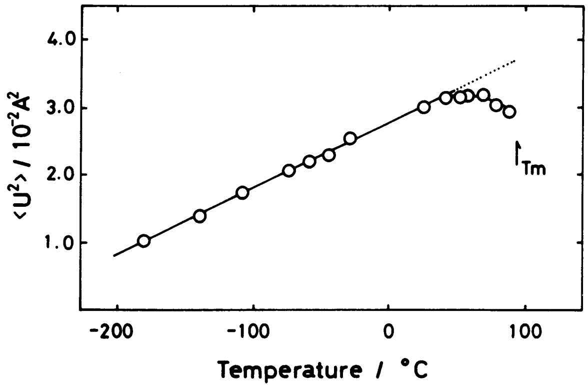

Fig. 2. Temperature dependence of the mean-square amplitude of the iron atoms in acetylferrocene.

[††] The complete, F_o-F_c data, atomic parameters of hydrogen atoms and bond distances are deposited as Document No. 8427 at the office of the Chemical Society of Japan.

ing point as shown in Fig. 2. The deviation from the dotted line suggests that the thermal motion cannot be explained by a simple harmonic oscillation model.

Crystal Structure. The C–C distances in the C_p rings are 1.392—1.442 Å; the Fe–C distances are 2.028—2.061 Å for the molecules I and II. These results agree with the values of the other ferrocene derivatives indicating no effect of the substituent on the Fe–C bondings.

Evidence for the reorientation in the substituent group and C_p ring of acetylferrocene has been deduced on the basis of the temperature dependence of the second moment of the ^{1}H-NMR lines.[4] The steep decrease of the line width and second moment between 50 and 210 K could be ascribed to the reorientation of the methyl groups about its triad axis and of th C_p rings about their five-fold axes of symmetry. The methyl group, unsubstituted C_p ring and substituted C_p ring, may initiate the reorientation in order of their moment of inertia with increasing temperature.

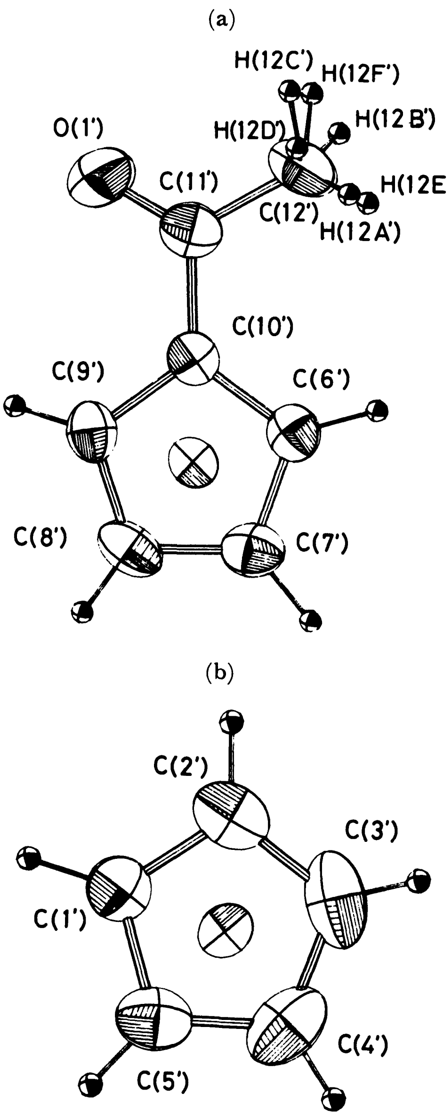

Fig. 3. Ellipsoids of the non-hydrogen atoms for molecule II are scaled at the 50 % probability. (a) substituted C_p ring and (b) unsubstituted C_p ring.

Figure 3 shows the vibrational ellipsoids of the C atoms in molecule II. A rigid-body analysis indicates that the principal libration axis of the C_p rings is nearly parallel to the five-fold molecular axis. The root-mean-square vibration amplitudes for the in-phase libration of the substituted C_p rings, 4.8° and 5.9°, are smaller than those of the unsubstituted C_p rings, 8.3° and 7.5° for molecules I and II, respectively, probably because steric hindrance of the acetyl groups reduces the thermal motion. On the other hand, the methyl hydrogen atoms in the acetyl groups take two alternative sets of positions with equal probability and the two orientations of the methyl groups are related by rotation of about 60° around the carbon–carbon bonds. The C and O atoms of the acetyl groups lie on approximately the planes of the aromatic rings owing to the existence of the complete conjugation between the acetyl groups and the C_p rings. The mean-square amplitudes of the C and O atoms in the direction perpendicular to the aromatic ring planes are about twice those estimated from the rigid-body motion, suggesting reorientation of the acetyl groups at high temperatures.

Figure 4 shows a projection of the structure along the b axis. There are two crystallographically independent molecules I and II in the unit cell. The eight iron atoms are located at *ca.* $y=1/4$ and 3/4. A prominent feature of the crystal structure is the pairing of two molecules with respect to a center of symmetry, such as II and IV, and I and III, respectively. There is no intermolecular distance shorter than the sum of the van der Waals radii. The disordered hydrogen atoms of the methyl groups are illustrated by shaded circles.

Figure 5 shows the view of the structure perpendicular to the face (102). The C_p planes incline by about 20 degrees against the b axis in order to avoid contact with each other, and oxygen atoms are packed in the interior of the pairs. Intermolecular nearest distances are 2.29 Å between H(2)–H(12C) for the molecule I and 2.32 Å

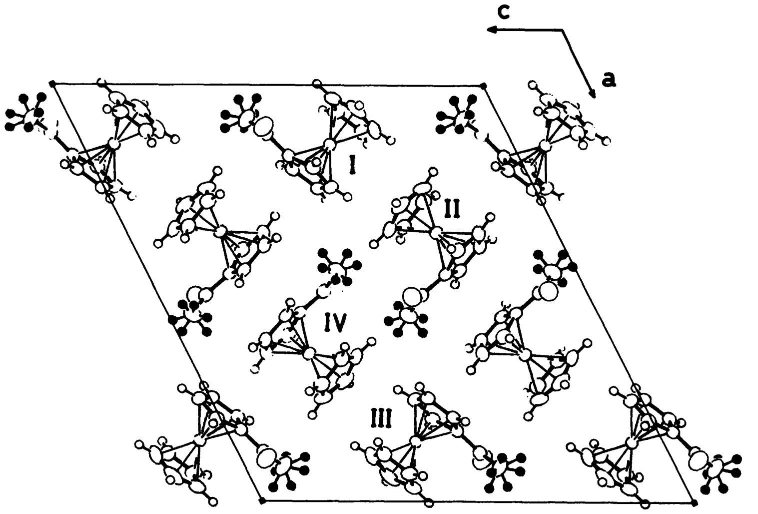

Fig. 4. Projection of the crystal structure of acetylferrocene along the b axis at room temperature. The disordered hydrogen atoms of acetyl groups are illustrated as shaded circles.

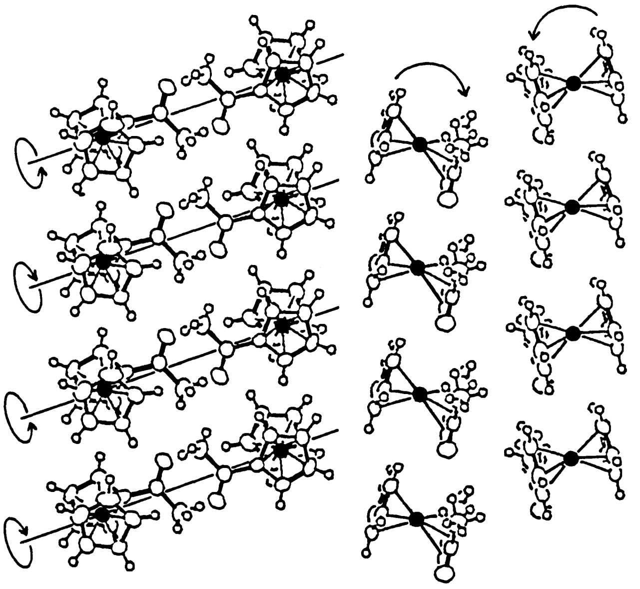

Fig. 5. View of the structure perpendicular to the face (102). The phase transition is associated with a cooperative phenomenon like in a series of rotating gears, that is, molecules reorient simultaneously around the iron-iron directions in the pairs.

between H(1′)-H(12C′) for the molecule II.

Rotational Phase Transition. Crystal specimens were heated in a stream of electrically heated air controlled with a precision of about ±0.25°. Both the Weissenberg and the oscillation photographs taken at temperatures up to the melting point (86 °C) showed that the diffraction pattern abruptly changed twice, at *ca.* 80 °C and 83 °C.

When the temperature was raised, the reflections split into two spots in the a*c* plane at *ca.* 80 °C. On increasing the temperature, the reflection intensities disappeared at *ca.* 83 °C except those corresponding to the 210, $\bar{1}12$, $\bar{3}02$, and 102 reflections in the original pattern. Those reflections are considered to be contributed largely by the iron atoms because they correspond to the planes containing the iron atoms at room temperature. Further, there appeared several additional satellite reflections along 3a*—2c* between 210 and $\bar{1}12$ as shown in Fig. 6. It was difficult to obtain the cell dimensions and the symmetry of the crystal owing to the deficiency of reflection data.

When the crystal specimen, heated once above *ca.* 83 °C, was cooled slowly back to room temperature, the Weissenberg photograph showed the same diffraction pattern as its original one or the two-fold rotated pattern. The latter photograph showed that the specimen remained as a single crystal but was rotated by 180° around the c axis with respect to the original orientation as shown in Fig. 7 by dotted lines. This indicates that the original structure, (A), shown by full lines, must be transformed into the rotated structure, (B), through a molecular motion at 83 °C. The interchange of the original structure with the resulting structure can be interpreted in the same way as the twinning shown in Fig. 1, assuming a small potential barrier between the crystal components A and B.

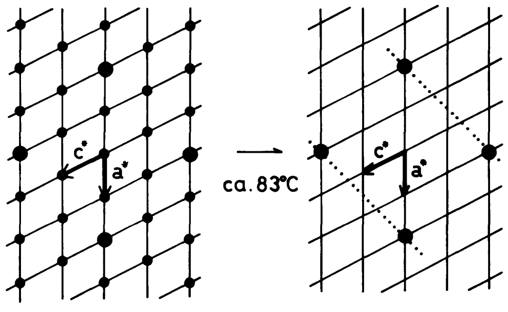

Fig. 6. Temperature dependence of Weissenberg photographs in the first layer.

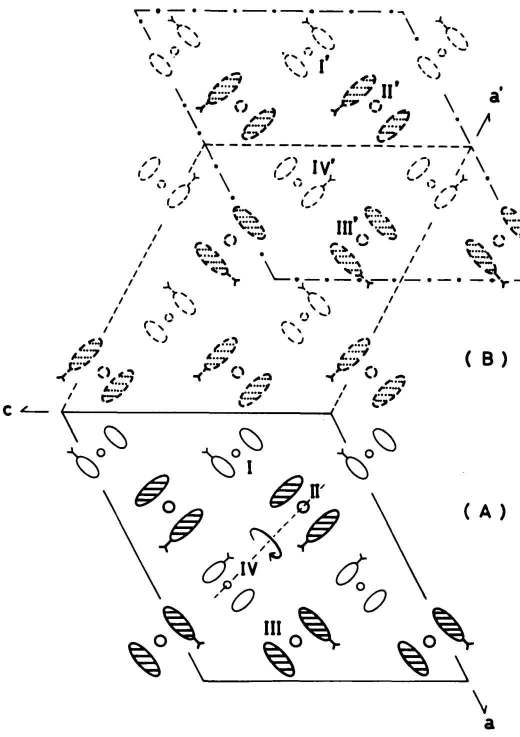

Fig. 7. Crystal structure of acetylferrocene at room temperature (A) before and (B) after heating to *ca.* 83 °C. The structure (B) shown by dotted lines is given by the rotation of the structure (A) shown by solid lines, around the c axis by 180 °, where the C_p rings are picturized with ellipses and the acetyl groups are Y-shaped symbols, and the molecular positions are expressed by different size of the ellipses and slant lines.

These observations enable us to propose a plausible model for the phase transition at *ca.* 83 °C as follows. The structure (B′) shown by the chain lines in Fig. 7 is given by the rotation of the structure (A) around the c axis by 180° in the same way as described for the twinning of this compound. Because of the specific molecular arrangement, the crystal structure of the ferrocene moieties in (B′) resembles that in (A) except for the position of acetyl groups; *i.e.*, molecules I, II, III, and IV correspond to molecules I′, II′, III′, and IV′, respectively. The structure (A) transforms to the structure (B′) by rotating the acetylferrocene molecules. This rotational interchange is considered to be effected by the simultaneous and cooperative rotation of pairs of adjacent molecules, such as II and IV, around the iron–iron direction in pairs as shown in Fig. 7. This model suggests that molecules jump rather than freely rotate between the two orientations, (A) and (B′), around the direction between the two adjacent iron atoms in the pairs of II and IV, and I and III, respectively, at *ca.* 83 °C. Each molecular reorientation may also be accompanied by a rotation of the acetyl group.

In the proposed model, the phase transition is assumed to be associated with a cooperative motion similar to that of a series of rotating gears as shown in Fig. 5. This model can also explain why there is no increase of the mean-square amplitude of the iron atoms with increasing temperature, as shown in Mössbauer spectra, since the central iron atoms would keep their positions in the transition state.

Mössbauer Spectra. Mössbauer spectra consist of a doublet with the isomer shift 0.40 to 0.42 mm s^{-1} and the quadrupole splitting 2.53 mm s^{-1} that reveals Fe(II) low-spin state. As shown in Fig. 8, there evidently occurs a progressive broadening above room temperature, although slight decrease of the line-width is expected in the high temperature region because of the decrease of the recoil-free fraction.

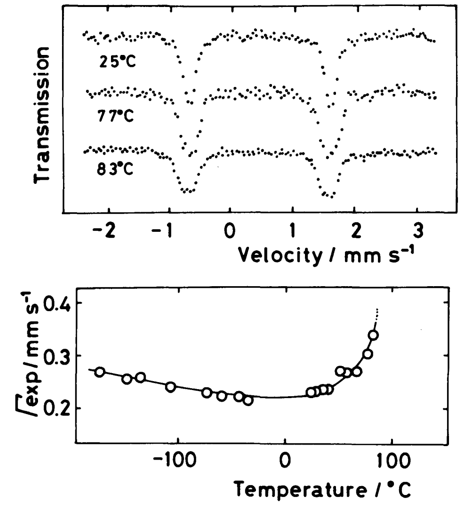

Fig. 8. Temperature dependence of the Mössbauer line-width for acetylferrocene.

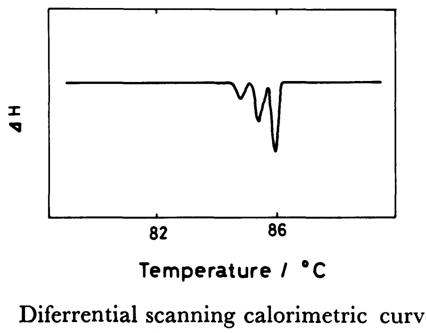

Fig. 9. Diferrential scanning calorimetric curve of acetylferrocene at heating rate 1 deg h^{-1}.

In addition to the fact of no increase of mean-square amplitude estimated by Mössbauer spectroscopy near the melting point, this behaviour may well be explained by assuming the relaxation effect of quadrupole split lines, caused by the fluctuation of the electric field gradient in the high temperature region. The process may be ascribed to a slow flipping between two equilibrium positions in the reorientational plane rather than to the rotational motion. The reorientational motion of acetylferrocene may be hindered by interaction with neighbouring molecules, for instance the steric hindrance of the acetyl groups.

Thermal Analysis. Figure 9 shows the results of Differential Scanning Calorimetry for acetylferrocene. Two endothermic peaks are observed below the melting point under an extremely slow heating rate, 1 deg h^{-1}. The peak closest to the peak of melting is ascribed to the molecular rotational phase transition, and the other peak to the rotation of acetyl groups, although further measurement are needed to justify more detailed discussion.

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