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MÖSSBAUER SPECTROSCOPIC STUDIES ON THE GLASS STATE IN DIETHYLFERROCENE

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The discontinuous temperature dependence of Mössbauer recoil-free fraction observed in diethylferrocene, reflects the transition from the glass state to the super-cooled liquid state followed by crystallization on heating the sample which was prepared by cooling quickly the liquid sample with liquid nitrogen. On cooling the crystallized diethylferrocene, the temperature dependence was similar to that found monoethylferrocene.

One of the typical molecular organoiron compounds, bis(η^5-cyclopentadienyl)iron, so-called ferrocene, consists of an iron atom sandwiched between pentadienyl rings in its molecule. A lot of ferrocene derivatives have been extensively studied, but the behaviour in the solid state is still not completely understood and there are few reports on phase transition and glass transition. All that is known is that ferrocene shows phase transition around 164K and that the X-ray crystal structure of ferrocene consists with a P2/a space group at room temperature. Specific-heat measurements have shown a second-order transition at 163.9K, with an entropy change of $\Delta S = R\ln 1.89 K^{-1} mol^{-1}$,1) whereas detailed studies of the X-ray powder pattern gives the evidence for a small discontinuity in the lattice parameters at 164K as if the transition were of first order.2) The fact that a significant deviation of areal intensity of Mössbauer spectra occurs at this temperature indicates a substantial modification in the lattice characteristic of the solid at the temperature of order-disorder transition.3) Although ferrocene and its derivatives have been used as probe solutes for Mössbauer spectroscopic studies of liquid crystal,4,5) there has so far been no report that molecular compounds containing Mössbauer atom form an amorphous state. In the present paper, we shall report that 1,1'-diethylferrocene is found in a glass state which seems to be the first among ferrocene derivatives.

The compounds $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4CH_2CH_3)$ and $(\pi\text{-}C_5H_4CH_2CH_3)_2Fe$ were prepared by following the method described in ref.6, and purified by the alumina-column chromatography with hexane. No impurity was detected by IR and NMR, but the Mössbauer results at high temperature indicated that the purified sample was contaminated with some ferric species. As it is known that low molecular-weight liquid alkylferrocene decomposes to a considerable extent after standing for several months even under nitrogen in dark,7) further purification was carried out by the sublimation method untill the ferric impurity disappeared to the Mössbauer spectrum.

Mössbauer spectra reported in the present work were extracted from the spectra obtained by the use of an Austin Science Associates Mössbauer spectrometer. By fitting the resonance line shape to a Lorentzian function, the Mössbauer parameters, isomer shift and quadrupole splitting were extracted. In the case of well resolved quadrupole splitting, the error in the isomer shift and quadrupole splitting is approximately $\pm 0.005 mm\cdot s^{-1}$. Differential thermal analyses (D. T. A.) and differential scanning calorimetry (D. S. C.) were carried out by raising temperature at the rate of 2.2 to 14.5deg·$\min^{-1}$ after cooling the sample at 78K.

Although many ferrocene derivatives are characterized by the stability of crystal state with high melting points, both mono- and 1,1'-diethylferrocene are exceptionally liquid at room temperature and the detailed property of these compounds has not been reported even on the precise melting points. Melting points of mono- and 1,1'-diethylferrocene were found by D. S. C. to be 2.6°C and -37.5°C, respectively. It was found that monoethylferrocene remains in a super-cooled liquid state without solidify about 30 degrees below its melting point, when the sample was cooled as fast as the scanning rate 100deg·$\min^{-1}$. There was essentially no hysteresis found in the scanning rate lower than 10deg·$\min^{-1}$, either on heating or cooling the sample. Repeated experiments show the high reproducibility in the temperature-dependence experiment for the Mössbauer recoil-free fraction.

As shown in Fig. 1, the D. T. A. data of 1,1'-diethylferrocene reveal that this compound in glass state turns into a super-cooled liquid state at 149K, the glass transition temperature, Tg. After heating beyond the glass transition temperature, crystallization takes place at 180K, Tc, the crystallizing temperature, followed by melting at 235.5K. Although the apparent Tg and Tc depended upon the scanning rate of temperature, the constant values of Tg and Tc were obtained with good reproducibility in various slow scanning rates. The peculiar behaviour which was first observed among the ferrocene derivatives was elucidated by studying the lattice dynamics based on the temperature dependence of the Mössbauer spectrum of these compounds.

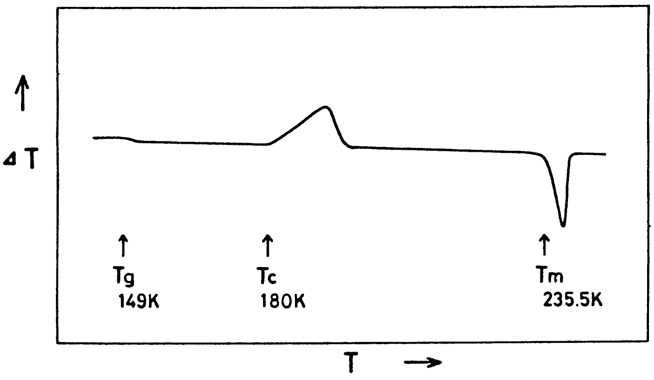

Fig. 1. Differential thermal curve of diethylferrocene at scanning rate of 2.2deg·$\min^{-1}$, Tg: Transition temperature from glass to super-cooled liquid state (glass transition temperature); Tc: Transition temperature from super-cooled liquid to crystal state (crystallizing temperature); Tm: Melting point.

The values of isomeric chemical shift and quadrupole splitting of mono- and 1,1'-diethylferrocene at 78K are 0.52mm·s^{-1} and 0.51mm·s^{-1} with respect to metallic iron and 2.34mm·s^{-1} and 2.38mm·s^{-1}, respectively, which are very closed to the typical values for ferrocene derivatives reported.[8)] Another important experimental parameter obtained from the Mössbauer studies in the recoil-free fraction whose temperature dependence reflects the lattice dynamics of the compound as follows.

In the approximation of simple harmonic oscillation of the Mössbauer atoms, the recoil-free fraction, f, estimated from the areal intensity of the Mössbauer spectrum is expressed by the mean-square amplitude of Mössbauer atom, $\langle U^2 \rangle$, as follows

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

where $\lambda\gamma$ is the wave length of Mössbauer γ-ray.

At a temperature high enough to assume kT as the thermal kinetic energy, it is known that the mean-square amplitude is proportional to the absolute temperature. Most of ferrocene derivatives were found to satisfy this approximation as illustrated for mono- and 1,1'-diacetylferrocene in Fig. 2, for the sake of comparison.

The results of lnf measurements for mono- and 1,1'-diethylferrocene are shown in Fig. 3a and b, respectively. The temperature dependence of lnf for monoethylferrocene deviates from a single straight line, showing anomaly at about 150K. One of the explanations for the anomaly may be the increased mobility of molecules in the process preceding the melting of crystal.

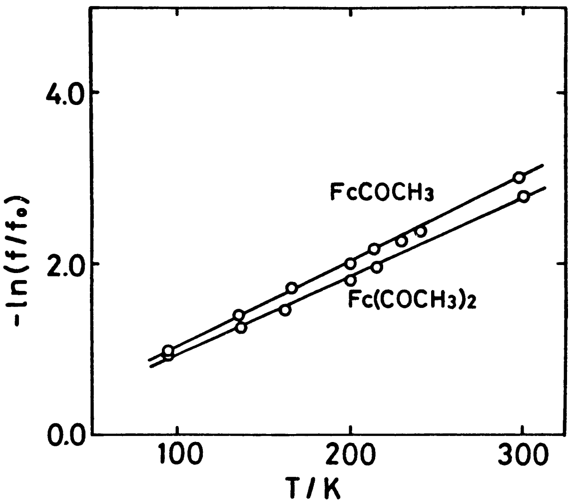

Fig. 2. Temperature dependence of lnf in monoacetylferrocene (m. p. 90°C) and 1,1'-diacetylferrocene (m. p. 128 °C). Recoil-free fraction, f, was normalized respect to the value at 0K.

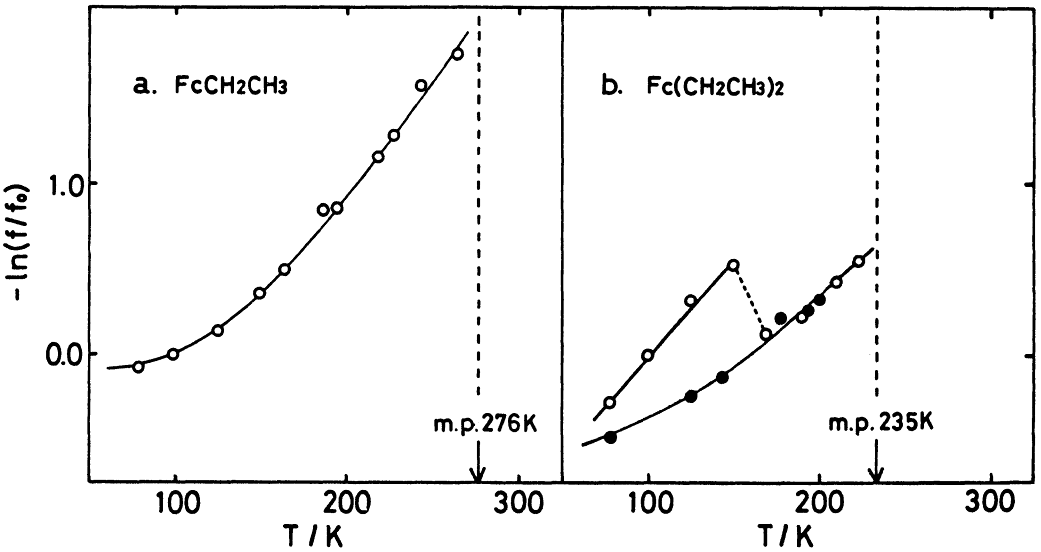

Fig. 3. Temperature dependence of lnf in monoethylferrocene (a) and in diethylferrocene (b). Open circles were obtained on heating the samples which was cooled down at first to liquid nitrogen temperature. Closed circles were obtained on cooling diethylferrocene heated up to 224K in the heating experiment. No hysteresis was found in monoethylferrocene. Recoil-free fraction, f, was normalized with respect to the value at 100K.

As shown by open circles in Fig. 3b, the value of lnf for 1,1'-diethylferrocene which was prepared by putting the liquid sample in liquid nitrogen, suddenly increases between 150-170K. The drastic anomaly observed at this point in the heating process is attributed to the transition from the glass to the crystal state via the supercooled liquid state, as based on the data of D. T. A. shown in Fig. 1. The apparent crystallizing temperature was observed at 180K in the scanning speed, 2.2deg$\cdot$min^{-1}, in D. T. A.. It is supposed, however, that the crystallizing temperature will be a little lower than 180K in a lower scanning speed, because higher apparent Tc is obtained at higher scanning speed than 2.2deg$\cdot$min^{-1} (e. g., 190K in 10deg$\cdot$min^{-1}). Since the measurement of Mössbauer spectra required about 24 hours at a constant temperature, the values of lnf from 80K to 149K are attributed to thermal motion of molecules in glass state. The values above 169K (corresponding to the Tc (180K) in D. T. A.) may reflect the thermal motion in the crystal state. The larger value of -lnf found near 149K indicates that molecules in the glass state are much more mobile compared to molecules near 200K in the crystal state in spite of the higher temperature.

Closed circles in Fig. 3 show the data of lnf obtained in the re-cooled process from 224K to 80K. Since it is impossible to transit from crystal state to glass state on cooling, the closed circles indicate the data obtained from the crystal state. It is clearly observed that lnf of 1,1'-diethylferrocene in crystal state differs from that of glass state at the same temperatures.

The temperature dependence of lnf in 1,1'-diethylferrocene on cooling also deviates from a single straight line as found in monoethylferrocene. The slopes estimated from the temperature dependence in the lower temperature region for mono- and diethylferrocene, come close to the slopes found for mono- and diacetylferrocene while the slopes increase as the temperature rise near to the respective melting points. The similarity of the temperature dependence between ethylferrocenes in the lower temperature and acetylferrocenes in any temperature observed can be interpreted by assuming similar molecular size and packing in the crystal state, because it is known that the intermolecular interaction dominates the recoil-free fraction in molecular compounds in the solid. The slope of lnf obtained for diethylferrocene in the crystal state near the melting point, becomes similar in the magnitude to that found in the glass state, indicating that the mean-square amplitudes of iron atom in the crystal state near the melting points, are similar to those in the glass state which are ca. 70K lower than the crystal state temperatures.

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