Metal atom motion, vibrational anisotropy and hydrogen bonding effects in octamethylferrocenylmethanol

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Abstract

Temperature dependent ^{57}Fe Mössbauer effect measurements of octamethylferrocenylmethanol, using ^{57}Fe enriched samples, have been carried out over the temperature range $90 \leq T \leq 320$ K, and analyzed to elucidate the dynamics of the metal atom motion in this solid ($T_{mp} = 484$ K). In consonance with earlier observation of related octamethylferrocenes (OMFcs), there is a significant drop in the recoil-free fraction at temperatures well below T_{mp}. However, the almost complete disappearance of the resonance effect observed earlier at $T \ll T_{mp}$ in OMFcs is absent, presumably due to a ring–ring interaction effected by hydrogen-bond coupling, consistent with room temperature infra-red data for this solid. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In several recent studies [1–4] it has been shown that temperature-dependent ^{57}Fe Mössbauer spectroscopy can be used to elucidate the motion of the metal atom in a number of iron-organometallics, and in particular the anisotropy of this motion over a wide temperature range. It was noted that in contrast to compounds such as ferrocene methanol and 1,1′-dimethyl ferrocene, in which the resonance effect was observable to within 0.5° of the melting point (T_{mp}), in a number of octamethyl ferrocene systems, the recoil-free fraction effectively becomes unobservable some 180° or more below T_{mp}. This observation has been accounted for by a 'gear-wheel' effect [5], in which the onset of rotation of the Cp ring with four methyl groups gives rise to a librational motion which, in turn, increases the mean square amplitude of vibration (msav) of the metal atom to the point where the recoil-free fraction (f_a) becomes vanishingly small. The abrupt onset of this increase in the msav of the metal atom is particularly evident in octamethylethynylferrocene (**I**) [201472-67-5] and its ethenyl congener [121429-48-9]. In the present study, the metal atom motion in octamethylferrocenyl-methanol (**II**) [128925-13-3] has been examined in detail over the temperature range $90 < T < 330$ K and compared to the corresponding data for **I** and the parent ferrocene (**III**) [102-54-3].

2. Results and discussion

As is true of all ferrocene-related diamagnetic solids, the Mössbauer spectra of such compounds consist of a well-resolved doublet. A typical spectrum of a sample of **II**, which had been prepared from ^{57}Fe enriched starting material (see Section 4), is shown in Fig. 1. From this figure it is seen that there is present a small impurity, having an isomer shift (IS) of ca. 0.4 mm s^{-1}

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and a quadrupole splitting of ca. 0.5 mm s^{-1}. In the subsequent analysis of the data, the presence of this impurity has been taken into account. It should be noted from Fig. 1 that there is a small but distinct intensity asymmetry in the two components of the spectrum. This intensity asymmetry, characterized by the ratio $R = A(+)/A(-)$, where the two areas refer to that at a positive and negative velocity with respect to the spectrum centroid, respectively, can arise from two major contributions. The first of these are referred to as the 'texture' effect, and is due to the preferential orientation of the crystallites with respect to the gamma ray axis of the experiment. This contribution is temperature independent. The second contribution arises from
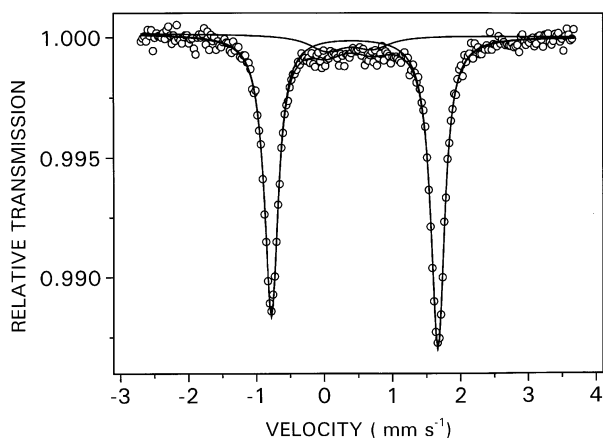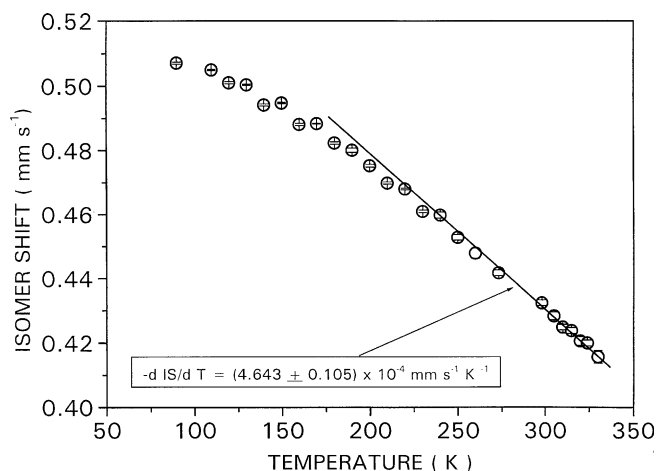
Fig. 2. Temperature dependence of the isomer shift parameter of **II**.

the anisotropy of the metal atom motion with respect to the major molecular symmetry axis, and is commonly referred to as the Gol'danskii–Karyagin effect (G.K.E.). This contribution is temperature dependent, and reaches a limiting value at low temperatures. The observed R values in **II** are, in fact, temperature dependent above ca. 200 K, and this observation is clearly indicative of an anisotropy in the iron atom motion relative to the orientation of the two Cp rings. Similar vibrational anisotropies have been reported [2] both for **III** as well as for a number of other ferrocenoid solids, and the present results are in no way unexpected. However, in the absence of detailed X-ray crystallographic characterization of **II**, it is not possible to assign quantitative values to this vibrational anisotropy on the basis of the currently available data. The hyperfine and related parameters are summarized in Table 1, together with the corresponding data for **I** and **III**.

The IS of **II** as a function of temperature is summarized graphically in Fig. 2. The high temperature $(240 < T < 330$ K) slope leads to an 'effective vibrating mass' [6], M_{eff}, of 90 da, in good agreement with the values reported [7] for related ferrocene solids. The IS at 90 K calculated from this regression is 0.527 ± 0.001 mm s^{-1}.

The temperature dependence of the quadrupole splitting (QS) parameter for **II** is summarized in Fig. 3, which clearly evidences a maximum at ca. 200 K. The decrease of the QS at higher temperatures is a result of both normal thermal expansion effects, as well as the onset of ring motion (vide infra).

The temperature dependence of the area under the resonance curve for **II**, which is related to the recoil-free fraction, f_a, is shown graphically in Fig. 4 and evidences two distinct regimes. In the region below ca. 200 K, $\text{d} \ln[A(T)/A(90)]/\text{d}T$ has a slope of ca. -8×10^{-3} K^{-1}, and this value, combined with the low-temperature d IS/dT value leads to a 'Mössbauer lattice temperature' [6], Θ_{M}, of ca. 85 K. Above the breakpoint the

Fig. 1. Mössbauer spectrum of ^{57}Fe labelled octamethylferrocenylmethanol (**II**) at 273 K. The velocity scale is with respect to the centroid of an α-Fe spectrum at room temperature. Because of the small value of f_a at this temperature, in excess of 26 million counts were scaled for each channel.

Table 1
Summary of Mössbauer data for the compounds discussed in the text

	I	**II**	**III**	Units
IS(90)	0.508(1)	0.507(1)	0.531(1)	mm s^{-1}
QS(90)	2.426(1)	2.459(1)	2.419(1)	mm s^{-1}
−d IS/dT	3.90(6)	3.19(15) [a]	3.29(7)	10^{-4} mm s^{-1} K^{-1}
		4.64(10) [b]		
M_{eff}	107	90 [e]	126	Da
−d ln[$A(T)$/$A(90)$]/dT		8.23(46) [a]	8.50(42)	10^{-3} K^{-1}
		17.00(16) [e]		
Θ_{M}		85 [d]	85	K
		71 [e]		

The figures in parentheses are the uncertainties in the last figures of the data.
[a] $90 \le T \le 225$ K.
[b] $240 \le T \le 330$ K.
[c] $260 \le T \le 330$ K.
[d] From low T data.
[e] From high T data.

$\ln A(T)$ curve has a slope of ca. $-17 \times 10^{-3} \text{ K}^{-1}$, and this value, combined with the high temperature slope of the IS leads to Θ_M of ca. 71 K. The distinct decrease, on warming, of the lattice temperature at ca. 200 K, that is, some 250° below the reported [8] melting point ($T_{mp} = 454$ K) is clearly indicative of a phase change in this solid. This lattice softening, as probed by the iron atom motion, is the result of a new intra molecular degree of freedom in the solid. It should be noted, however, that in contrast to the sudden change in $\ln A(T)$ observed in **I** and in octamethylethynylfer-

rocene, inter alia, at temperatures well below T_{mp}, the high temperature regime for **II** evidences a significantly slower decrease in the recoil-free fraction. In the case of the compounds reported earlier [5,7], the sharp decrease in the recoil-free fraction has been ascribed to the onset of rotation of one (or both) of the methyl-substituted cyclopentadienyl rings. The presence of one ring site with a hydrogen (instead of a methyl) substituent leads to the onset of a librational motion which, in turn, strongly influences the msav of the iron atom. A very similar behavior is observed in **II** at ca. 200 K, but only one of the two rings is free to rotate. The other ring, bearing the hydroxymethyl substituent, is involved in hydrogen bonding to a neighboring molecule, as indicated schematically in Fig. 5. This type of hydrogen bonding is also evident in the crystal structures which have been reported [9] for a number of α-ferrocenyl alcohols, albeit not of the octamethyl congeners of the present study. The hydrogen bonding in **II** is clearly observed in the room temperature IR spectrum (KBr) of this solid which shows a broad absorbance centered at ca. 3240 cm^{-1}, a region which is characteristic and diagnostic for this type of interaction. Consistent with this identification is the fact that a comparable IR spectrum of octamethylferrocene carbaldehyde, [128925-12-2], which differs structurally from **II** in the double bond of the oxygenated carbon substituent, thus implying the absence of a hydroxylic proton, shows no absorbance of the kind noted for **II** in the corresponding region between 3700 and 3000 cm^{-1}.

Because of the ^{57}Fe enriched nature of these absorbers, all samples are optically 'thick', especially at low temperatures, and hence the area under the resonance curve can be taken as only a qualitative measure of the temperature dependence of the msav of the iron atom. To correct for the saturation effects associated with optically 'thick' samples, the resonance curve data have been analyzed using a transmission integral fitting procedure [10]. Such an analysis permits the calculation of the quantity $k^2 \langle x^2 \rangle$, where k is the wave vector of the 14.4 keV gamma radiation of the Mössbauer transition. The results of this analysis are summarized in Fig. 6 for **II**, as well as for ferrocene (**III**) [11] and octamethylethynylferrocene (**I**). The data for **I** show the onset of the sudden increase in the metal atom msav at the transition temperature, while those for **III** do not show any major effect of the onset of ring rotation in the solid. The data for **II** are clearly of an intermediate behavior, and reflect the competition between the effects of ring rotation of the tetra-methyl substituted Cp ring, and its concomitant 'gear-wheel' effect, on the one hand, and the hydrogen bonding interaction between adjacent molecules, on the other.

It is worth observing that the quantitative determination of $k^2 \langle x^2 \rangle$, using the transmission integral formalism, is sensitive to assumptions made concerning the
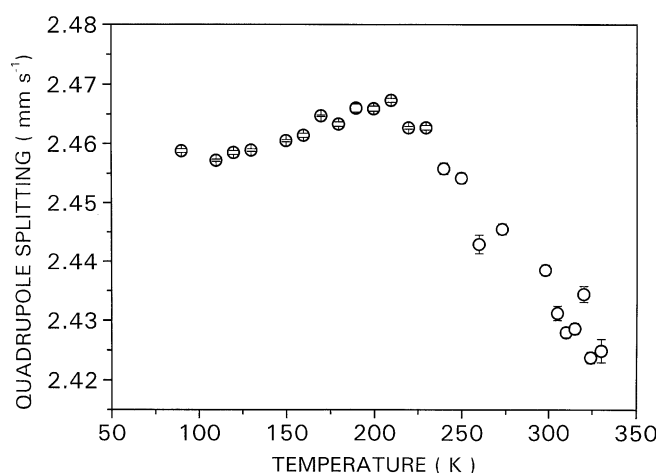

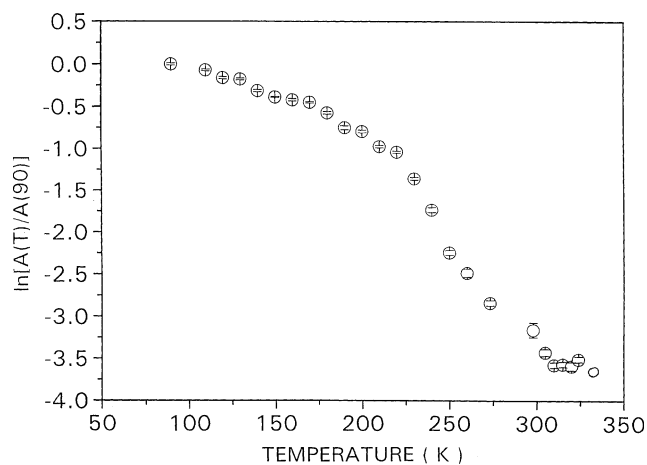Fig. 3. Temperature dependence of the quadrupole splitting parameter of **II**.

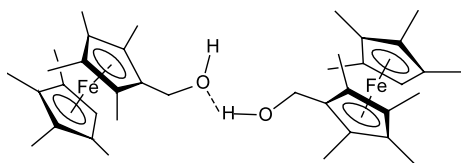Fig. 4. Temperature dependence of the logarithm of the area under the resonance curve of **II**.

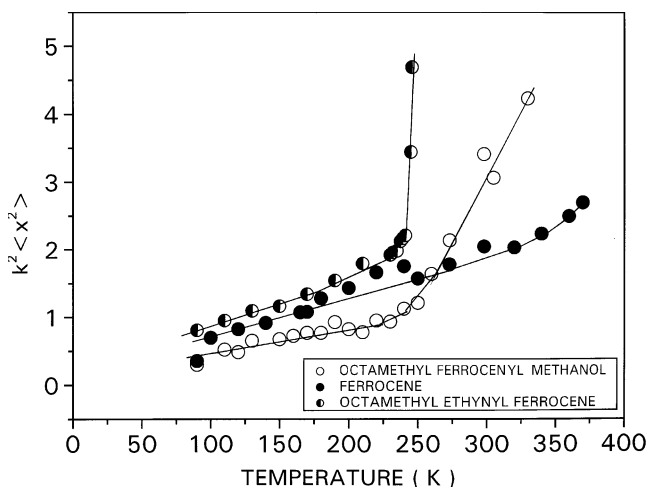Fig. 5. Postulated intra-molecular hydrogen bonding interaction in **II** in the solid state.

Fig. 6. Temperature dependence of $k^2\langle x^2\rangle$ of **II** (open circles), **I** (half-filled circles), and **III** (filled circles).

line width of the source and that of the absorber, and a number of other parameters involved in the fitting procedure. Thus, in the absence of X-ray diffraction U_{ij} data, which can serve as normalization points, the indicated values of $k^2\langle x^2\rangle$ can only be taken as having relative significance. In this context, however, it is interesting to note that the root-mean-square-amplitude of vibration of the iron atm in **II** is ca. six times larger at room temperature than at 90 K. If the quasi-linear behavior of $k^2\langle x^2\rangle$ at low temperatures is extrapolated to room temperature, this ratio is only ca. 2. This factor of three difference is a clear indication of the lattice softening above the ca. 200 K transition—as probed by the iron atom—referred to above.

3. Summary and conclusions

The temperature-dependent Mössbauer data accumulated in this study demonstrate clearly two competing effects which influence the metal atom motion in octamethylferrocenylmethanol (**II**). The first of these is the increase in the msav of the metal atom due to the 'gear wheel' effect noted earlier for related octamethyl ferrocene systems. The second effect is related to the postulated hydrogen bonding between adjacent molecular units in the solid, and this interaction, also inferred from relevant infra-red data, mediates the msav of the Fe atom arising from the motion of one of the two methyl-substituted Cp rings of solid **II**.

4. Experimental

4.1. Sample preparation

Starting with ^{57}Fe enriched iron powder (> 95%, Advanced Materials Technologies, Or Yehuda, Israel)

an optimized synthesis of ^{57}Fe labelled octamethylferrocene has been developed, and is to be published in detail [12]. Subsequently, a Vilsmeyer formylation to ^{57}Fe octamethylferrocene carbaldehyde, and a final hydride reduction to ^{57}Fe octamethylferrocenylmethanol (**II**) was performed by a slight modification of the procedure of Zou and Wrighton [8].

4.2. Instrumentation

Nicolet 510 FT-IR (IR); melting point determinations (uncorrected) were performed on a Kofler hotplate apparatus (Leica Galeen III).

4.3. Mössbauer spectroscopy

The crystals obtained by the synthetic procedure detailed above were finely ground in an agate mortar, and mixed with a large excess of BN to optimize random sample orientation. This mixture was transferred to plastic sample holders which were, in turn, mounted in a transmission geometry cryostat. The sources, detectors, temperature control system and spectrometer calibration have been described earlier [1,4]. All IS are reported with respect to the centroid of an α-Fe absorber spectrum at room temperature. In general, in excess of 4 million counts per channel (of 256) were recorded at each temperature, with the data at the high temperature end of the range involving as many as 40 million counts per channel, due to the small value of f_a in this region.

Data analysis was effected using either a Lorentzian fitting program for optically 'thin' samples, or a transmission integral procedure [10] for samples for which thickness broadening is significant. Temperature control over the several hour periods of data accumulation is considered to be accurate to within $\pm 0.2°$.

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