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STUDIES ON THE PHASE TRANSITION NEAR THE MELTING POINTS IN ACETYL AND CARBOXYL FERROCENES

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Phase transitions were found in the entitled compounds near the melting points by means of Mössbauer spectroscopic study. In order to investigate the phase transition, the crystal structure of monoacetylferrocene was determined by X-ray diffraction at room temperature and oscillation and Weissenberg photographs were taken at high temperatures. The phase transition was also confirmed by differential thermal analysis.

The well-known second-order transition for ferrocene at 163.9K has been investigated by specific-heat measurement, X-ray diffraction and Mössbauer spectroscopy.1) Thiourea-ferrocene clathrate shows the process of reorientation of ferrocene molecules in the channels with phase transition.2) Based on the temperature dependence of the intensity of the Mössbauer spectrum, it was reported that ferrocene carboxaldehyde exhibits a plastic phase in which the molecules are randomly orientated about their centers of mass.3) 1,1'-Diethylferrocene was found to have a glassy state by measuring the temperature dependence of the mean square amplitude of iron atoms.4)

Mössbauer spectra provide us with information about the electronic state and the mean square amplitude of Mössbauer atoms which are extracted from the isomer-shift and quadrupole splitting, and the recoil-free fraction, f , estimated from the areal intensity. In the approximation of simple harmonic oscillation of Mössbauer atoms, it is known that the mean square amplitude is proportional to the absolute temperature. Although most ferrocene derivatives are found to satisfy this approximation, deviation from the linear temperature dependence of lnf is found in a few ferrocene derivatives. In the present paper, we found that a kind of transition occurs a little below the melting points in monosubstituted ferrocene, and particularly in monoacetylferrocene, the crystal structure was determined at room temperature by X-ray diffraction and the transitional process was investigated by taking oscillation and Weissenberg photographs in order to clarify the phase transition.

These compounds were prepared by following the method described in Ref. 5, and purified by recrystallization and sublimation. The purity was confirmed by checking the melting points and by elemental analysis. No impurity was detected in IR, NMR and Mössbauer spectra. Mössbauer spectra were determined by using an Austin Science Associate 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 measurement was preformed by using a CA thermocouple embedded in a copper sample holder in a cryostat. The precision of this measurement was approximately ± 1° over a period of several hours. A high-temperature apparatus was constructed with a heater, in a vacuum furnace. The samples were sealed, being prevented from sublimation. Temperature was checked by a CA thermocouple, and had the precision of about ± 0.1°.

Crystals of monoacetylferrocene for X-ray work were grown from benzene-hexane solution. They are brown needles. The dimensions of the crystal used for intensity measurements were 0.30 x 0.25 x 0.35 mm. The crystal specimen was sealed into a Lindemann-glass capillary. Intensities were measured on a four-circle diffractometer with Mo *Kα* radiation monochromated by a graphite plate. Refinement of the structure by the block-diagonal least-squares method reduced the R value to 0.036 for 3194 independent reflections with $|F_o| > 3\sigma(|F_o|)$ up to $2\theta = 55°$. The crystals are monoclinic at room temperature with space group $P2_1/c$, $a = 20.595(2)$, $b = 5.790(4)$, $c = 18.840(2)$ Å, $\beta = 116.87(7)°$. $V = 2004.37(1)$ Å^3 and $Z = 8$.

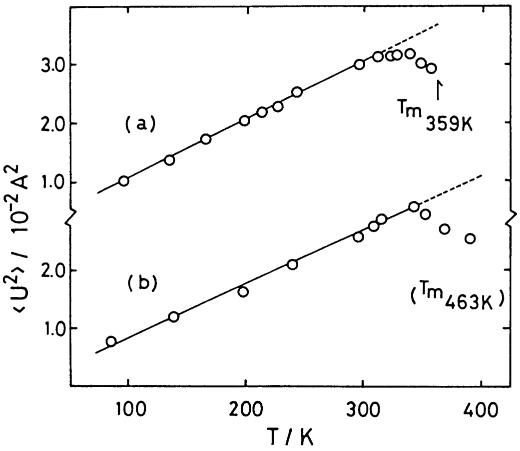

Fig. 1 Temperature dependence of the mean square amplitude for (a) monoacetylferrocene and (b) ferrocenemonocarboxylic acid.

Figure 1 shows the temperature dependence of the mean square amplitude estimated from the areal intensities of Mössbauer spectra for iron atoms in acetyl and carboxyl ferrocenes. Although the mean square amplitude increases in proportion to the absolute temperature up to room temperature, an appreciable anomaly in the temperature dependence of the mean square amplitude is found near their melting points, indicating that a transition occurs before melting in these compounds.

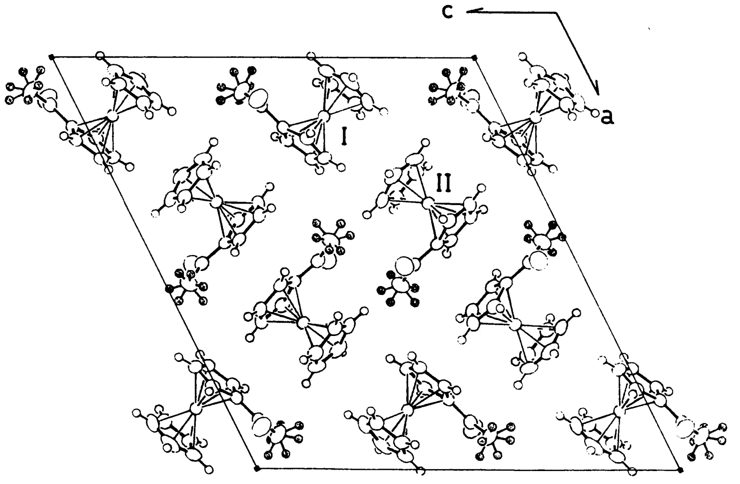

Fig. 2 Projection of the crystal structure of monoacetylferrocene along b axis at room temperature. The disordered hydrogen atoms of acetyl groups are illustrated as shaded circles.

Figure 2 shows a projection of the structure along b axis. There are two crystallographically independent molecules I and II in the unit cell. The eight iron atoms are located in *ca.* y = 1/4 and y = 3/4. A prominent feature of the crystal structure is the pairing of two molecules with respect to a center of symmetry. The mutual interaction between the pairs in the a and c directions is ascribed to van der Waals force because there is no intermolecular distance shorter than the sum of van der

Waals radii. It was found that the methyl hydrogen atoms exhibit orientational disorder and that they take two alternative sets of position with equal probability, which are rotated by about 60° around the carbon-carbon bond.

Crystal specimens were heated in a stream of electrically heated air controlled in the precision of about ± 0.25°. Both the Weissenberg and oscillation photographs around b axis taken at the temperature up to the melting point (86°C) show that the diffraction pattern changes abruptly twice, at 80 and 83°C. When the temperature was raised, the reflections split into two spots in the a^*c^* plane at 80°C. With further rise of temperature, in the first layer of the Weissenberg photograph taken around the b axis, intensities of the reflections completely diminished at 83°C except for the 210 and $\bar{1}12$ refelctions. Those reflections are considered to be contributed largely by iron atoms because they correspond to the reflections based on the planes containing iron atoms at room temperature. This observation suggests that iron atoms keep a three dimensional periodicity and other atoms mutilate the periodical ordering, probably because of a reorientational phase transition at a temperature a little below the melting point. Further, there appear several additional satellite reflections along $2a^* - 3c^*$ between 210 and $\bar{1}12$.
When the crystal specimen, heated once above 83°C, was cooled slowly again to room temperature, the Weissenberg photograph showed the same diffraction pattern as its original one. The photograph showed that the specimen remained as a single crystal but it was rotated around the c axis by 180° with respect to the original orientation as shown in Fig. 3 by solid lines, where the cyclopentadienyl rings were picturized with ellipses and the acetyl groups Y-symbols and the molecular positions were expressed by different size of the ellipses and slant lines. These observations enable us to propose a plausible model for the phase transition at 83°C as follows; a molecular motion in which molecules I and II turn into molecules II' and I', respectively, rotating the molecules around the iron atoms, as shown in Fig. 3. In the rotation of molecules I and II, the adjacent molecules III and IV are expected to rotate simultaneously around the iron-iron direction in the pairs of I and III, and II and IV, respectively, in order to minimize the steric hindrance. For each molecular rotation the rotation of acetyl group may also be accompanied. In the proposed model, the phase transition is assumed to be associated with a cooperative phenomenon like in a series of rotating gears. This model can explain why iron atoms keep the three dimensional periodicity while other atoms lose the periodicity above 83°C, by assuming that the cooperative motion should converge the position of iron atoms as a center of molecular rotation. No increase of mean square amplitude with increased temperature can be attributed to the cooperative motion as well.

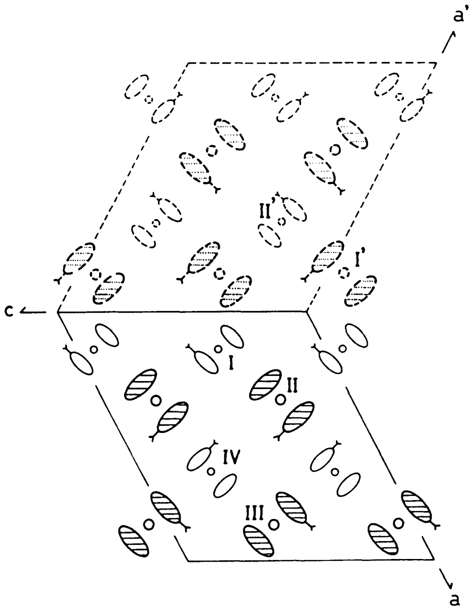

Fig. 3 Crystal structures of monoacetylferrocene at room temperature before and after heating to 83°C.

Figure 4 shows the results of DTA for monoacetylferrocene. Two endothermic peaks are observed at 80 and 83°C below the melting point under an extremely slow heating rate, 1 deg/h. The peak closest to the peak of melting may be ascribed to the molecular rotational phase transition, while another indistinct peak to the rotation of acetyl groups, although further measurement should be carried out for more detailed discussions.

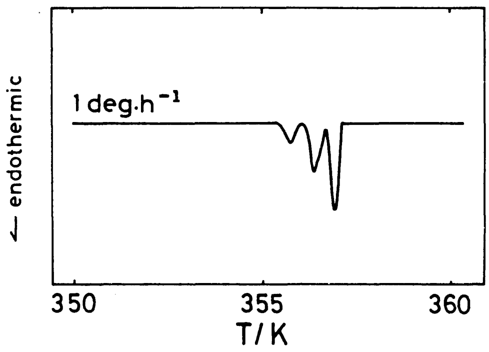

Fig. 4 Differential thermal analysis curve of monoacetylferrocene at heating rate 1 deg/h.

Finally, the support of this model may also be provided by the temperature dependence of line-width in Mössbauer spectra. As shown in Fig. 5, although the slight decrease of the line-width is ascribed to the decrease of the recoil-free fraction in the low temperature region, evidently there occurs a progressive broadening above room temperature. This behaviour may well be explained by assuming the relaxation effect of quadrupole split lines, caused by the fluctuation of electric field gradient due to the rotational molecular motion 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. Gibb reported on the relaxation of the electric field gradient in the Mössbauer spectra of a thiourea-ferrocene clathrate caused by anisotropic reorientation of the ferrocene molecules.[2)] Because the reorientational motion of monoacetylferrocene may be hindered due to the interaction with the neighbouring molecules, for instance the steric hindrance of acetyl group, it is concluded that the phase transition is barely observed at a temperature a few degrees below the melting point. Similar X-ray studies on ferrocenemonocarboxylic acid are in progress and will be published elsewhere.

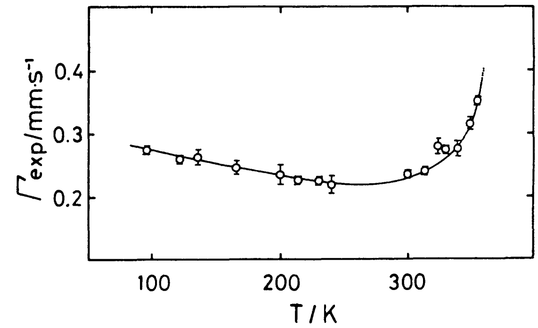

Fig. 5 Temperature dependence of the Mössbauer line-width for monoacetylferrocene.

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