A STUDY OF IRON PALMITATE BY MÖSSBAUER SPECTROSCOPY

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ABSTRACT

Mössbauer spectra of iron palmitate were measured in the temperature range from 77 K to 362 K. They were found to be consistent with the weak antiferromagnetically exchange coupled binuclear structure of the compound. From the temperature dependence of the spectral areas a phase transition at 185 K was determined. Vibrations of the iron palmitate molecules as a whole are suggested above this temperature. Spectral line widths were related to the medium to fast spin relaxation.

INTRODUCTION

Binuclear compounds with antiferromagnetically exchange coupled spins have so far presented various features of interest, in particular their special magnetic properties and structure. Among them, iron soaps have also been studied for their ability to form complex organometallic catalysts of the Ziegler-Natta type[1,2] and lyotropic mesophases in some organic solvents[3]. Iron stearate is one of the most studied iron soaps, to which X-ray diffraction[4,5], IR spectroscopy[1] and magnetic susceptibility measurements[6,7] have been applied. Mössbauer spectra of iron stearate have been measured indicating that iron ions were in the high spin state ($S = 5/2$), but no detailed physical interpretation was attempted[2]. It has been suggested[7] that iron stearate exists in the form of metal-metal bound dimers with a quasi aromatic ring formed by the π-molecular orbitals of the stearic acid carbonyl groups to which ferric d-electrons may contribute.

Thus, it was of interest to study the compound $Fe(C_{15}H_{31}COO)_3$ (i.e. iron palmitate) by means of Mössbauer spectroscopy. As will be shown later on in this work, this compound is isostructural with iron stearate.

EXPERIMENT AND RESULTS

Iron palmitate was prepared according to ref. 4 and X-ray diffraction patterns were taken. Dry samples of 9.2 mg/cm^2 of natural iron served as absorbers for Mössbauer measurements in transmission geometry. A 25 mCi $^{57}Co/Rh$ source was used and spectra were recorded with a 512 multichannel analyser. The velocity scale and the centre shifts were calibrated with natural iron. The measurements were done in the temperature range from 77 K to the melting point of the sample. This was optically determined to be: $T_m = 89^oC \pm 2^oC$ in fair agreement with ref. 8.

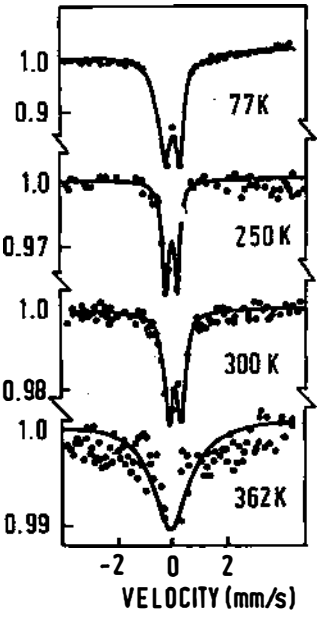

Fig.1 Some typical Mössbauer spectra of iron palmitate.

Some resulting Mössbauer spectra of iron palmitate are shown in Fig. 1. They consist of a slightly asymmetric quadrupole doublet with rather broad lines of not exactly Lorentzian shape, indicating the presence of a relaxation process. In any case, they were analysed by a least square fitting routine assuming a Lorentzian line shape, although the more rigorous treatment considering the appropriate relaxation Hamiltonian is in progress. The values of the centre shift and quadrupole coupling at 77 K are 0.49 ± 0.02 mm/s and 0.69 ± 0.02 mm/s respectively; very close to those reported for iron stearate[1,2], This, and also the similar X-ray diffraction patterns for the two compounds indicate

that they are isostructural. We may thus assume iron palmitate to exist in the form of dimers with the iron spins antiferromagnetically coupled by the exchange interaction: $H = -2JS_1S_2$. The value of the exchange integral (J) could be deduced from the temperature dependence of the magnetic susceptibility[9]. Our re-interpretation of the data from ref. 6 for iron stearate and laureate in terms of the exchange interaction yielded $J = -25 \pm 5\ cm^{-1}$ and the total spin $S_T = 3$, for both compounds. Since iron palmitate is isostructural to them, the exchange interaction must also be practically the same in this compound. Thus the ground state of dimer is diamagnetic and due to the relatively weak exchange interaction even at 77 K, higher states, which are paramagnetic, are considerably populated. These can in turn produce a magnetic field at the site of the iron nucleus and thus the line broadening if their relaxation time, due to interaction with the neighbouring spins, is not too short. The nearly constant line width as determined for iron palmitate (Fig. 2a) up to about 190 K is thus in agreement with the rather small value of J as suggested above.

Fig. 2b represents the temperature dependence of -lnA. A is the total peak area, which is directly proportional to the recoilless fraction (f). As seen, there is an abrupt change in the recoilless fraction at 185 ± 10 K, whereas the other Mössbauer parameters remain unchanged. This suggests a transition with a change of lattice dynamics, but not affecting the structure of the immediate vicinity of the iron ions. Namely, the recoilless fraction is proportional to the mean square displacement ($\langle x^2 \rangle$) of the iron ion, which is mostly sensitive to the long wavelength vibrations[11].

Assuming the Debye model for the lattice vibrations, $\langle x^2 \rangle$ can be related to the Debye temperature (θ) and the recoilless fraction in the high temperature limit ($T \geq \theta/2$) becomes:

$$f = I \exp\left(-\frac{3}{2}\frac{E_R}{k\theta} - \frac{6E_R}{k\theta^2}T\right) \qquad (1)$$

where E_R is the recoil energy and I the factor coming from the possible vibrational anisotropy.

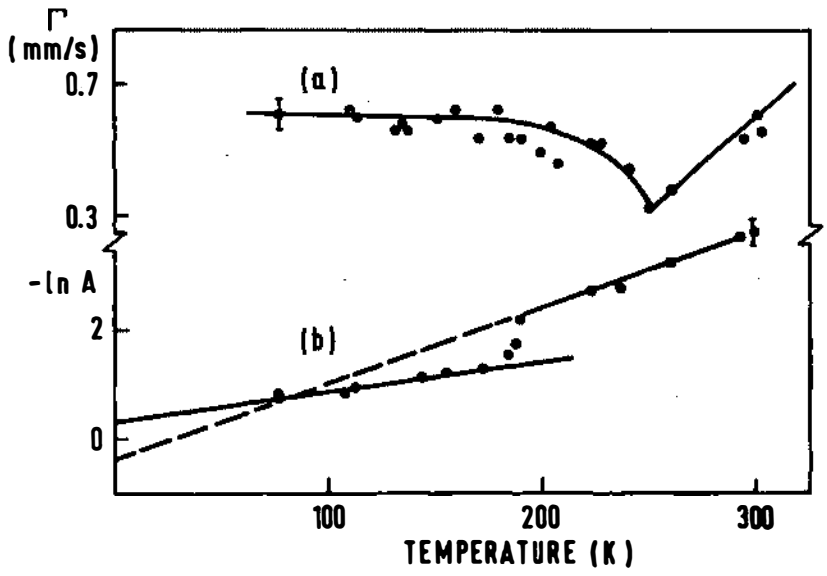

Fig. 2 Temperature dependence of the low energy line width (a) and negative logarithm of the spectral area of the sample $Fe(C_{15}H_{31}COO)_3$ (b).

Note that in Fig. 2b -lnA extrapolated to zero temperature gives a higher value in the low temperature region then in the higher one. This difference can come only from the first term in Eq. (1), since all other contributions to -lnA are constant experimental parameters. Even vibrational anisotropy (factor I) does not change significantly in this temperature range, for no change in the peak area ratio was detected. But the observed difference is just contrary to that expected if the recoil energies are the same in both regions. This discrepancy can be explained by considering at low temperatures only the vibrations of iron ion, but at higher ones the iron palmitate molecule must vibrate as a whole, thus reducing the recoil energy. At the phase transition at 185 K the palmitic acid chains which at lower tem-

perature were rigidly fixed in the crystal lattice, probably reorient so that the molecules of iron palmitate can vibrate as a unit.

Our data yield $\theta = 146 \pm 5$ K for the low temperature region and $\theta = 25.6 \pm 5$ K for the high temperature one. The average amplitude of the ferric ion in iron palmitate can be then approximated by $\sqrt{\langle x^2 \rangle}$, which is 0.26 Å ± 0.04 Å at 250 K. Considering that in iron stearate the intermolecular and intramolecular distances at room temperature are 3.6 Å and 4.1 Å respectively[5], the vibrational amplitudes of about 0.25 Å should be enough for the intermolecular distance to reduce to the value of the intramolecular one. Thus the line width minimum at 250 ± 10 K can be explained by the decrease of the spin-spin relaxation time due to the intermolecular intraction. The increase in line width and spectral asymmetry at still higher temperatures could be due to diffusion and anisotropic vibrations of the iron palmitate molecule.

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REFERENCES

1. A.R.Brodskii et al., J. Organomet. Chem. 178, 325 (1979)
2. A.S.Khlystov et al., J. Phys. (Paris), 41, C1-343 (1979)
3. R.P.Varma and H.K.Bhargava, Anali di Chimica 66, 773 (1976)
4. R.D. Vold and G.S.Hattiangdi, Ind.and Engin.Chem. 41, 2311 (1948)
5. V.A.Tulupov et al., Zh. Fiz. Khim. 40, 850 (1966)
6. R.C.Herron and R.C.Pink, J. Chem. Soc. (London), 1956, 3948
7. V.A.Tulupov, Zh. Fiz. Khim. 39, 2341 (1965)
8. G.S.Hattiangdi et al., Ind. and Engin. Chem. 41, 2320 (1948)
9. W.M.Reiff, in: "Mössbauer Effect Methodology", ed. I.J. Gruverman, Vol. 7, 213, Plenum Press. New York 1971
10. M.Blume, Phys. Rev. Lett. 18, 305 (1967)
11. Y.Hazony and R.H.Herber, J. Phys. (Paris) 35, C6-131 (1974)