Plastic Phase of Formylferrocene Studied by X-Ray Diffraction and Mössbauer Spectroscopy

Kumiko SATO,* Makoto IWAI, Hirotoshi SANO, and Michiko KONNO†
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158
†*The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106*
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The structures of both the crystal and the plastic phases of formylferrocene have been determined to be orthorhombic by single-crystal X-ray diffraction. The structural change proposes a mechanism of the transition that postulates the translational molecular motion along the a-axis. Mössbauer spectra observed in the plastic phase show little fluctuation of the electric field gradient ascribed to the orientational disorder between x, y, and z axes of the molecule.

It is known that organometallic compounds, such as ferrocene derivatives, exhibit various kinds of mesophase transitions. Malthete and Billard have reported that ferrocene derivatives of *N*-(*p*-benzoyloxybenzylidene)aniline exhibit mesomeric properties.[1] The plastic crystal (PC) phases of formyl- and polychloroferrocenes were studied and the former especially has been widely investigated by Daniel *et al.*[2-4] Although the structure of the ordered low-temperature phase of formylferrocene was determined to be orthorhombic (space group $P2_12_12_1$; Z=4, a=7.635, b=10.520, c=11.281 Å) by using a single crystal, the structure of the PC phase was assinged to a simple face-centered cubic (f.c.c.) lattice with a unit-cell parameter a=9.99 Å accompanied by orientational disorder based on a Debye-Scherrer pattern.

In the present paper the plastic phase transition in formylferrocene has been studied by means of single crystal X-ray diffraction and Mössbauer spectroscopy. Although the present X-ray diffraction data determined at room temperature agreed essentially with those reported by Daniel *et al.*, the results obtained for the PC phase determined by oscillation and Weissenberg photographs were found to be orthorhombic, with a'=11.9, b'=16.4, c'=7.0 Å at 50 °C. The temperature dependence of the Mössbauer spectra was determined in order to confirm dynamic molecular motion.

Experimental

Formylferrocene was synthesized by acylation of ferrocene with *N*,*N*-dimethylformamide. The products were separated by column chromatography on an alumina and purified by recrystallization and sublimation. The purity was checked by melting point and elemental analysis. The thermal properties of formylferrocene were determined by a Rigaku Thermoflex Differential Scanning Calorimeter (DSC). The thermal parameters at transition and melting points were found to be ΔH=12.09±0.04 and 2.184±0.008 kJ mol^{-1} and ΔS=38.37±0.12 and 5.82±0.04 J mol^{-1} deg^{-1}, respectively, which agreed with the values reported in the previous paper.[2]

Mössbauer spectra were determined by using an Austin Science Associated Mössbauer spectrometer. Velocity calibration was carried out based on the room-temperature spectra of metallic iron. By fitting the resonance line with a Lorentzian function, the Mössbauer parameters were extracted. A high-temperature apparatus was constructed with a heater in a vacuum furnace. The sample was sealed to suppress sublimation. Temperature was checked by using a CA thermocouple with a precision of about ±0.05°.

Because our results on the structural analysis of the PC phase of formylferrocene contradicted those reported by Daniel *et al.*, the crystal structure of this compound at room temperature was determined in order to confirm that the compound used here has the same crystal structure in the crystal phase as the one used by them.

Single crystals suitable for X-ray study were obtained by a slow sublimation method. A crystal specimen with approximate dimensions of 0.28×0.25×0.23 mm was used, kept in a Lindemann-glass capillary filled with nitrogen gas. Intensity data were collected on a four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate.

The crystals are orthorhombic with space group $P2_12_12_1$, a=10.525(9), b=11.294(10), c=7.639(5) Å, V=908.1(13) Å^3 and Z=4 at room temperature. The details of the basic crystal data have been omitted in the present paper as the results obtained at room temperature agree essentially with those reported by Daniel *et al.* in 1981.[3] There are, however, some comments in connection with the crystal structure. The positions of hydrogen atoms could be determined and are shown in Table 1. In refinement, incorporating the model with two-fold disorder, the cyclopentadienyl rings are found to be twisted approximately by 36° around the molecular axis with respect to one another, as shown by the solid circles in Fig. 1. The disordered model involves two alternative ring orientations in a ratio of occupancy of 0.85:0.15. A composite structure, which attempts to model the disorder, gives R=3.72% over 1001 independent reflections with $|F_o|>3\sigma(|F_o|)$ up to 2θ=60°.†† The disordered structure at room temperature provides a useful clue to understanding the molecular motion of this compound at the transition point as described later.

Results and Discussion

Crystal Structure. Formylferrocene exists approximately on the a and c plane and a prominent feature of the molecular structure is the layer structure along b axis. There exist the 020 reflections with a significant intensity characteristic of a layer structure.

The molecules occupying in the ratio of 0.85 exhibit an appreciable interaction between neigh-

†† The complete F_o—F_c data are deposited as Document No. 8401 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

Table 1. Fractional atomic coordinates ($\times 10^3$) and equivalent isotropic thermal parameters

	x	y	z	U_{eq}/10 Å
H(1)	−90(6)	366(6)	228(10)	97(23)
H(2)	−122(5)	88(5)	233(8)	60(18)
H(3)	38(5)	28(5)	463(8)	52(19)
H(4)	146(6)	204(6)	561(8)	71(21)
H(5)	64(6)	436(6)	426(9)	80(24)
H(6)	115(6)	302(6)	−78(8)	83(22)
H(7)	91(7)	63(6)	−89(10)	104(28)
H(8)	268(8)	−2(8)	179(10)	104(28)
H(9)	354(6)	152(5)	234(9)	73(21)
H(11)	224(7)	470(6)	43(10)	82(25)

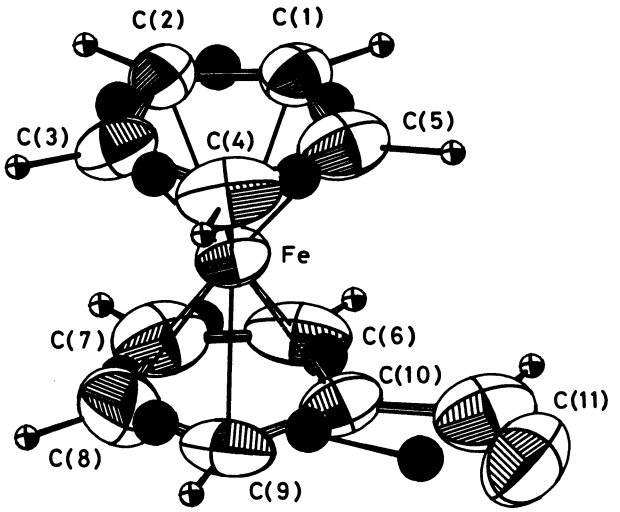

Fig. 1. View of the compound. Solid circles refer to disordered molecule.

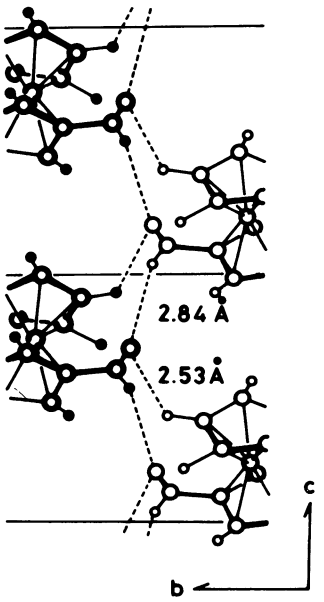

Fig. 2. The conformation of the network of weak intermolecular bonding along c axis. The intermolecular bonding C(5)-H(5)···O′(1) and O(1)-H(11)··· O′(1) are indicated by broken lines.

bouring molecules along the b axis. The nearest distance between O(1) and H(5) is estimated to be 2.53 Å and the C(5)-H(5)···O′(1) bond angle 128°. The H(11)-O′(1) distance is estimated to be 2.84 Å, the O(1)-H(11)···O′(1) bond angle 148° and the H(2)-O′(1) distance 2.81 Å the C(2)-H(2)···O′(1) bond angle 132°. There is a network of intermolecular interaction along c axis as shown by broken lines in Fig. 2.

The molecules occupying in the ratio of 0.15 are twisted approximately by 36° around the molecular axis and too far separated to form an intermolecular bonding network. At room temperature the probability of molecules sitting in the disordered positions is about 15% and the possibility may increase with increasing temperature.

Plastic Crystalline Structure. The crystal specimen was heated by electrically heated air, controlled with a precision of about ±0.25°. In the PC phase, oscillation and Weissenberg photographs were taken at temperatures from 45 to 70 °C. After the transition at 43.5 °C, there remained only five independent reflections with significant intensity, 111, 210, 030, 121, and 220. Oscillation and Weissenberg photographs indicate that the PC phase is orthorhombic, $a'=11.9$, $b'=16.4$ ($b'=3/2b$, where b stands for the lattice constant at room temperature), $c'=7.0$ Å at 50 °C. The lattice constant exhibits no serious change up to 70 °C.

These results contradict the f.c.c. structure with the lattice constant 9.99 Å concluded by Daniel *et al.*,[3] since the observed reflections cannot be interpreted by the f.c.c. structure. The X-ray powder pattern at 50 °C exhibits two characteristic reflections with very strong intensity. Although these reflections seem to correspond to 111 and 200 in f.c.c. lattice, they consist of five overlapped reflections, *i.e.*, 111, 210, 030, 121, and 220 in the orthorhombic lattice. The results indicate that the PC phase of formylferrocene is explained not by f.c.c. but by an orthorhombic structure, although there are few reports suggesting any orthorhombic PC phase.

Phase Transition Model. The PC phase yeilds only a few diffracted X-ray reflections at low Bragg angles, as a consequence of the very high Debye-Waller factors owing to orientationally disordered molecules, but a detailed comparison of the structural data of the crystal phase with those of the PC phase permit a hypothetical structure for the PC phase.

A structural model of the PC phase may be proposed based on the structure determined at room temperature having six molecules in a unit-cell as shown in Fig. 3. The iron atoms lie in the mirror planes at $Z'=0$ and 1/2 as illustrated with open and solid circles, respectively. There exist four crystallographically independent molecules, I, II, III, and IV, in the unit cell. Furthermore, molecules III and IV are located in the mirror planes both at $y'=1/2$ and there is a two fold axis along a'. Although the space group could not be unequivocally determined, the PC phase exhibits an increase in symmetry compared to the crystal phase.

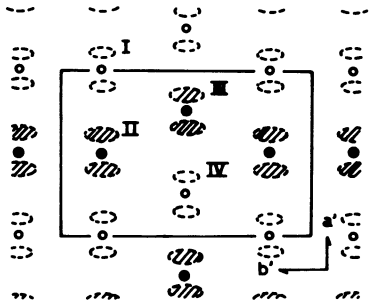

Fig. 3. A proposed structure of the PC phase projected along c′ axis. Open circles refer to iron atoms in each molecule lying on the mirror plane at $z=0$. Solid circles refer to iron atoms in each molecule lying on the mirror plane at $z=1/2$.

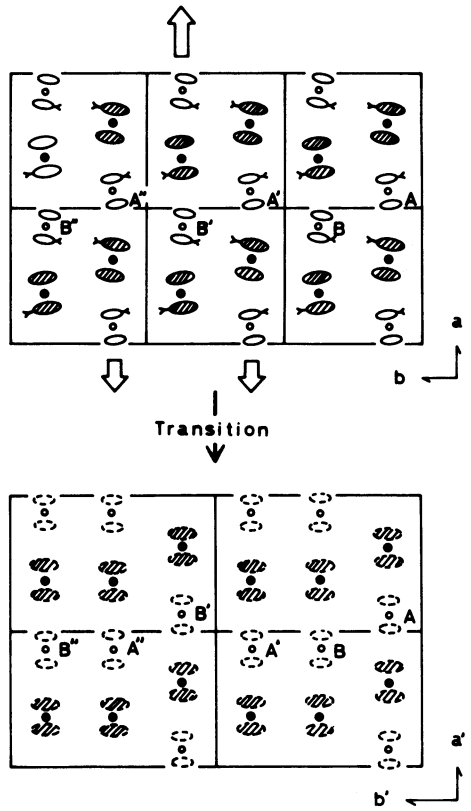

Fig. 4. The upper part shows schematically the crystal structure at room temperature and the lower part the proposed PC phase structure (a triad structure).

The structure proposed for the PC phase dose not give rise to any essential deviations of molecular positions from the crystal structure in the crystal state at room temperature.

The projections of the structures of modifications viewed along the c axis of the crystal phase and the c′ axis of the PC phase are given in the upper and lower parts of Fig. 4, respectively. Bragg reflections observed in the PC phase have little contribution from carbon and oxygen atoms, because of the large Debye-Waller factors ascribed to the large thermal motion of cyclopentadienyl rings and the formyl groups which make their scattering factors much

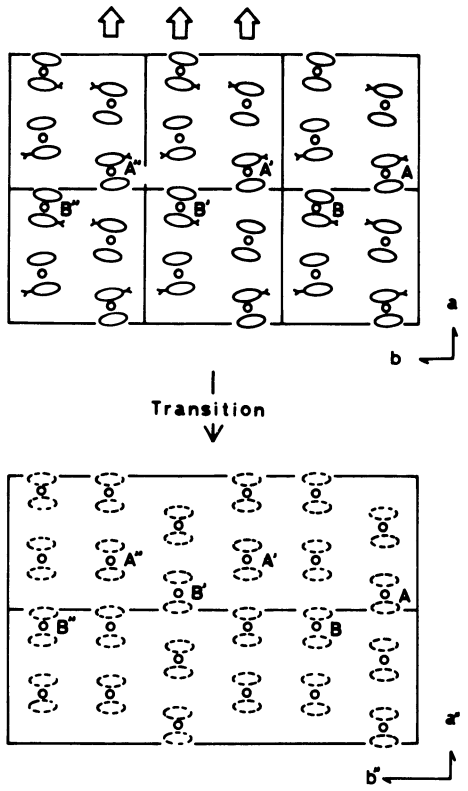

Fig. 5. The upper part shows schematically the crystal structure at room temperature and the lower part the proposed PC phase structure (a hexa-periodical structure).

weaker compared with that of iron atoms.

The 030 reflections with significant intensities indicate a triad structure for the PC phase. The lattice constant of the b′ axis in the PC phase *vs.* that of b axis in the crystal phase gives a ratio of 3:2. The structural change which accounts for the different lattice suggests a cooperative slide of the layer consisting of molecules on the a and c planes along the a axis. As shown in Fig. 4, in the crystal phase, the molecules A, A′, and A″ are equivalent in each cell separated by translating molecules to the nearest molecular position along the b axis. In the PC phase, the molecule B′ will probably be equivalent with the molecule A because of the reason described above. The molecules A, A′, A″, B, B′, and B″ in the crystal phase correspond to those in the PC phase, respectively. There is an indication that the iron atoms cooperatively slide along the a axis at the phase transition point. The schematic features of the phase transition are indicated by downward and upward arrows in Fig. 4, although the model described above seems to overestimate the sliding motion up and down along the a axis.

An alternative model is shown in Fig. 5, where the PC phase is considered to have a hexa-periodical structure. The 030 reflections with significant intensities are regarded as the 060 reflections. As shown in Fig. 5, in the PC phase the molecule A can be described as equivalent to the molecule A in the adjacent unit-cell repeatedly appearing along the b′ axis. This model requires that all the molecules slide upward along the a axis as

shown by the arrows in Fig. 5. In this case, the positional deviation from the original molecular position in the crystal phase is also considered to occur in the direction of the c axis, causing the change of molecular positions undetectable by X-ray analysis.

Although it remains undetermined whether a triad or a hexa-periodical structure is to be prefered for the PC phase, it is concluded that formylferrocene acquires a considerable degree of translational freedom in the direction of the a axis above the transition point.

When the plastic crystalline molecules are almost spherical, the entropy of melting is expected to be close to the value of $3R/2$ which is expected for molecules possessing freedom in three dimensional translation based on the classic theory. Because each molecule can rotate without significant translational motion of the centers of gravity in the crystal phase, the molecule may have as much rotational entropy in the plastic crystal as in the liquid phase. On the other hand, formylferrocene with the first-order transition has an entropy of melting of 1.39 entropy units which is less than $3R/2$. Molecules that have anisotropic structures may need translation of the center of gravity, such as the translational motion to the adjacent position, so that they can start rotating and a kind of cooperative motion, making the transition first order at the transition point from crystal to PC phase. Since a part of the translational entropy has already been consumed below the melting point, the entropy of melting is interpreted to be less than $3R/2$.

There exists no significant change of the lattice constant between 50 °C and room temperature, except that the b axis in the PC phase *vs.* the b′ axis in the crystal phase is in the ratio of 3:2, and the PC phase remains orthorhombic. This is one of strong pieces of evidence supporting the anisotropic molecular rotation in the PC phase. The a axis in the PC phase lengthens by *ca.* 13%, while the c and b axes become shortened by *ca.* 8 and 3% of each axis in the crystal phase at room temperature. It has generally been known that the lattice constant in the PC phase is larger than that in the crystal phase. The present data, which indicate an anisotropic expansion, also suggest an anisotropic orientation such as a partial rotation around the molecular axis. The results of the crystal structure in the crystal phase, involving occupancy of two alternative ring orientations in the ratio of 0.85:0.15 provide us with additional evidence supporting rotational motion around the molecular axis. The orientational disorder in the PC phase may have the effect of deteriorating a weak intermolecular bonding network found along the b and c axes in the crystal phase at room temperature. This model provides a possible explanation for the contraction of the b and c axes, although further investigations should be carried out for more detailed discussions.

Mössbauer Spectra. The values of the isomer shift and quadrupole splitting are 0.43 and 2.23 mm s^{-1} at room temperature, respectively, and the electronic state of the iron atom is found to be divalent with a low-spin state. The characteristically large quadrupole splitting is attributed to the large electric field gradient: that is, a larger population of electrons in the x, y directions than in the z direction for iron atoms.

In the Mössbauer spectra there exists no serious difference between the crystal and the plastic crystal phase, as shown in Fig. 6. If there is any fluctuation of the electric field gradient owing the orientational disorder between x, y, and z axes, one can expect a change in the spectral line shape. In the case of acetylferrocene, an orientational phase transition was observed at a temperature a few degrees below the melting point in X-ray diffraction. The temperature dependence of the recoil-free fraction in the Mössbauer spectra of acetylferrocene was ascribed to the quadrupole relaxation effect caused by the orientational disorder.[5] In the PC phase of formylferrocene, the unchanged line-width indicates either that there may be little orientational disorder around x or y axes of the molecule or that the quadrupole relaxation time may be very long.

Mössbauer spectra cannot be detected above 85 °C

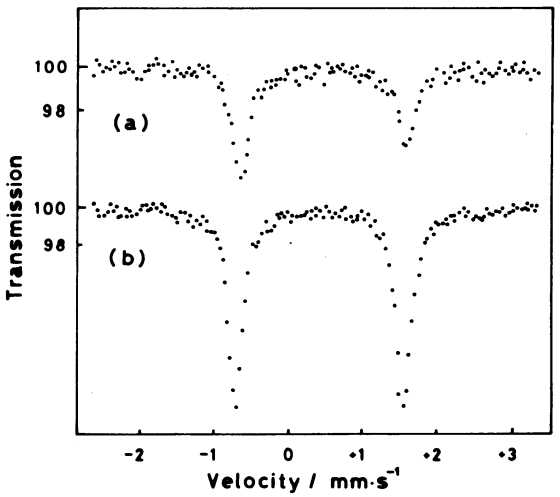

Fig. 6. (a) Mössbauer spectrum of the PC phase at 75 °C, which indicates an asymmetric quadrupole split line. (b) Mössbauer spectrum of the crystal phase at room temperature.

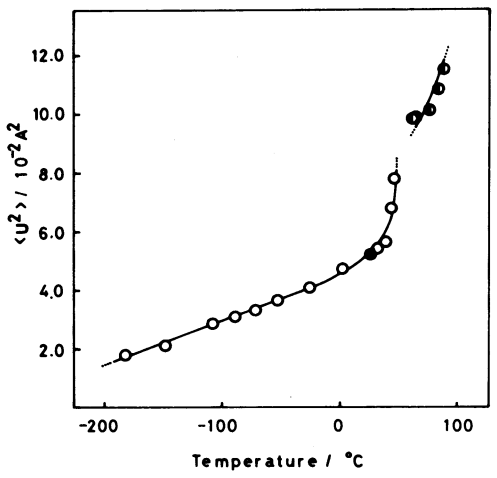

Fig. 7. The temperature dependence of the mean-square amplitude. The solid circle shows the value estimated from the thermal factor based on the X-ray study.

because of a rapid decrease of the recoil-free fraction in the higher temperature phase. The areal intensity of the Mössbauer spectrum abruptly decreases at the transition point, as shown in Fig. 7, and is related to the mean-square amplitude of Mössbauer atoms $<U^2>$ as follows:

$$A \propto f = \exp\left[-\frac{4\pi^2}{\lambda_\gamma^2}\langle U^2\rangle\right],$$

where λ_γ is the wavelength of the Mössbauer γ-ray and f is the recoil-free fraction. In the high-temperature approximation, $<U^2>$ can be estimated from the areal intensity. The solid circle in Fig. 7 is the value of the isotropic mean-square amplitude estimated from the thermal factor determined by the X-ray analysis for the crystal phase at room temperature, which agrees with the value obtained by the Mössbauer spectrum.

The mean-square amplitude shows a linear temperature dependence in the temperature range from about -200 °C to 0 °C, indicating an harmonic lattice vibration, but a significant deviation is found near the transition temperature, *e.g.*, an abruptly increased value, 0.07 $Å^{-2}$, is given before the transition. This indicates a substantial modification in the lattice characteristics of the solid. Although a thin sample, 32.8 mg cm^{-2}, shows no detectable spectra after the transition, because of the decreasing spectral intensity, definite spectra are successfully obtained with a thick sample, 97.5 mg cm^{-2}. The percent effects of the spectrum cannot precisely be normalized with those obtained for the thin sample because of a saturation effect. Therefore, the mean-square amplitude in the PC phase shown in Fig. 7 may be underestimated.

The PC phase of formylferrocene is characterized by the abnormally large translation similar to that expected in the liquid phase. The ratio, δ, between the mean square-root amplitude and the mean intermolecular distance has been used as an estimation of lattice vibrations in metallic solids and crystals of metal halides.[6] The value of δ is estimated at approximately 5% for formylferrocene at temperatures from 50 °C to 85 °C below the melting point, 123.5 °C, while other ferrocene derivatives, mono- and diacetylferrocene and ferrocenemono- and dicarboxylic acid, reveal the values of 2 to 3% even near the melting points. The anomalous value of δ for formylferrocene in the PC phase below the melting point suggests an unusual lattice vibration in the crystal phase. There may exist an anisotropic translation of molecules in the PC phase as was proposed for the transition in the previous section.

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