

## THE EFFECTIVE MAGNETIC FIELDS IN CUBIC FERRICYANIDES

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The effective magnetic fields at the iron nuclei in ferricyanides  $Mn_3[Fe(CN)_6]_2$ ,  $Ni_3[Fe(CN)_6]_2$ ,  $Cu_3[Fe(CN)_6]_2$ , and  $Co_3[Fe(CN)_6]_2$  studied at 4.2°K are  $195 \pm 15$ ,  $269 \pm 10$ ,  $266 \pm 10$ , and  $160 \pm 15$  kOe, respectively. Mössbauer spectra of  $Ni_3[Fe(CN)_6]_2$  were taken at several temperatures between 4.2°K and  $T_c = 19^\circ K$ . The form of the observed spectra and the slow variation of the effective field with temperature suggest that the atomic spin-flip frequency is comparable with Larmor frequency of the iron nucleus. The most explicit relaxation pattern corresponding to  $S = 1/2$  was observed in  $Co_3[Fe(CN)_6]_2$ . The origin of the magnetic field in low-spin ferricyanides is discussed. The contributions of orbital and dipolar terms are estimated.

*Introduction*

Ferricyanide metal complexes  $Me_3^{2+}[Fe^{III}(CN)_6]_2$  are peculiar iron compounds in which the hyperfine magnetic interaction of  $^{57}Fe$  nuclei with a low-spin ( $S = 1/2$ ) atomic shell may be studied. Some of them are magnetically ordered above liquid helium temperature [1], [2]. The nature of magnetic order in cubic ferricyanides has not been established as yet. We can make the presumption that magnetic ordering arises owing to the indirect superexchange interactions between ferric ions and  $Me^{2+}$  ions via molecular orbitals of  $CN^-$  ligands ( $t_{2g} - \pi - t_{2g}$ ).

*Experimental results and discussion*

Table I gives some results of magnetic and Mössbauer effect studies in ferricyanides. As it is seen, the transition temperatures  $T_c$  obtained from magnetic measurements [1], [2] differ considerably. Our values determined from the temperature variation of the Mössbauer absorption at zero relative velocity are more accurate.

The effective magnetic fields in  $Mn_3[Fe(CN)_6]_2$ ,  $Ni_3[Fe(CN)_6]_2$  and  $Cu_3[Fe(CN)_6]_2$  at 4.2°K. have been determined previously [3]. The obtained Mössbauer spectra are presented in Fig. 1.

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TABLE I

Experimental data for ferricyanides.  $T_c$  is the magnetic transition temperature measured by the magnetic method MM (Ref. [1] and [2]) and the Mössbauer effect ME.  $H$  is the effective magnetic field at the nucleus at 4.2°K measured by the Mössbauer effect. Data for  $K_3[Fe(CN)_6]$  taken from Ref. [4]

Me—Fe <sup>III</sup> (CN) <sub>6</sub>	$T_c$ [°K]		$H$ [kOe]	
	MM [1]	ME		
Mn <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	2	11	15.8±0.5	195±15
Ni <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	19	27	18.9±0.5	269±10
Cu <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	11	16	16.2±0.7	266±10
Co <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	12	21	>4.2	160±15
Ca <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>			<4.2	
Cd <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>			<4.2	
Cr[Fe(CN) <sub>6</sub> ]			<4.2	
V <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>4</sub>			<4.2	
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0.13			193

In order to study the character of the magnetic ordering in low-spin complexes measurements of Mössbauer spectra in Ni<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> at several temperatures below its Curie temperature were performed. The temperature of the sample was increased above liquid helium temperature by means of a small heater wound on the absorber holder. The temperature,

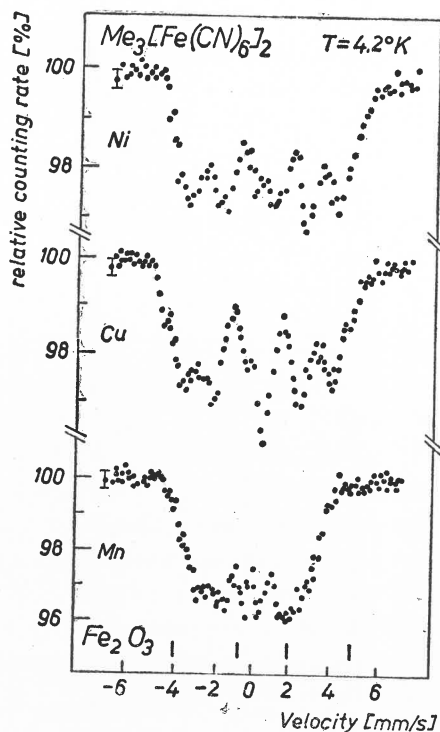


Fig. 1. The Mössbauer spectra of Ni<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>, Cu<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> and Mn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> at liquid helium temperature

measured with a germanium thermometer, was stable and uniform up to  $\pm 0.5^\circ\text{K}$ . Three of the obtained spectra are presented by way of illustration in Fig. 2.

First, we notice an unusual form of the Mössbauer spectra and the considerable broadening of the peaks. As the temperature is raised the outer peaks become broader, decrease in height, and finally fade away, leaving only two central peaks. At  $22.5^\circ\text{K}$  a pure, slightly

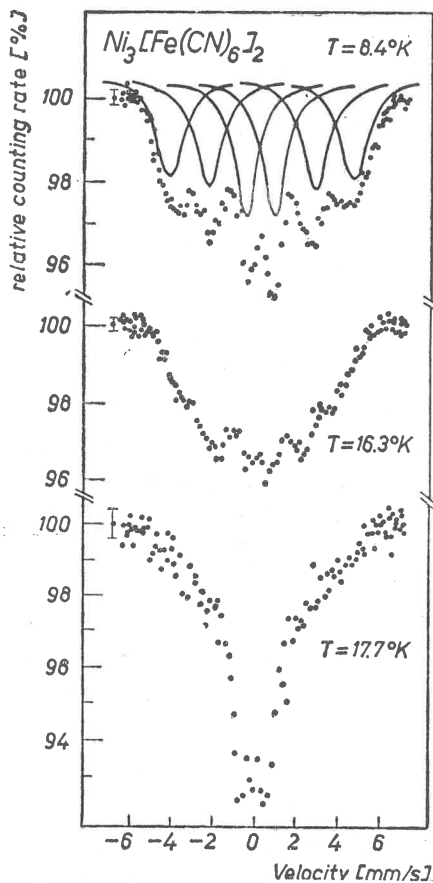


Fig. 2. The Mössbauer spectra of  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$  at  $8.4^\circ\text{K}$ ,  $16.3^\circ\text{K}$  and  $17.7^\circ\text{K}$

asymmetrical, quadrupole doublet was observed. The transition temperature determined in this way corresponds to that measured from the change of absorption at zero velocity.

Assuming a Lorentzian form of the peaks and using the ratio  $g_0/g_1 = 1.77$ , the spectra were decomposed and the effective magnetic fields were determined from the peak positions. The effective magnetic field  $H$  as a function of temperature  $T$  is given in Fig. 3. It is clearly seen that at higher temperatures the points do not fit to a spontaneous magnetization  $vs T$  curve, calculated on the basis of the Brillouin function  $B_{1/2}$ .

Referring to the discussion of van der Woude and Dekker [5] concerning the relation between electron spin relaxation and the shape of Mössbauer spectra in magnetic materials,

our observation may be explained as follows. The effective magnetic field measured in Mössbauer experiments will follow the magnetization only if the Larmor frequency of the nucleus  $\omega_L$  in internal magnetic field  $H$  is much lower than the electron spin-flip frequency  $\Omega$  ( $\omega_L \ll \Omega$ ) for all temperatures between  $0^\circ\text{K}$  and  $T_c$ . In the case of  $^{57}\text{Fe}$  with  $H = 300$  kOe,  $\omega_L \sim 10^8$  rad/s. This condition may not be satisfied at low temperatures in slightly ordered systems

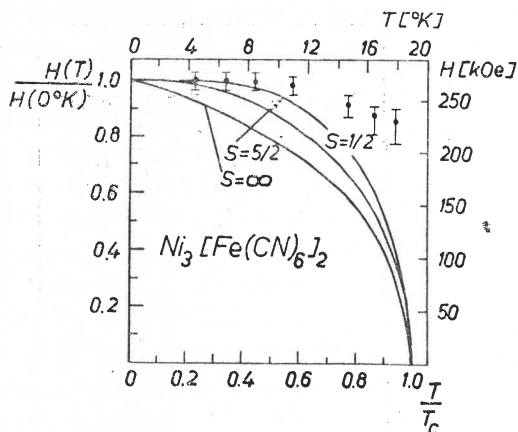


Fig. 3. The effective magnetic field in  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$  vs temperature

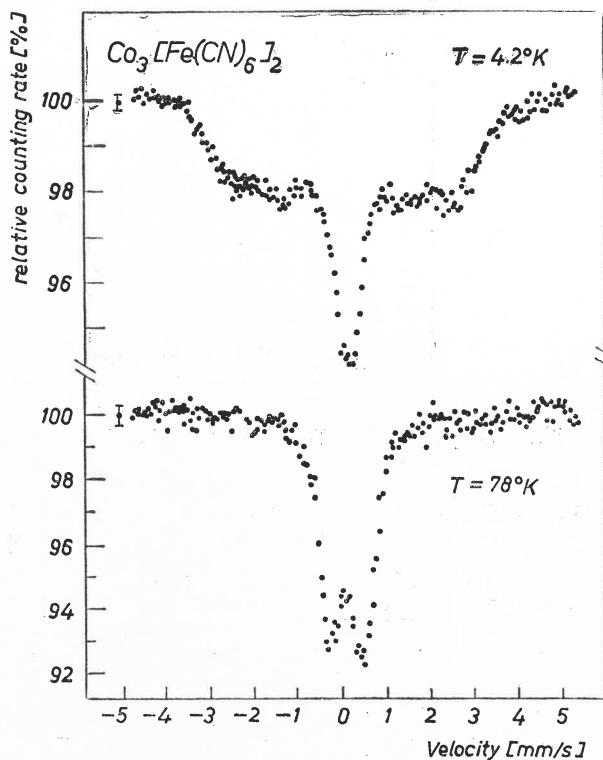


Fig. 4. The Mössbauer spectra of  $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$  at  $4.2^\circ\text{K}$  and  $78^\circ\text{K}$

of spins or in the case of incomplete magnetic lattices. If  $\omega_L > \Omega$  one can observe in  $S = 1/2$  ferromagnet below its  $T_c$  the six-line pattern in which the positions of the peaks are independent of the degree of magnetic order; the effective magnetic field measured by the position of the peaks should remain independent of temperature. As a result of the increase of  $\Omega$  with temperature, in a region where  $\omega_L \sim \Omega$ , one should observe a considerable broadening of the peaks and a reduction of the peak heights. For certain values of the  $\Omega/\omega_L$  ratio the intensity of the two central peaks could be considerably larger than that of the other four peaks. Thus, it seems that in the case of the examined  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$  the electron spin-flip frequency below  $T_c$  is of the same order as the Larmor frequency of the iron nucleus.

The relaxation phenomenon was observed most distinctly in the case of  $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ . In Fig. 4 the Mössbauer spectra take for this material at 4.2°K and 78°K are compared. The presence of a pronounced central peak in combination with broadened hyperfine splitting at 4.2°K does not require the coexistence of paramagnetic and magnetically ordered regions in the sample. It represents the Mössbauer spectrum of a slightly ordered system of spins which the collective behaviour has practically broken down. According to calculations by van der Woude and Dekker [5], as well as by Pál [6], the observed pattern may be explained if the electron spin-flip frequency is ca. 5 times the Larmor frequency of the iron nucleus. It should be emphasized that the spectra taken by us for this substance below 78°K are markedly asymmetrical. The asymmetry of the quadrupole doublets increases as the temperatures decreases, leading to an almost single, broadened line below 30°K. This means that the spin-lattice relaxation frequency decreases drastically to ca.  $10^9$  rad/s, which is consistent with the Blume effect [7].

A detailed treatment of the phenomena reported here will be given separately. Further experiments with low-spin magnetic materials are in progress.

Let us now turn our attention to the observed effective field intensities in ferricyanides and discuss their origin.

Thy hyperfine field  $H$  is the sum of three contributions,

$$H = H_c + H_L + H_d$$

where  $H_c$  is the Fermi contact term produced by the polarization of the core  $s$ -electrons *via* the  $3d$ -electrons,  $H_L$  is the field due to the orbital moment, and  $H_d$  is the spin dipolar field. According to Watson and Freeman's [8] spin-polarized Hartree-Fock computations for iron series ions, the contact term  $H_c$  per unpaired spin in the  $3d$ -shell should be roughly constant:  $\chi = -125$  kOe. This suggests that the polarizability of the  $s$ -core is linear in spin of the  $3d$ -shell. The  $1s$ - and  $2s$ -shells, which lie inside the  $3d$ -shell give a negative contribution to  $H_c$ . The  $3s$ -shell lies neither "inside" nor "outside" the  $3d$ -shell. The "outside" part gives a positive and predominant contribution to  $H_c$ . In the case of high-spin  $\text{Fe}^{3+}$  ion individual  $1s$ -,  $2s$ - and  $3s$ -shell contributions to the resulting  $H_c = -630$  kOe are  $-50$  kOe,  $-1790$  kOe and  $+1210$  kOe, respectively.

The intensities of fields observed in ferricyanides range from 160 kOe to 270 kOe. They are much lower than in the case of high-spin ferric compounds; however, they markedly exceed the spin-polarized Hartree-Fock estimations (125 kOe). Previously we have noticed [3] that the strong delocalization of  $3d$ -electrons *via* back donation may induce a large negative

polarizability of  $s$ -electrons leading to the higher  $H_c$  negative contribution to the effective field in the case of ferricyanides. It is known that in ferricyanides the ratio  $\langle r^{-3} \rangle / \langle r^{-3} \rangle_0$  is considerably reduced. Hence, the mean radius of the  $3d$ -shell increases remarkably as compared with the ionic one. Owing to the increased  $3d$ -shell radius in the ferricyanide complex the positive contribution to  $H_c$  from the  $3s$ -shell should become weaker, leading to a larger negative effective field in the iron nucleus.

It is possible to estimate the contribution of orbital term  $H_L$  if one knows the  $g$ -factor of the iron ion,

$$H_L = -2\mu_B \langle r^{-3} \rangle (g-2) \langle S \rangle.$$

We have measured the magnetic susceptibilities of the series of ferricyanides in the temperature range from 78°K. to 400°K [9]. Preliminary estimates indicate that effective magnetic moments of ferric ions in cubic ferricyanides  $\text{Ca}_3^-$ ,  $\text{Cd}_3^-$ ,  $\text{Mn}_3^-$ ,  $\text{Co}_3^-$ ,  $\text{Ni}_3^-$  and  $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$  lie between 1.7 and 1.9  $\mu_B$ , close to the spin only value of 1.73  $\mu_B$ . Therefore, we expect the angular momentum  $L$  in cubic ferricyanides to be almost completely quenched, giving a negligible orbital contribution to the effective field. In the case of non-cubic  $\text{K}_3[\text{Fe}(\text{CN})_6]$  we obtained  $\mu_{\text{eff}} = 2.5 \mu_B$  in good agreement with the existing data [10]. When discussing an effective magnetic field intensity in the latter substance a positive orbital field must be taken into account.

The spin dipolar term  $H_d$  can be estimated from the formula [11]:

$$H_d = \mu_B \frac{q_z}{2} \langle S \rangle.$$

As in the case of cubic ferricyanide complexes the maximum value of electric field gradient  $q_z$  and the  $\langle S \rangle$  value, is almost four times smaller than in the case of high-spin  $\text{Fe}^{2+}$ , the dipolar term should also be very small, *viz.*,  $|H_d| < 5 \text{ kOe}$ .

In conclusion we find that the most important contribution to the effective magnetic field in cubic ferricyanides is due to the Fermi contact term. Its high value should be attributed to the radial expansion of  $3d$ -orbitals in the  $[\text{Fe}^{\text{III}}(\text{CN})_6]$  complex.

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