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Lattice dynamics, phase transitions and spin relaxation in $[Fe(C_5H_5)_2]$ PF_6

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Abstract The organometallic compound ferrocenium hexafluorophosphate, $[Fe(C_5H_5)_2]$ PF_6, has been studied by Mössbauer spectroscopy in the past, mainly to determine the crystal structure at high temperatures. Here we present studies at 95 K to 305 K and analyze the spectra in terms of spin relaxation theory which yields accurately the hyperfine interaction parameters and the spin-spin and spin-lattice relaxation rates in this paramagnetic compound. The spectral area under the resonance curve yields the recoil free fraction and thus the mean square of the vibration amplitude $<x^2>$. One observes a large discontinuity in the slope of $<x^2>$versus T at ≈210 K, indicative of a phase transition. The analysis of the spectra proves that the quadrupole interaction is small but certainly negative, $½e^2qQ = -0.12(2)$ mm/s, and causes the asymmetry observed in the spectra. The detailed analysis yields also, for the first time, the fluctuating effective magnetic hyperfine field, $H_{eff} = 180(50)$ kOe.

Keywords Mössbauer spectroscopy · Lattice dynamics · Phase transitions · Spin relaxation · Ferrocenium hexafluorophosphate

1 Introduction

When diamagnetic iron-organometallics are subjected to one-electron oxidation, the normal Mössbauer spectrum of the former, which consists of two well-separated components of the quadrupole split (QS) absorbance, is replaced by an absorption spectrum that consists of an asymmetric broad line that can be associated with spin relaxation of the paramagnetic

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oxidation product. The fundamental theoretical treatment of the QS ”collapse” in ferrocene ($Fe(C_5H_5)_2$, Fc) was reported in a classical study by Collins [1]. Accordingly, Mössbauer spectroscopy has been employed to monitor, in addition to conventional hyperfine interaction parameters, also electron-transfer processes and mixed valence species involving ferrocenes. Here we present an extension of a research by Webb *et al* [2] who have studied $[Fe(C_5H_5)_2]PF_6$ but were interested mainly in the crystal structure at high temperatures. We summarize here studies of $[Fe(C_5H_5)_2]PF_6$ at 95 K to 305 K and analyze the spectra in terms of spin relaxation theory which yields accurately the hyperfine interaction parameters and the spin-spin and spin lattice relaxation rates in this paramagnetic compound.

2 Experimental details

(a) Reagent grade $Fc^+PF_6^-$ was obtained commercially and not further purified prior to use. A 50 milligram sample was mixed with BN and transferred to a perspex sample holder.

(b) ^{57}Fe Mössbauer spectroscopy was effected in transmission geometry as described previously [3]. Spectrometer calibration was based on a room temperature spectrum of metallic iron, and the isomer shifts here reported are with respect to the centroid of these data. To monitor sample integrity relative to evaporation or sublimation, the transmission rate through the sample was determined both before and after each temperature point data acquisition. Temperature control was monitored using the Megadaq [4] software.

3 Results and analysis

3.1 Relaxation spectra

The observed Mössbauer spectra at 95 K to 305 K in this paramagnetic material display a broad asymmetric absorption line due to spin relaxation phenomena, as discussed before for other ferrocenium compounds, such as octamethylferrocenium tetraflouroborate [5], octamethylferrocenium hexafluorophosphate [6], and decamethylferrocenium tetraflouroborate [7], among others. Representative spectra are shown in Fig. 1. Mössbauer spectroscopic observations of paramagnetic spin relaxation phenomena are common for ionic, trivalent compounds and were studied since the early sixties [8]. The spectra are, in most cases, analyzed in terms of a fluctuating effective magnetic hyperfine field corresponding to the ionic ground state Kramers' doublet (around 500 kOe for $S_z = \pm 5/2$, for trivalent iron). In ferrocene and related compounds the iron is held by both covalent and ionic bonds and is diamagnetic. When subjected to one-electron oxidation, it becomes paramagnetic with an effective spin of 1/2. The fluctuating magnetic hyperfine field cannot generally be determined because even at 4.2 K the spectra do not have well-resolved magnetic structure, probably due to temperature-independent spin-spin relaxation. In our case of $[Fe(C_5H_5)_2]PF_6$ the spectra were of good statistics (Fig. 1), and the least squares fit of the spectra using the frequently used formula [9, 10] yield the effective magnetic hyperfine field $H_{eff} = 180(50)$ kOe, the quadrupole interaction $½e^2qQ = -0.12(2)$ mm/s and the relaxation rate to the accuracy shown in Fig. 2.

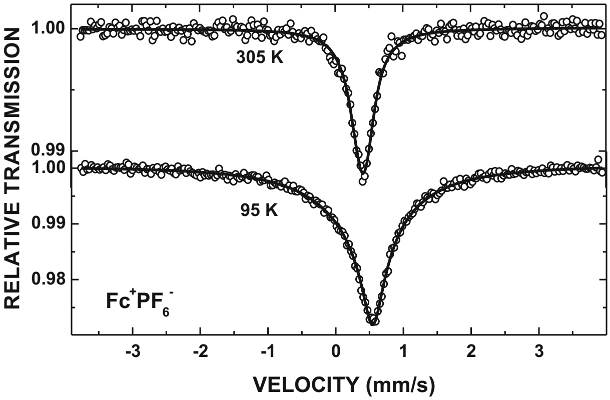

Fig. 1 The Mössbauer spectra of $[Fe(C_5H_5)_2]PF_6$ at lowest and highest temperature of measurement

The temperature dependence of the relaxation rate $1/\tau$ was fitted as in Ref. [5], but by the approximate ($\Delta >> T$) formula;

$$1/\tau = r_{ss} + r_o \exp(-\Delta/T) \tag{1}$$

where r_{ss} is the temperature independent spin-spin relaxation rate, and the exponential portion is that due to the spin-lattice Orbach process [11], and where Δ is the energy of the first excited state above the iron ground doublet state.

3.2 Determination of the recoil free fraction

The direct determination of the recoil free fraction from a spectrum is quite difficult. However if the absorber is thin enough to assume that the spectral area A(T) at temperature T is proportional to the recoil free fraction f(T) of the absorber, namely

$$A(T) = Cf(T) \tag{2}$$

and the recoil free fraction f (T) is given by the expression [12]

$$f(T) = \exp(-k^2 <x^2>) \tag{3}$$

where k is the wave number of the γ-ray, and $< x^2>$ is the mean square amplitude of vibration in the direction of the γ-ray then one obtains:

$$k^2 <x^2> = -\ln(A(T)/C) \tag{4}$$

In any model in which the density of the vibration modes of a crystal are temperature independent, the high temperature limit of $k^2<x^2>$is linear in temperature T (for example in

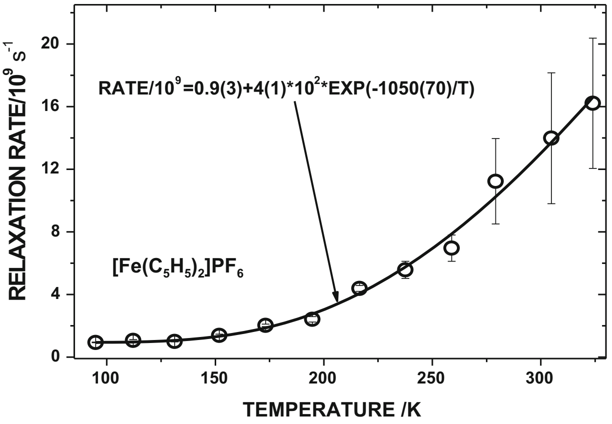

Fig. 2 The temperature dependence of the spin relaxation rate, the solid line represents the theoretical fit with spin-spin (at very low T) and the spin-lattice Orbach relaxation process at high T

the Debye model, for $T>O_D/2$, $k^2<x^2>$is proportional to $T/\ O_D^2$). Thus in order to derive $k^2<x^2>$one calculates the high temperature experimental value of the slope of -ln(A(T)), which is also the slope of $k^2<x^2>$and the constant C is obtained from the requirement that the high temperature values of $k^2<x^2>$the straight line extrapolated to zero temperature will reach the value $k^2<x^2>=0$, making the assumption that the zero-point vibration amplitude is negligibly small compared to the values in the T regime of the ME study. This procedure was applied in the present case as has been reported previously [5]. The absorber $[Fe(C_5H_5)_2]PF_6$ used in the present experiment was thin enough to permit this application and the results are shown in Fig. 3.

3.3 Phase transitions

Many of the diamagnetic [13] and paramagnetic [14] ferrocene derivatives display crystallographic phase transitions, observable by several conventional methods. In particular we stress here the contribution of Mössbauer spectroscopy in revealing such transitions, observable by the sudden change, as a function of temperature [15], in one or several [16] of the hyperfine interaction parameters. Even pure ferrocene displays a phase transition at 169 K, observable by a sharp change in the large quadrupole splitting [13] and to a lesser extent in the slope of $k^2<x^2>$as a function of T. In $Fc^+\ PF_6^-$ however the quadrupole interaction is very small, hardly observable, but the change in slope of $k^2<x^2>$as a function of T is shown in Fig. 3.

3.4 Hyperfine field

The metal atom ground state Kramers' doublet was assumed to have an effective spin 1/2, with an effective magnetic hyperfine field fluctuating up-down along the major symmetry axis. To determine the magnitude of the hyperfine field originating from this spin state, the goodness of the fit (χ^2) was determined for various initial values of the hyperfine field. The minimal value of χ^2 was obtained for $H_{eff} = 180\pm50$ kOe. This is the first determination of the value of the magnetic field fluctuating in ferrocenium compounds.

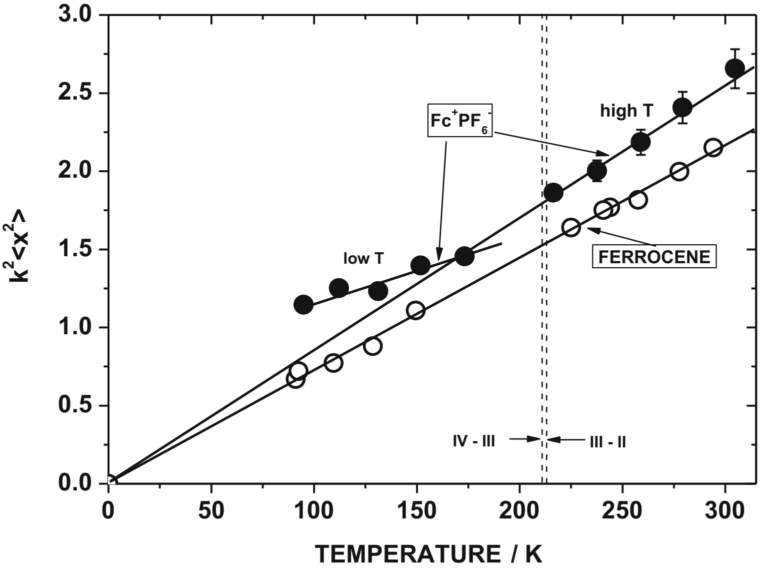

Fig. 3 The mean square of the vibration amplitude, times the square wave number of the γ ray, in $[Fe(C_5H_5)_2]PF_6$ and in $Fe(C_5H_5)_2$.

4 Conclusions

The detailed Mössbauer spectroscopy study of $[Fe(C_5H_5)_2]PF_6$ as a function of temperature reported here yields: All of the hyperfine interaction parameters including, for the first time, the value of the fluctuating magnetic hyperfine field. The analysis of the spin relaxation spectra yields the temperature dependence of the spin relaxation rates. The spectral area temperature dependence yields the mean square amplitude of vibration of the iron atom in the paramagnetic complex, $k^2<x^2>$, and can be compared to that in the neutral ferrocene parent compound as a function of T and displays the presence of the phase transition discussed by Webb *et al.* [2].

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