THE POSITIVE SIGN OF THE INTERNAL MAGNETIC FIELD
IN Ni_3 $(Fe(CN)_6)_2$

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Ferricyanides $M_3(Fe(CN)_6)_2$ have a cubic unit cell and symmetry $O_h^5(Fm3m)$. There is a trigonal crystal field at Fe sites in one of the (111) directions. $Fe^{III}(t_{2g}^5)$ ion is in a low-spin state $S = 1/2$.

Ferricyanides with M = Mn, Co, Ni, Cu were found to be ferromagnetic at low temperatures[1]. Ferricyanides with M = Mn, Ni, Cu were examined down to 4.2 K by the Mössbauer effect[2], and those with M = Co and Cd down to 0.04 K, additionally[3]. The saturation values of H_{int} ranged between 160 and 270 kOe but the sign of B_{int} has not yet been determined.
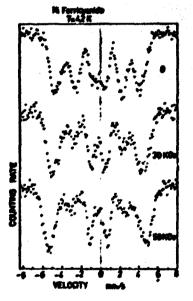
In the present work the sign of H_{int} was measured for $Ni_3(Fe(CN)_6)_2$. The polycrystalline absorber was placed in an external longitudinal magnetic field of a superconducting solenoid. The temperature of the sample, 4.2 K, was sufficiently below the Curie point $T_c = 19.5$ K, and the magnitude of H_{ext} used ($H_{ext} = 30$ and 58 kOe) was strong enough to orient the magnetic domains, also stronger than any possible induced fields.

The experimental spectra are presented in Fig. 1. The value of H_{int} at 4.2 K amounts to 265 ± 10 kOe, in agreement with earlier data[2]. The observed expansion of the Zeeman pattern in the external field signifies the positive sign of H_{int} ($H_{tot} = 295 \pm 10$ kOe at $H_{ext} = 30$ kOe and $H_{tot} = 317 \pm 10$ kOe at $H_{ext} = 58$ kOe). An induced field H_{ind} has a negligible value.

We associate the above result with the interesting question whether the contact contribution H_c to the internal field at the iron nucleus could be positive. As follows from the theoretical results of Watson and Freeman[4] as well as from Nozony's discussion of covalency effects and H_c-QS-IS correlations in octahedral iron compounds[5], a decrease in magnitude or even reversal of the sign of $H_c/2S$-value might be expected in covalent complexes owing to significant radial expansion of the 3d wave functions.

In the highly covalent $Fe^{III}(CN)_6$ the $3d(t_{2g}^5)$ density is spread over the entire complex rather than localized on the central ion. This is evident, at least, from Mössbauer data, for both IS and QS parameters. The covalency factor $a_c^2 = <r^{-3}>/<r_0^{-3}>$ determined from QS data for the series of $M_3(Fe(CN)_6)_2$ compounds amounts to ~ 0.2, which corresponds to $<r^{-3}> \gtrsim 1$ a.u.[6]. Such a large increase in the 3d charge density is due to non-bonding π molecular orbitals where t_{2g} electrons of Fe are displaced towards unoccupied π (2p) orbitals of CN ligands (back donation).

In figure 2 the contact contribution H_c per one unpaired electron in the 3d shell of iron is plotted against $<r^{-3}>$ values for some compounds[5]. The point for $Ni_3(Fe(CN)_6)_2$, without correction for possible orbital H_l and dipole H_d contributions, fits well to the correlation of H_c and the covalency suggested by Hazony. One may of course wonder whether these last two contributions are really negligible[7]. However our susceptibility data between 77 K and 300 K indicate effective magnetic moments close to the "spin-only" value.
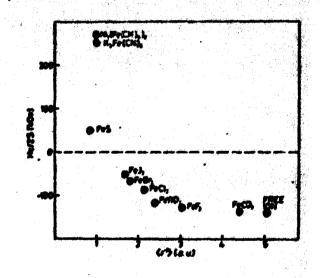

Fig.1 : Mössbauer spectra of $Ni_3(Fe(CN)_6)_2$ at 4.2 K in 0, 30 and 58 kOe longitudinal field.

Fig.2 : H_c vs. $<r^{-3}>$ for some iron compounds. Points other than for $Ni_3(Fe(CN)_6)_2$ taken from ref.5.

References :

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