[June, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 1961—1966 (1987) 1961

Studies on the Lattice Dynamics in Ferrocene Derivatives by Means of Recoil-Free Fraction and Thermal Shift in Mössbauer Spectra

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(Received October 4, 1986)

Lattice dynamics in ferrocene derivatives, mono- and disubstituted acetyl-, carboxy-, and ethylferrocenes, tetrachloro(1,1′-diacetylferrocenato-*O,O′*)tin(IV) and tetrachlorobis(acetylferrocenato-*O*)tin(IV) have been studied by determining the temperature dependence of the recoil-free fraction and the thermal shift in the Mössbauer spectra. It was found that the lattice vibrations in acetyl- and carboxyferrocenes and adducts could be satisfactorily explained by assuming a harmonic oscillation model, while those of ethyl-substituted ferrocenes could not be interpreted by assuming harmonic vibrations.

Ferrocene derivatives are of great interest to the authors, since they exhibit various kinds of mesophase transitions associated with intermolecular interactions.[1–4] In order to investigate the effect of substituent groups on the lattice dynamics, such ferrocene derivatives as mono- and disubstituted acetyl-, carboxy-, and ethyl-ferrocene have been synthesized and the lattice dynamical nature of these compounds investigated in the solid state by comparing their Mössbauer spectra with the crystal structures and thermal data.

Lattice dynamics in more complicated systems, tetrachloro(1,1′-diacetylferrocenato-*O,O′*)tin(IV) and tetrachlorobis(acetylferrocenato-*O*)tin(IV), were also studied by Mössbauer spectroscopy. The temperature dependence of the recoil-free fraction and the thermal shift were determined for each of two the Mössbauer nuclides, ^{57}Fe and ^{119}Sn, included in the adducts, in order to investigate the total vibration of molecules.

Experimental

Preparation of Mono- and Disubstituted Ferrocenes. Mono- and disubstituted ferrocenes were prepared by following the method described in Ref. 5. The purification was carried out by repeated sublimations and recrystallizations. The purities were confirmed by checking the melting point and by elemental analyses. No impurity was detected in infrared(IR), NMR, and Mössbauer spectra.

Preparation of Adducts. Tetrachloro(1,1′-diacetylferrocenato-*O,O′*)tin(IV) and tetrachlorobis(acetylferrocenato-*O*)tin(IV) were prepared by modifying the method described in Ref. 6. Since the adducts are very sensitive to air, the samples for IR and Mössbauer measurements were mounted under nitrogen in a glove box. The IR spectra agreed with those of the literature.[6] However, the data of elemental analyses are not in good agreement with the calculated values, since the partial decomposition of adducts seems to occur upon exposure to air.

Mössbauer Spectra. Mössbauer spectra were measured using an Austin Science Associate Mössbauer spectrometer. A velocity calibration was carried out based on the spectra of metallic iron at room temperature. By fitting the resonance line-shape to a Lorentzian function, the Mössbauer parameters could be extracted. Low-temperature measurements were carried out by using a CA thermocouple embedded in a copper sample holder in a cryostat. The precision of this measurement was approximately ±1°.

Structure Determination and Refinement for Ferrocenecarboxylic Acid. A yellow-needle single crystal suitable for an X-ray study was obtained by slowly evaporating a methanol solution. The crystal size employed for data collection was approximately 0.05 m×0.15 mm×0.35 mm. Intensity data were collected on a four-circle diffractometer using an ω-2θ scan technique. A total of 2356 reflections were measured with Mo $K\alpha$ radiation ($2\theta<55°$); of these, 1252 were considered to have a significant intensity ($|F_o|>3\sigma|F_o|$). The intensities of the four standard reflections remained almost constant during data collection.

Crystal data for ferrocenecarboxylic acid are tabulated in Table 1. The positions of carbon and iron atoms were deduced from sharpened Patterson maps and all of the hydrogen atoms were deduced from difference syntheses. The block-least-squares program HBLS-4[7] was employed using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The atomic scattering factors were taken from the International Tables for X-ray Crystallograpy (1974).[8] Unit weights were adopted for all reflections. The R value reduced to 0.040 and final atomic parameters are given in Table 2. The complete F_o-F_c data have been deposited as Document No. 8736 at the

Table 1. Summary of Crystallographic Data for Ferrocenecarboxylic Acid at 24°C

Molecular formula	$C_{11}H_{10}O_2Fe$
Molecular weight	M.W. 235.0
Crystal system	Monoclinic
Space group	$P2_1/c$
a	5.8183(5) Å[a)]
b	12.8535(11) Å
c	13.2064(13) Å
β	108.734(8)°
V	935.32(14) Å^3
D_c	1.67 g cm^{-3}
Z	4
R	4.0%

a) 1 Å=10^{-8} cm.

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Table 2. Positional Parameters ($\times 10^4$; for $\mathrm{H}\times 10^3$)

	X	Y	X	$U_{eq}\times 10^2$(Å^2)		X	Y	X	$U_{eq}\times 10^2$(Å^2)
Fe	3066(1)	1807(1)	1791(1)	31(1)	O(1)	−94(8)	4392(3)	1084(4)	65(2)
C(1)	−129(10)	1047(5)	1184(6)	61(3)	O(2)	2921(8)	4341(3)	377(4)	65(2)
C(2)	1651(12)	363(5)	1770(5)	55(2)	H(1)	−159(10)	127(4)	121(4)	59(17)
C(3)	3495(10)	339(4)	1297(4)	46(2)	H(2)	166(12)	−6(5)	242(5)	89(23)
C(4)	2870(11)	1014(4)	429(4)	47(2)	H(3)	497(12)	4(6)	155(5)	95(24)
C(5)	633(11)	1468(5)	353(5)	57(2)	H(4)	384(10)	113(5)	−2(5)	72(20)
C(6)	2597(9)	2953(4)	2770(4)	38(2)	H(5)	−18(12)	196(5)	−11(5)	80(21)
C(7)	4422(11)	2264(5)	3354(4)	47(2)	H(6)	108(8)	313(4)	291(4)	36(13)
C(8)	6283(10)	2244(5)	2878(4)	49(2)	H(7)	442(9)	179(4)	391(4)	50(15)
C(9)	5664(9)	2914(4)	2003(4)	42(2)	H(8)	766(9)	180(4)	313(4)	44(14)
C(10)	3358(10)	3371(4)	1921(4)	38(2)	H(9)	661(10)	309(5)	154(4)	67(18)
C(11)	1929(11)	4070(4)	1097(5)	45(2)	H(10)	194(12)	479(6)	−18(5)	95(24)

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Results and Discussion

First, suitable model compounds having similar molecular weights and volumes but different intermolecular interactions caused by the substituent groups (mono- and disubstituted acetyl-, carboxy-, and ethylferrocenes) were synthesized and the temperature dependence of Mössbauer spectra was measured in order to elucidate the relationship between the recoil-free fraction or the thermal shift and the lattice vibration in these ferrocene derivatives.

The recoil-free fraction, f, can be estimated from the areal intensity of Mössbauer spectrum and is expressed by the mean-square amplitude of a Mössbauer atom, $<U^2>$:

$$f=\exp[-4\pi^2<U^2>/\lambda_\gamma^2] \qquad (1)$$

where λ_γ is the wavelength of a Mössbauer γ-ray. It is difficult to obtain an absolute recoil-free fraction by using the areal intensity method, because of the absence of a suitable standard sample. Therefore, the mean-square amplitude was estimated by a high-temperature-approximation method.[2] At a temperature sufficiently high to assume $T \gg \Theta_D/2$ (where Θ_D is the Debye characteristic temperature), it is known that the mean-square amplitude is proportional to the absolute temperature. The values of the mean-square amplitude are estimated from the slope of the linear relationship.

Figure 1 shows the temperature dependence of the mean-square amplitude estimated from the areal intensities of the Mössbauer spectra for iron atoms in acetyl- and carboxyferrocenes. The mean-square amplitude is considered to be proportional to the absolute temperature nearly up to room temperature, indicating that the molecules are in harmonic vibration. The values of the mean-square amplitude at room temperature determined by applying the high-temperature approximation from 78 K to room temperature are 2.6×10^{-2}, 2.8×10^{-2}, 3.0×10^{-2}, and 4.5×10^{-2} Å^2 for ferrocenecarboxylic acid, 1,1′-diacetylferrocene, acetylferrocene, and 1,1′-ferrocenedicarboxylic acid, respectively, while those determined based on the isotropic thermal factors in X-ray diffraction study are 3.1×10^{-2}, 2.8×10^{-2},[10] 3.2×10^{-2},[3] and 4.0×10^{-2} Å^2,[11] respectively. Both values for the same compound are in fairly good agreement with each other. The value of the mean-square amplitude of ferrocenecarboxylic acid is slightly less than those of acetylferrocenes, while the value of 1,1′-ferrocenedicarboxylic acid was estimated to be about 1.5-times larger than those of other compounds.

Figure 2 shows the crystal structure of ferrocenecarboxylic acid determined by X-ray diffraction. The C-C distances in the cyclopentadienyl rings are 1.289—1.426 Å; the Fe-C distances are 2.019—2.045 Å. These results are in good agreement with acetylferrocene[3] and 1,1′-diacetylferrocene,[10] as well as molecules that exhibit an eclipsed conformation. The C(11), O(1), and O(2) atoms lie approximately on the plane of the aromatic rings, because of a existence of a

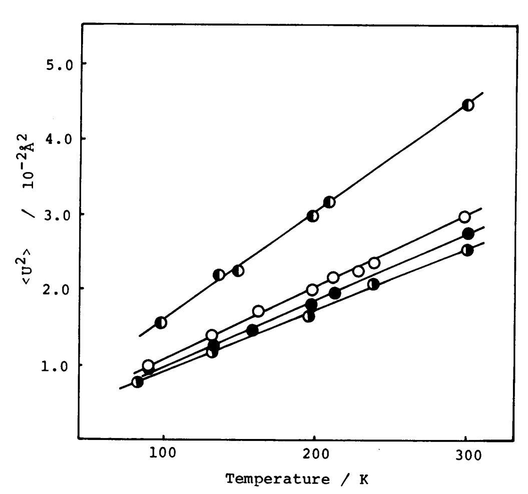

Fig. 1. The temperature dependence of mean-square amplitude for acetylferrocene (O), 1,1′-diacetylferrocene (●), ferrocenecarboxylic acid (◑), and 1,1′-ferrocenedicarboxylic acid (◐).

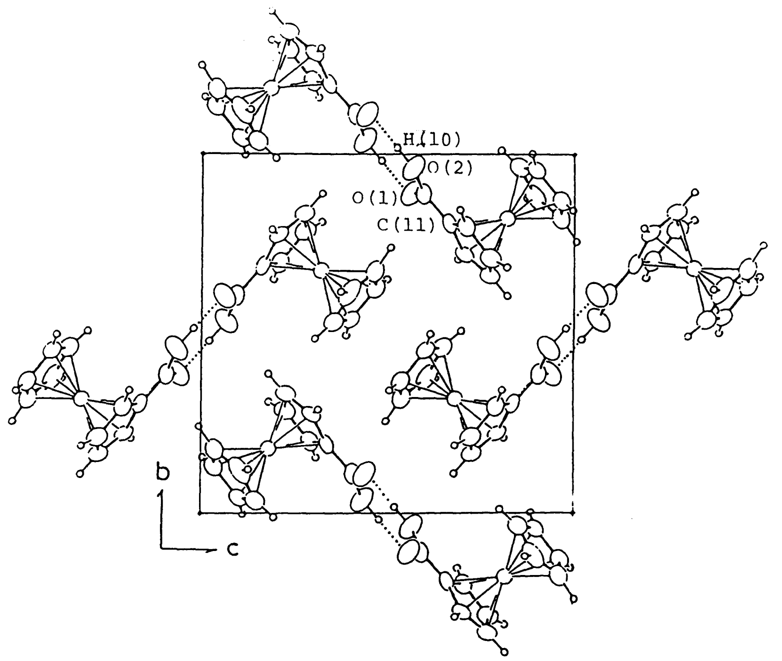

Fig. 2. Projection of the crystal structure of ferrocenecarboxylic acid along the a axis at room temperature. The hydrogen bonding O(1)···H(10) is indicated by broken lines.

complete conjugation between the carboxyl group and cyclopentadienyl rings. Two molecules of ferrocenecarboxylic acid have an intermolecular hydrogen bonding as shown in Fig. 2. The hydrogen-bonding distance between O(1) and H(10) is 1.69 Å and that between O(1) and O(2) is 2.65 Å. The H(10) is covalently bonded to the O(2) on one side of the carboxyl group. Molecules of ferrocenecarboxylic acid seem to be rigid in the crystal state owing to a significant interaction of hydrogen bonding between carboxyl groups.

On the other hand, the values of the mean-square amplitude of iron atom in 1,1′-ferrocenedicarboxylic acid are about 1.5-times larger than those found in other ferrocene derivatives. It was found by means of X-ray diffraction measurements that two 1,1′-ferrocenedicarboxylic acid molecules form a dimer through two intermolecular hydrogen bonds.[11] The present sample was determined to be a monoclinic form by Weissenberg photographs. The intermolecular hydrogen bonds seem to be so strong that the dimer molecules of 1,1′-ferrocenedicarboxylic acid behave like one molecular unit in regard to the molecular motion.

An attempt to interpret the molecular motion for 1,1′-ferrocenedicarboxylic acid was made by applying a rigid-body model. The center of gravity for this compound associated with the molecular motion is assumed to be located at the center of a dimer. Since iron atoms are far apart from the center of gravity in a dimer and its moment of inertia for librational vibration seems to be large, the large values of the mean-square amplitude for iron atoms could be explained by assuming both translational and librational motion. For the other compounds, it is roughly assumed that all the iron atoms sit at the center of mass of the molecules and, thus, the mean-square amplitudes of iron atoms have been estimated to be much smaller than that of 1,1′-ferrocenedicarboxylic acid.

As can be seen in Fig. 3, the temperature dependence of the mean-square amplitude for mono- and 1,1′-diethylferrocene derivates from a single straight line, which shows anomaly at about 150 K. There seems to

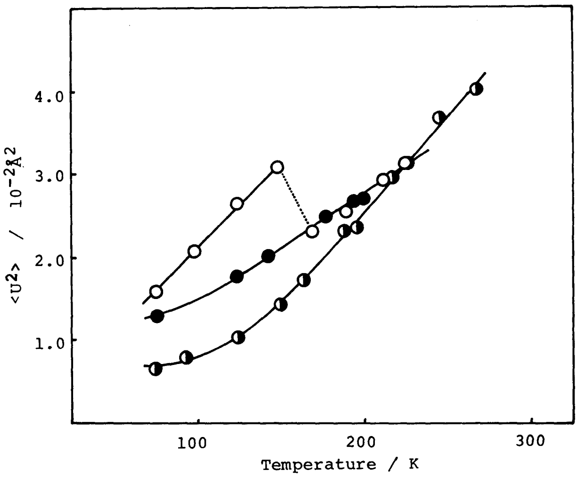

Fig. 3. The temperature dependence of mean-square amplitude in ethylferrocene (◑) and in 1,1′-diethylferrocene (○) and (●), in which open circles were obtained by heating the samples where were first cooled down to liquid nitrogen temperature; closed circles were obtained on cooling 1,1′-diethylferrocene heated up to 224 K in the heating experiment.

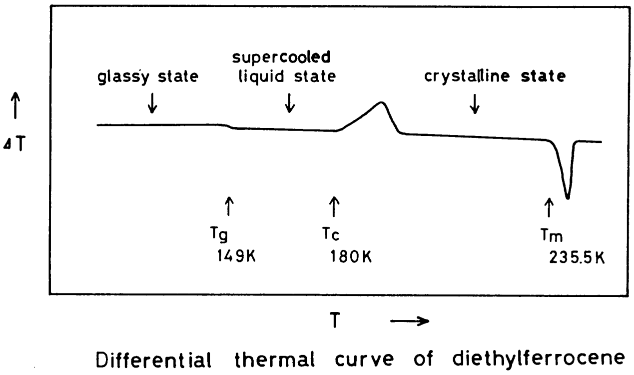

Fig. 4. Differential thermal curve of 1,1′-diethylferrocene at scanning rate of 2.2 deg min^{-1}, *Tg*: Transition temperature from glass to supercooled liquid state (glass transition temperature); *Tc*: Transition temperature from supercooled liquid to crystal state (crystallizing temperature); *Tm*: Melting point.

exist an anharmonicity of the intermolecular vibration in the low-temperature region owing to a loosely packed crystal structure caused by the flexibility of the ethyl groups. This observation suggests that the thermal vibration in acetyl- and carboxy-substituted ferrocenes differs considerably from that in the ethyl-substituted ones.

1,1′-Diethylferrocene was found to have a glassy state through a thermal analysis (Fig. 4).[2)] The Differential Thermal Analysis (DTA) data of 1,1′-diethylferrocene reveal that this compound in a glassy state turns into a supercooled liquid state at 149 K, the glass transition temperature, T_g. After heating beyond T_g, crystallization takes place at 180 K, the crystallizing temperature, T_c, followed by melting at 235.5 K. Although the apparent T_g and T_c depend upon the scanning rate of the temperature, nearly constant values of T_g and T_c are obtained with good reproducibility at various slow scanning rates (<2 deg min^{-1}).

In Fig. 3, the open circles indicate the data obtained while heating a sample which was first cooled down to liquid-nitrogen temperature. The closed circles indicate the data obtained while cooling 1,1′-diethylferrocene (heated to 224 K during the heating experiment). The drastic anomaly observed in the recoil-free fraction at 150—170 K during the heating process could be attributed to a transition from the glass to the crystal state via a supercooled liquid state (based on the DTA data shown in Fig. 4). The apparent crystallizing temperature is a little lower than 180 K for a lower scanning speed than 2.2 deg min^{-1}. Since a measurement of the Mössbauer spectra requires about 24 h at a constant temperature, values of the mean-square amplitude between 80 and 149 K are attributed to the thermal motion of molecules in a glass state. The values above 169 K (corresponding to the T_c (180 K) in DTA) may reflect the thermal motion in a crystal state. The larger value of the mean-square amplitude found near 149 K indicates that the molecules in a glass state are much more mobile compared to the molecules near 200 K in a crystal state. Since it is impossible to change from a crystal state to a glass state during cooling, the data of the mean-square amplitude obtained in the recooled process from 224 to 80 K are ascribed to the values for the crystal state. It has been clearly observed that the mean-square amplitude of 1.1′-diethylferrocene in the crystal state differs from that in the glassy state at the same temperature. The value of the mean-square amplitude obtained for 1,1′-diethylferrocene in the crystal state near the melting point is similar in magnitude to that found at the glass transition point.

Lattice dynamics in tetrachlorobis(acetylferrocenato-*O*)tin(IV) and tetrachloro(1,1′-diacetylferrocenato-*O,O′*)tin(IV) have been observed by Mössbauer spectroscopy in order to investigate the total vibration of molecules.

These adducts were synthesized by Pavlik et al. in 1968 and were suggested to have a molecular structure in which oxygen atoms of acetyl groups are coordinated to tin atoms. The isomer shift and quadrupole splitting values of iron atoms in the Mössbauer spectra at nitrogen temperature for the sample mounted under nitrogen are 0.51 and 2.17 mm s^{-1} for tetrachlorobis(acetylferrocenato-*O*)tin(IV) and 0.49 and 1.98 mm s^{-1} for tetrachloro(1,1′-diacetylferrocenato-*O,O′*)tin(IV), respectively. The values of quadrupole splitting are smaller than other ferrocene derivatives because of the electron-attracting effect of the acetyl group coordinating to the tin atom. The isomer shift values of tin atoms in the Mössbauer spectra at nitrogen temperature are 0.46 mm s^{-1} for tetrachlorobis(acetylferrocenato-*O′*)tin(IV) and 0.39 mm s^{-1} for tetrachloro(1,1′-diacetylferrocenato-*O,O′*)tin(IV), respectively, which are smaller than those, 1,45—1.55 mm s^{-1}, of starting materials, $SnCl_4$. These adducts are found to have an octahedral structure which consists of an sp^3d^2 orbital since the s-electron density around tin atoms in these adducts is lower than that of $SnCl_4$. Mössbauer spectroscopic data support the results offered by Pavlik et al.

Figure 5 shows the temperature dependence of the mean-square amplitude obtained for these adducts. The values of the mean-square amplitude of iron atoms were found to be larger than those of tin atoms. The reason may be that iron atoms require not only a translational motion of the center of gravity but also a librational motion around the center of gravity, since iron atoms are located far from the center of gravity and possess a large moment of inertia for librational motion around the center of gravity. Although the crystal structures of these adducts cannot be determined because of instability in air and the difficulty of preparing a single crystal, the results obtained from the temperature dependence of the mean-square amplitude indicate that the mean-square amplitude of iron and tin atoms are apparently proportional to the

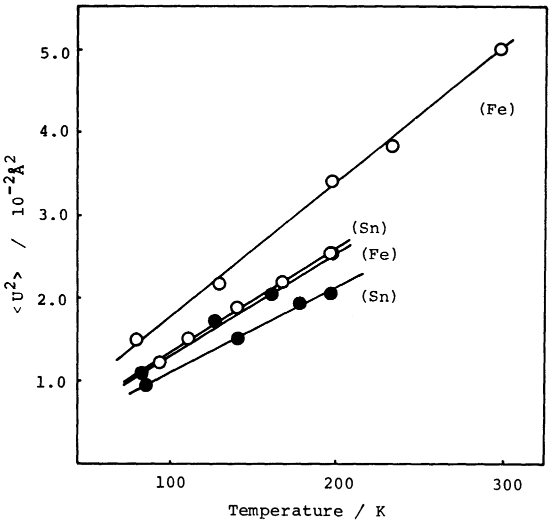

Fig. 5. The temperature dependence of mean-square amplitude determined for each of two Mössbauer nuclei, iron and tin atoms, included in the respective adducts, in which open circles were obtained for tetrachlorobis(acetylferrocenato-*O*)tin(IV); closed circles were obtained for tetrachloro(1,1′-diacetylferrocenato-*O*,*O*′)tin(IV).

absolute temperature in the temperature range studied and that the molecular vibration for these adducts can be explained by assuming the harmonic vibration and the rigid-body model.

The thermal shift, so-called 2nd-order Dopplar Shift, extracted from the Mössbauer spectra also gives significant information about the lattice dynamics in the solid state. The thermal shift originates from the mass defects of the Mössbauer nuclei associated with a γ-ray transition. When the high-temperature approximation of the Debye model is applied, the thermal shift, ΔE, can be expressed as,

$$\Delta E = 3kTE_{\gamma}/2c^2M, \qquad (2)$$

where E_{γ} is the energy of the Mössbauer γ-ray and M is the effective vibrational mass. It was known that the Mössbauer spectra shift position by both thermal and isomer shifts. Since the former depends on the temperature, the temperature dependence of center shifts in Mössbauer spectra can provide information concerning the magnitude of the thermal shift.

Figure 6 shows the temperature dependence of the center shifts. It was found that all the values are proportional to the absolute temperature and that their slopes are constant in spite of the different molecular structure. When the thermal shifts was interpreted by applying the Debye model (as shown in Eq. 2) the effective vibrational mass was estimated to be ca. 100 for all the studied samples. This fact indicates that the thermal shift dose not depend on the intermolecular interaction and that the iron atom and some atoms in its neighbourhood are involved as a unit in the molecular vibration.

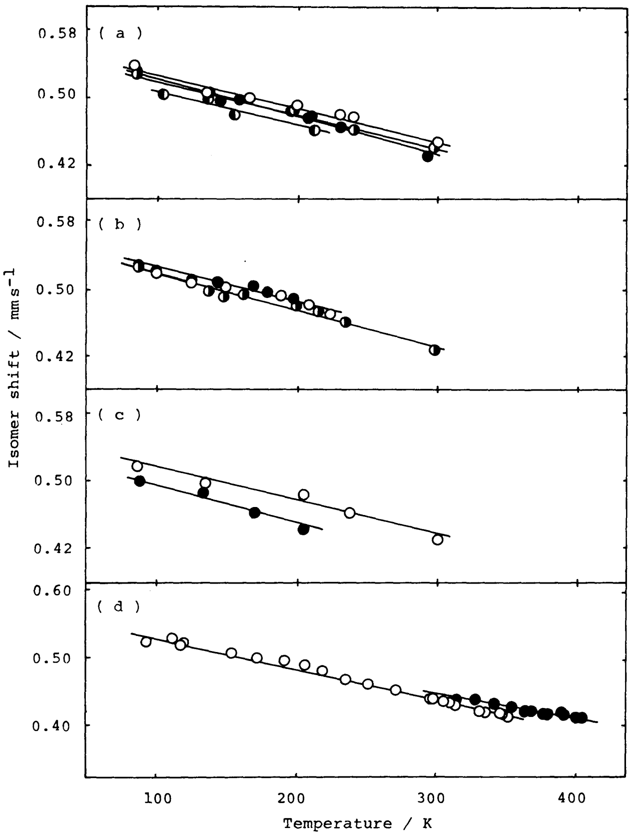

Fig. 6. The temperature dependence of thermal shift for (a) acetylferrocene (○), 1,1′-diacetylferrocene (●), ferrocenecarboxylic acid (◑), and 1,1′-ferrocenedicarboxylic acid (◐), (b) ethylferrocene (◑) and 1,1′-diethylferrocene (○) and (●), in which open circles were obtained in the crystal state; closed circles were obtained in the glassy state, (c) tetrachlorobis(acetylferrocenato-*O*)tin(IV) (○) and tetrachloro(1,1′-diacetylferrocenato-*O*,*O*′)tin(IV) (●), (d) formylferrocene (○) and 1,1′,2,2′-tetrachloroferrocene (●).

It is interesting to note that the values of the thermal shifts obtained in the crystal phase and the glassy phase for 1,1′-diethylferrocene are apploximately equal (Fig. 6(b)) in spite of the drastic difference in the mean-square amplitude between the crystal and glassy phases. The results were also observed in other ferrocene derivatives having a mesophase. The authors have reported that the mean-square amplitudes of formylferrocene and 1,1′,2,2′-tetrachloroferrocene drastically change at the plastic crystal phase transition points, 296.5 and 391 K, respectively.[4] In the case of the formylferrocene, the value of the mean-square amplitude in the plastic phase is about 4-times larger than those in the crystal phase. However, as shown in Fig. 6(d), the thermal shift of formylferrocene shows no significant change in the range from 78 to 343 K. For formyl- and 1,1′,2,2′-tetrachloroferrocene, the effective masses were estimated to be ca. 100, similar to the values obtained in the present work.

It is concluded that acetyl- and carboxyferrocene and adducts exhibit harmonic thermal vibrations in the range of whole temperature but that ethyl-substituted ferrocenes do not exhibit harmonic thermal vibration at low temperatures. The values of the mean-square amplitude of iron atoms significantly depend upon the position of the iron atom in the compound associated with the moment of inertia in molecular motion. The magnitude of the mean-square amplitude is affected by the molecular arrangement in the solid state, such as the crystal and the glassy states. On the other hand, the thermal shift dose not depend on the intermolecular interaction for ferrocene derivatives studied and the values of vibrational mass estimated from Debye model remain in a constant value. It was found that the thermal shift depends on the bonding state between the Mössbauer atoms and the atoms around the Mössbauer atom.

The authors are indebted to Prof. Michiko Konno at Ochanomizu University for her kind help regarding the use of the X-ray diffractometer at the Institute for Solid State Physics, The University of Tokyo and for discussions concerning the results.

References

1) F. L. Hedberg and H. Rosenberg, *J. Therm. Anal.*, **6**, 571 (1974); J. Malthete and J. Billard, *Mol. Cryst. Liq. Cryst.*, **34**, 117 (1976); M. F. Daniel, A. J. Leadbetter, R. E. Meads, and W. G. Parker, *J. Chem. Soc., Faraday Trans. 2*, **1978**, 456.

2) K. Sato, M. Katada, and H. Sano, *Chem. Lett.*, **1980**, 217.

3) K. Sato, M. Katada, H. Sano, and M. Konno, *Bull. Chem. Soc. Jpn.*, **57**, 2361 (1984).

4) K. Sato, M. Konno, snd H. Sano, *Chem. Lett.*, **1984**, 17; K. Sato, M. Iwai, H. Sano, and M. Konno, *Bull. Chem. Soc. Jpn.*, **57**, 634 (1984).

5) M. Rosenblum and R. B. Woodward, *J. Org. Chem.*, **80**, 5443 (1958); K. L. Rinehart, Jr. K. L. Motz, and S. Moon, *J. Org. Chem.*, **79**, 2749 (1957); R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Org. Chem.*, **74**, 3458 (1952); R. A. Benkeser and J. L. Bach, *J. Org. Chem.*, **86**, 890 (1964).

6) I. Pavlik, J. Klikorka, and K. Handlir, *Z. Chem.*, **8**, Jg. 10, 390 (1968).

7) T. Ashida (1976) UNICS. The Universal Crystallographic Computing System, The Crystallographic Society of Japan.

8) "International Tables for X-Ray Crystallography." Kynoch Press, Birmingham (1974), Vol. IV.

9) H. Sano, Mössbauer Spectroscopy The Chemical Applications, Kodansha Ltd., 1972.

10) G. J. Palenik, *Inorg. Chem.*, **9**, 2424 (1974).

11) F. Takusagawa and T. F. Koetzle, *Acta. Cryst.*, **B35**, 2888 (1979); G. J. Palenik, *Inorg. Chem.*, **8**, 2744 (1969).