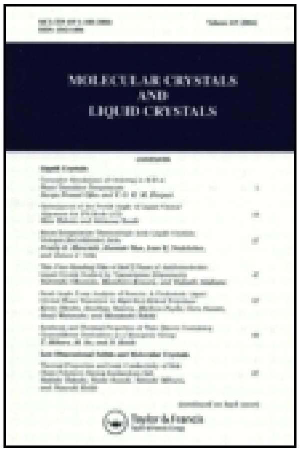

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mössbauer Spectroscopic Studies of $\{Nr_4Fefe(Ox)_3\}_X$ and Related Compounds ($R = N\text{-}C_3H_7$, $N\text{-}C_4H_9$)

Seiichiro Iijima [a] & Fumio Mizutani [a]

[a] National Institute of Bioscience and Human-Technology, 1-1 Higashi Tsukuba, Ibaraki, 305, Japan

Version of record first published: 04 Oct 2006

To cite this article: Seiichiro Iijima & Fumio Mizutani (1997): Mössbauer Spectroscopic Studies of $\{Nr_4Fefe(Ox)_3\}_X$ and Related Compounds ($R = N\text{-}C_3H_7$, $N\text{-}C_4H_9$), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 227-234

To link to this article: http://dx.doi.org/10.1080/10587259708044570

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 227–234
Reprints available directly from the publisher
Photocopying permitted by license only

MÖSSBAUER SPECTROSCOPIC STUDIES OF $\{NR_4FeFe(ox)_3\}_x$ AND RELATED COMPOUNDS ($R = n\text{-}C_3H_7$, $n\text{-}C_4H_9$)

SEIICHIRO IIJIMA AND FUMIO MIZUTANI
National Institute of Bioscience and Human-Technology, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Abstract Oxalate-bridged metal complexes, $\{NBu_4[FeFe(ox)_3]\}_x$ **(1)**, $\{NPr_4[FeFe(ox)_3]\}_x$ **(2)**, $\{NPr_4[FeCr(ox)_3]\}_x$ **(3)** and ^{57}Fe(II)-doped $\{NPr_4[MnCr(ox)_3]\}_x$ **(4)** were investigated by using ^{57}Fe Mössbauer spectroscopy, where NBu_4^+, NPr_4^+ and ox^{2-} are the tetra(*n*-butyl)ammonium ion, tetra(*n*-propyl)ammonium ion and oxalate ion, respectively. Magnetically split features of the Mössbauer spectra of **1** and **2** below Néel temperature were similar to each other, while a great difference in magnetization behavior between these compounds was reported. From the temperature dependence of the quadrupole splitting in the paramagnetic states, it was suggested that the axial field splitting of the t_{2g} orbitals of Fe(II) is somewhat larger in **1** than in **2**. The direction of the internal field at Fe(II) was observed to be approximately parallel in **1-3** and perpendicular in **4** to the honeycomb layers consisting of an alternate array of the bivalent and tervalent metal ions through ox^{2-} ligands.

INTRODUCTION

^{57}Fe Mössbauer spectroscopy provides significant information regarding the electronic, magnetic and lattice-dynamical properties of materials containing iron atoms. Several members of the molecular-based magnets found by Ōkawa et al., $\{NBu_4[M(II)M'(III)(ox)_3]\}_x$,[1-3] have been revealed by this spectroscopy to show three-dimensional magnetic ordering under zero applied field,[4-7] where NBu_4^+ = tetra(*n*-butyl)ammonium ion, ox^{2-} = oxalate ion. Recently, Day et al. have reported that five $\{A[FeFe(ox)_3]\}_x$ compounds (A^+ = quaternary ammonium, phosphonium or arsonium ion) including $\{NBu_4[FeFe(ox)_3]\}_x$ **(1)** exhibit a crossover from positive to negative magnetization near 30 K on lowering the temperature.[8,9] On the other hand, some other $\{A[FeFe(ox)_3]\}_x$ compounds such as $\{NPr_4[FeFe(ox)_3]\}_x$ **(2)** give magnetizations which increase monotonically below the Néel temperature (T_N) as conventionally found in materials with finite spontaneous magnetization,[8,9] where $NPr_4{}^+$ = tetra(*n*-propyl)ammonium ion. We reported preliminary results about the temperature dependence of the Mössbauer spectrum of **1** in the previous paper.[4] In the present work, the Mössbauer spectroscopic behavior of **2** was compared with that of **1** in order to obtain further insight into the magnetic ordering phenomena of the $\{A[FeFe(ox)_3]\}_x$ system. In addition, Mössbauer spectra were measured for two other compounds, $\{NPr_4[FeCr(ox)_3]\}_x$ (**3**) and ^{57}Fe(II)-doped $\{NPr_4[MnCr(ox)_3]\}_x$ (**4**) in connection with this purpose.

EXPERIMENTAL

Compound **1** was obtained as microcrystals by the reaction of $K_3[Fe(ox)_3]\cdot 3H_2O$ with $FeSO_4\cdot 7H_2O$ in the presence of NBu_4Br.[3] Compound **2** was prepared similarly by using NPr_4Br in place of NBu_4Br.[9] Compound **3** was prepared from $K_3[Cr(ox)_3]\cdot 3H_2O$, $FeSO_4\cdot 7H_2O$ and NPr_4Br according to the procedure for the preparation of $\{NBu_4[FeCr(ox)_3]\}_x$.[2] The ^{57}Fe-doped compound **4** was obtained by mixing an aqueous solution of $K_3[Cr(ox)_3]\cdot 3H_2O$ and NPr_4Br with an aqueous solution of $MnCl_2\cdot 4H_2O$ which contains $^{57}Fe^{2+}$ formed by the reaction of ^{57}Fe metal powder with H_2SO_4. Microanalyses for C, H, N, Cr, Mn and Fe afforded **4** the formula $\{NPr_4[Fe_{0.03}Mn_{0.97}Cr(ox)_3]\}_x$.

Mössbauer spectra were measured with an instrument described previously.[4] The hyperfine parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shifts are reported relative to metallic iron foil. The temperature accuracy was estimated to be ±0.5 K.

RESULTS AND DISCUSSION

The Mössbauer spectra of **2** were measured at 16 different temperatures between 4.2 and 298 K. Some of these spectra are shown in Figure 1. Above 40K, the spectrum consisted of two quadrupole doublets showing the presence of two kinds of iron atoms, high-spin Fe(II) and high-spin Fe(III), in paramagnetic states. At 78 K, for example, the isomer shift (δ) and the quadrupole splitting (ΔE_Q) were obtained for the Fe(II) as 1.30 and 1.83 mm/s, respectively, and for the Fe(III) as 0.48 and 0.68 mm/s, respectively. At 35 K, the centered absorption lines broadened and the base line was somewhat winding (Fig. 1c). The spectra below 35 K can be understood as a superposition of the line components of Fe(II) and Fe(III) split magnetically, as shown in Figure 1e. The above spectral change with temperature clearly indicates that the T_N of **2** is around 35 K, in accord with the results of cryomagnetic measurements.[9] The H_n (the magnitude of the internal magnetic field at the ^{57}Fe nucleus[10-12]) *vs.* temperature plots for the Fe(II) and Fe(III) are shown in Figure 2b.[13] Both H_n values increased rapidly on lowering the temperature below T_N (~35 K), and reached substantially saturated values at 4.2K (62 kOe for the Fe(II) and 536 kOe for the Fe(III)).

A great difference in the temperature dependence of magnetization between **1** and **2** was reported as mentioned in the Introduction.[8,9] The crossover from positive to (strongly) negative magnetization of **1** on lowering the temperature was explained by the idea that the Fe(II) and Fe(III) sublattices have

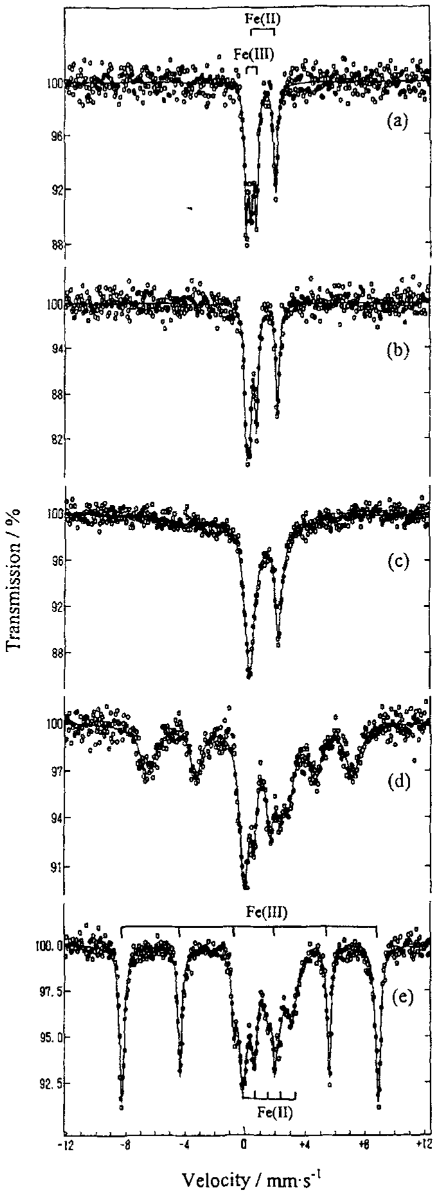

FIGURE 1 Mössbauer spectra of Compound **2** at (a) 140 K, (b) 40 K, (c) 35 K, (d) 28 K and (e) 4.2 K.

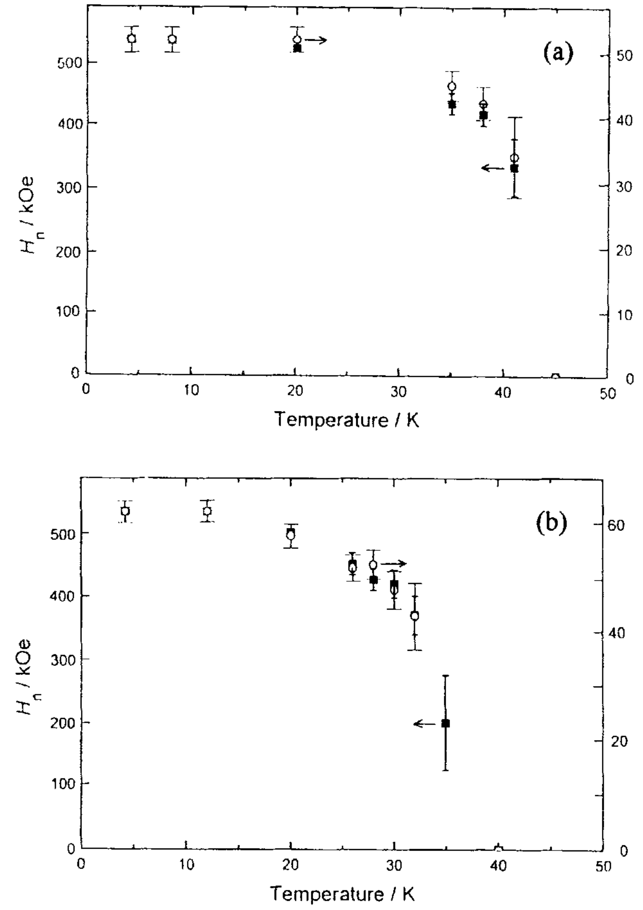

FIGURE 2 Temperature dependences of H_n of Fe(II) (○) and Fe(III) (■);[13] (a) Compound **1**, (b) Compound **2**.

different temperature dependences of the magnetization (the "compensation temperature[14]" ~ 30 K),[9] and the small H_n of the Fe(II) (52 kOe[4], ~40kOe[6] at 4.2 K) was thought to evidence this idea.[9] However, it is revealed in this work that the H_n of **2** is comparable to that of **1**. Similar H_n values are also obtained for the ferromagnets, $\{NBu_4[FeCr(ox)_3]\}_x$ (38 kOe[4], 45 kOe[5] at 4.2 K) and **3** (54 kOe at 4.2 K). The exceptionally small H_n values of high-spin Fe(II) of these compounds would be understood by a large positive contribution of the orbital moment to H_n, which is comparable in magnitude to the negative Fermi contact term.[4,5]

On the other hand, if some difference in the saturation behavior of H_n on lowering the temperature is observed between the Fe(II) and Fe(III), it is evident that the Fe(II) and Fe(III) sublattices do not become magnetized to an equivalent extent at the same temperature. The H_n *vs.* temperature plots for the Fe(II) and Fe(III) of **1** are shown in Figure 2a.[13] No clear difference was found between the plots for Fe(II) and Fe(III) in this figure, although a slight tendency that the H_n of Fe(II) saturates more rapidly than that of Fe(III) may be suggestive, from the comparison with the case of **2** (see Figure 2b).

High-spin Fe(II) ions often exhibit a large temperature dependence of ΔE_Q, and the temperature dependence can be analyzed primarily by the energy separation of the t_{2g} orbitals (Δ).[15,16] The $\Delta E_Q/\Delta E_Q(78)$ *vs.* temperature plots for **1** and **2** in the paramagnetic state are shown in Figure 3, and some difference was seen between them, where $\Delta E_Q(78)$ represents the ΔE_Q value at 78 K. On the assumption of D_3 symmetry around Fe(II),[17] the plots for **1** and **2** fitted well below *ca.* 180 K to the calculated curves[12,16] with Δ = 330 and 310 cm^{-1}, respectively. The Δ value, reflecting the degree of the trigonal distortion around the Fe(II), would affect the single ion magnetic anisotropy at the Fe(II) site, which in turn influences the temperature dependence of the Fe(II) sublattice.[9] The above results about Δ show the possibility that a small enhancement of the anisotropy at Fe(II) in **1** causes its unusual magnetization behavior through the process of different temperature dependences in the magnetization between the sublattices.[9]

The temperature dependence of the area intensity of the Mössbauer absorption (A = total area intensity of Fe(II) and Fe(III)) is shown for **1** and **2** in Figure 4. An anomaly in the logarithm of A *vs.* temperature plot was found for each compound, similarly to the case of $\{NBu_4[FeCr(ox)_3]\}_x$,[5] and it indicates a broad phase transition between 180-220 K. The Debye temperature was estimated for **1** to be 159 K in the low temperature range (below 180 K) and 100 K in the high temperature range (above 220 K). The $\Delta E_Q/\Delta E_Q(78)$ *vs.* temperature plots in Figure 3 deviate from the calculated lines at higher temperatures, probably due to this phase transition.

The Mössbauer spectrum of the ^{57}Fe(II)-doped Mn(II)-Cr(III) compound, **4**, measured at 4.2 K is shown in Figure 5. Every absorption line of Fe(II) in **1-3** and $\{NBu_4[FeCr(ox)_3]\}_x$[4,5] apparently consists of a doublet at the lower energy side and a triplet at the higher energy side below T_N or Curie temperature, as shown for **2** in

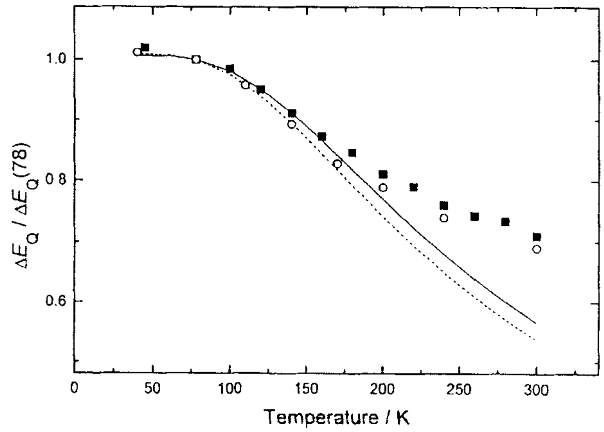

FIGURE 3 $\Delta E_Q/\Delta E_Q(78)$ *vs.* temperature plots for the Fe(II) of Compound **1** (■) and Compound **2** (○). The lines —— and ----- are calculated with the Δ values of 330 cm^{-1} and 310 cm^{-1}, respectively.

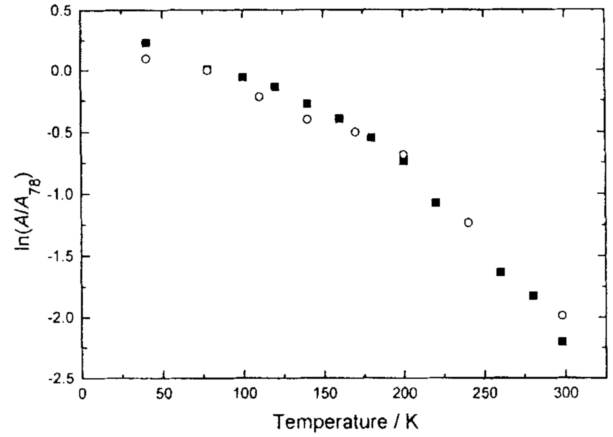

FIGURE 4 Area intensity (A) vs. temperature plots of Compound **1** (■) and Compound **2** (○).

Figure 1e, because the Fe(II) ions in these Fe(II)-Fe(III) and Fe(II)-Cr(III) compounds have the same values of the angle between the internal magnetic field and the principal axis of V_{zz} (θ = 90°) and the asymmetry parameter (η = 0),[10,11] where V_{zz} is the principal component of the electric field gradient tensor and is negative herein. On the other hand, Compound **4** gives a different type of Mössbauer spectrum, which apparently consists of a doublet at the lower energy side and broad singlet at the higher energy side. The Mössbauer line-shape of **4** can be understood on the grounds of a reduced θ value. The values of θ, H_n, δ and ΔE_Q were roughly estimated to be 10°, 30 kOe, 1.3 mm/s and 1.6 mm/s, respectively.[10,11] By magnetization measurements of a single crystal of $\{NBu_4[MnCr(ox)_3]\}_x$ (**5**), it was reported that the magnetic moments of Mn(II) and Cr(III) are aligned along the direction perpendicular to the basal planes[17] in **5**.[5] The nearly-zero value of θ observed for **4**[17] suggests that $\{NPr_4[MnCr(ox)_3]\}_x$ is an Ising ferromagnet like **5**.

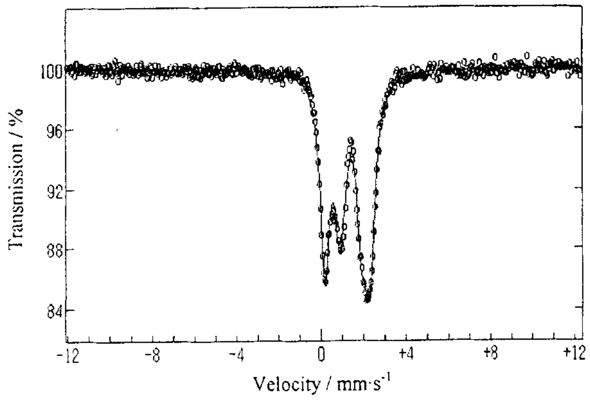

FIGURE 5 Mössbauer spectrum of Compound **4** at 4.2 K.

REFERENCES AND NOTES

1. Z. J. Zhong, N. Matsumoto, H. Ōkawa and S. Kida, Chem. Lett., 1990, 78.
2. H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Ōkawa, J. Am. Chem. Soc., 114, 6974 (1992).
3. H. Tamaki, M. Mitsumi, K. Nakamura, N. Matsumoto, S. Kida, H. Ōkawa and S. Iijima, Chem. Lett., 1992, 1975.
4. S. Iijima, T. Katsura, H. Tamaki, M. Mitsumi, N. Matsumoto and H. Ōkawa, Mol. Cryst. Liq. Cryst., 233, 263 (1993).
5. N. S. Ovanesyan, G. V. Shilov, L. O. Atovmyan, R. N. Lyubovskaya, A. A. Pyalling and Yu. G. Morozov, Mol. Cryst. Liq. Cryst., 273, 175 (1995).
6. W. M. Reiff, J. Kreisz, L. Meda and R. U. Kirss, Mol. Cryst. Liq. Cryst., 273, 181 (1995).
7. S. Iijima, F. Mizutani, M. Mitsumi, N. Matsumoto and H. Ōkawa, Inorg. Chim. Acta, in press.

8. C. Matnonière, S. G. Carling, D. Yusheng and P. Day, J. Chem. Soc., Chem. Commun., 1994, 1551.
9. C. Matnonière, C. J. Nuttall, S. G. Carling and P. Day, Inorg. Chem., 35, 1201 (1996).
10. S. V. Karyagin, Sov. Phys. Solid State, 8, 391 (1966).
11. W. Kündig, Nucl. Instrum. Methods, 48, 219 (1967).
12. W. M. Reiff, Coord. Chem. Rev., 10, 37 (1973).
13. The scale for the H_n of Fe(II) is expanded to equalize in the figure the magnitudes of H_n of the Fe(II) and Fe(III) at 4.2 K, in order to compare the saturation behaviors of H_n between the two kinds of Fe ions each other.
14. E. W. Gorter, Philips Res. Rep., 9, 403 (1954).
15. H. Ingalls, Phys. Rev., 133, A787 (1964).
16. A. Z. Hrynkiewicz, B. D. Sawicka and J. A. Sawicki, Phys. Status Solidi, 38, K111 (1970).
17. D_3 symmetry around M(II) was confirmed for some $\{A[MnCr(ox)_3]\}_x$ compounds in References 18 and 19. In general, it is expected that the crystal lattice of an $\{A[M(II)M'(III)(ox)_3]\}_x$ compound consists of the honeycomb layers consisting of alternate array of M(II) and M'(III) ions through ox^{2-} ligands. The principal axis of V_{zz} of Fe(II) in $\{A[Fe(II)M'(III)(ox)_3]\}_x$ is supposed to coincide with the D_3 axis which is perpendicular to the basal layers.
18 L. O. Atovmyan, G. V. Shilov, R. N. Lyubovskaya, E. I. Zhilyaeva, N. S. Ovanesyan, S. I. Pirumova, I. G. Gusakovskaya and Yu. G. Morozov, JETP Lett., 58, 766 (1993)
19 S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gütlich and A. Hauser, Inorg. Chim. Acta, 216, 65 (1994).