14. Valence Delocalization in Prussian Blue $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot xD_2O$, by Polarized Neutron Diffraction

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Summary

Polarized neutron diffraction has been used to investigate the spin delocalization from the high-spin Fe(III) sites to the low-spin Fe(II) in deuteriated Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot xD_2O$. Measurements of the 111, 200, and 400 reflections were made on a powdered sample at 3 K and 4.8 T using a neutron wavelength of 1.074 Å. The expectation value of S at the Fe(II) site is -0.008 ± 0.028 corresponding to an upper limit of about 5% of an electron for the spin delocalization.

Introduction. - Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot xD_2O$ (x = 14-16), is a classical mixed valence compound, belonging to Class II of the *Robin-Day* classification [1]. The overall structure of the cubic Fe(III)–N–C–Fe(II) framework corresponds to the face-centered space group Fm3m [2]. That there is substantial interaction between the two kinds of Fe-ions is indicated by the appearance of a broad intense absorption band at 14100 cm^{-1}, assigned as the Fe(II)→Fe(III) charge transfer transition [3]. Another feature of Prussian Blue is that at 5.5 K the Fe(III) spins order ferromagnetically [4], behaviour which is highly unusual for a coordination complex. Furthermore, the shortest superexchange pathway between the Fe(III)-ions is no less than 10.16 Å so the existence of magnetic ordering even at 5.5 K requires some explanation. A plausible mechanism [5] is the mixed-valence interaction, *i.e.*, mixing of the Fe(II)-to-Fe(III) charge-transfer excited state into the ground state. One consequence of such mixing would be a small transfer of spin density from Fe(III) to the low-spin Fe(II) which, to a first approximation, carries no net spin.

One of the most sensitive and direct methods for determining the distribution of unpaired electron-spin density in solids is by diffraction of polarized neutrons [6].

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In brief, the cross-section for elastic scattering of neutrons by unpaired electrons depends on the relative orientation of the electron and neutron spins. Since the cross-section for scattering by the nuclei is independent of the neutron-spin orientation, one can separate the nuclear and magnetic contributions to the total scattering cross-section by aligning the electron spins and then carrying out two diffraction experiments with the spins of the incident neutrons polarized parallel and antiparallel to the spins of the unpaired electrons in the solid. The earliest experiments of this kind were performed on ferromagnetic elements and alloys [7] and only very few have concerned non-metallic inorganic compounds [8]. Although in principle, one could magnetically saturate most paramagnetic substances by using a sufficiently high applied magnetic field at a sufficiently low temperature, compounds which order spontaneously as ferromagnets have a substantial advantage. This encouraged us to search for spin transfer from the high-spin Fe(III) to the low-spin Fe(II) in Prussian Blue by means of polarized neutron-diffraction. Unfortunately, because of its polymeric structure which makes it extremely insoluble, Prussian Blue has only been grown into single crystals of, at most, 0.1 mm on edge. This is too small for single crystal polarized neutron diffraction so our experiments had to be performed on polycrystalline samples. Prussian Blue is cubic so the number of reflections available is in any case limited.

Experimental Part. - The microcrystalline sample of Prussian Blue was prepared by slowly diffusing H_2O-vapour into a solution of $FeCl_3$ and $H_4Fe(CN)_6$ in concentrated HCl-solution [2]. Deuteriation was achieved by stirring a suspension of Prussian Blue (14.6 g) in D_2O (100 ml, 99.9%) at 80° for two days and collecting the solid by filtration. This procedure was repeated twice to yield a

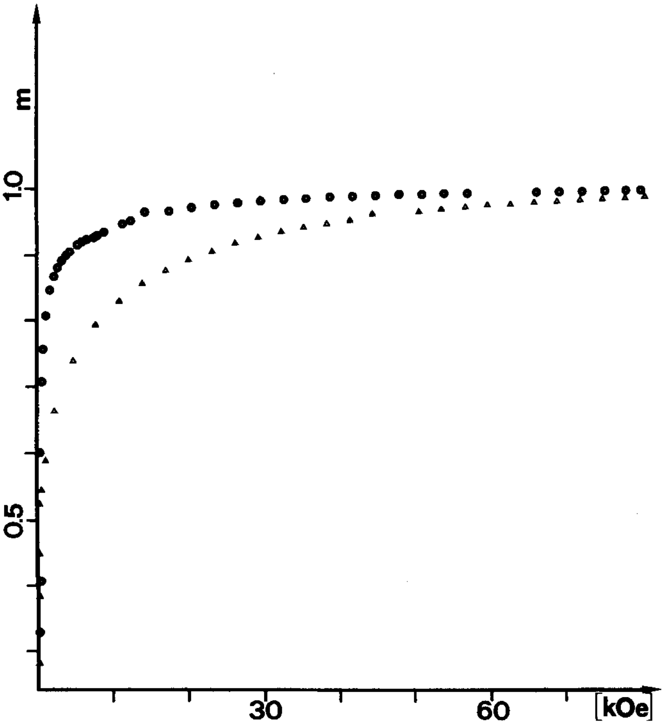

Fig. 1. *Magnetization isotherms of Prussian Blue powder at 1.7 K (○) and 4.4 K (△)*

sample deuteriated to 97.9% (by atoms) as determined by mass spectrometry. It has previously [2] been characterized by chemical analysis and x-ray powder diffraction. The sample contains a small amount of $Fe(CN)_6^{3-}$ which can be detected in the IR. spectrum showing a weak signal at 2130 cm^{-1}. This amount was determined by dissolving the sample in 2N KOH, filtering and measuring the absorbance at 420 nm. A calibration curve was obtained by measuring the absorbance of mixtures of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ (in the same ratio as expected in the Prussian Blue sample) in 2N KOH.

The magnetic susceptibility was measured by a moving sample magnetometer [9] between 1.3 and 300 K. It shows perfect *Curie-Weiss* behaviour between 10 and 300 K with a *Curie* constant of 17.92 ± 0.02 cm^3/mol and $\theta = 6.74 \pm 0.07$ K. This gives a $\mu_{eff} = 2.828\ \sqrt{C/4} = 5.98 \pm 0.02$ B.M. per Fe(III) corresponding to the spin-only moment of high-spin Fe(III). Two magnetization isotherms were measured at 1.7 and 4.4 K, respectively *(Fig. 1)*. In a field of 4.8 T the magnetization m is 0.99 at 1.7 K and 0.96 at 4.4 K.

The polarized neutron-diffraction measurements were carried out on the D5 instrument at the *Institut Laue-Langevin* high flux reactor, Grenoble, using a neutron wavelength of 1.074 Å. The polarization measured at two positions in the beam with a Fe-Co single crystal was $P = 0.970 \pm 0.002$. At 4.2 K no depolarization by the sample was detected, but after pumping the cryostat a depolarization of $\beta = 7.3 \pm 0.4 \times 10^{-2}$ cm^{-1} was measured, giving $P_{eff} = 0.928 \pm 0.003$ [10]. The efficiency of the flipping coil was $E = 0.99$. The counting time for the two polarizations was chosen approximately inversely proportional to the expected intensities. The sample was placed in a vanadium container

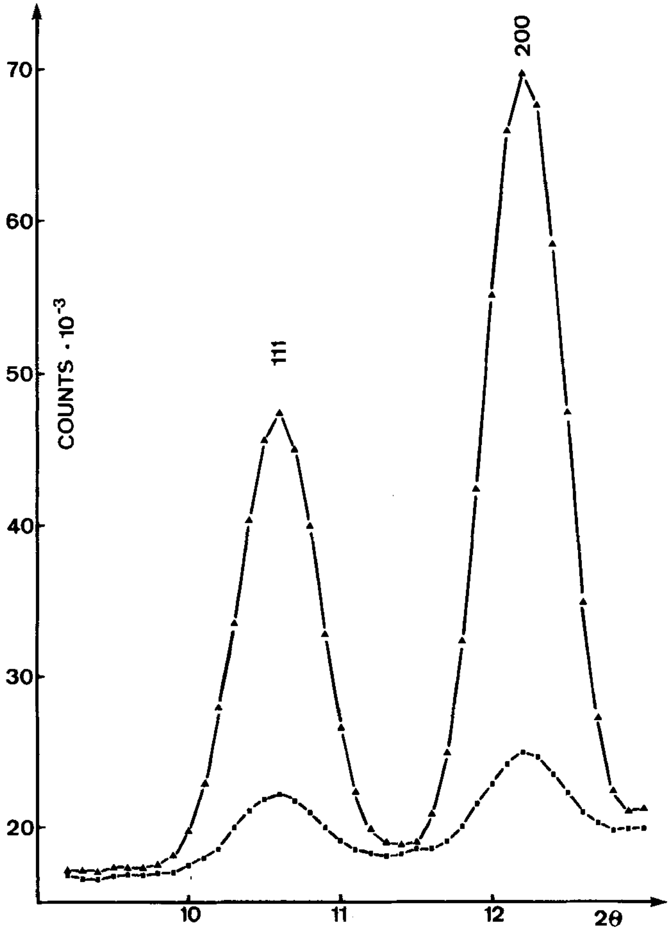

Fig. 2. *Neutron diffraction profiles of Prussian Blue powder for neutron spin up* ($I^{\uparrow}$; ▲) *and down* ($I^{\downarrow}$; ■) *at 3 K and 4.8 T.* $I^{\downarrow}$ has been scaled to the same monitor count as $I^{\uparrow}$.

(diameter = 12 mm) in a superconducting cryomagnet (4.8 T). The magnetic field was perpendicular to the scattering vector and the neutron spins were polarized parallel (↑) and antiparallel (↓) to the magnetic field. The temperature, measured with a carbon resistor, was 3 K. Interpolating the magnetic data between 1.7 and 4.4 K gives a magnetization $m = 0.98 \pm 0.01$ at 3 K. The maximum signal/background ratio was 4.1 and the linear absorption coefficient μ of the sample was 0.166 cm^{-1}, giving a negligible absorption correction.

Initially, powder diffraction profiles were scanned out to $2\theta = 30°$. However, given the limited number of reflections observable, any possibility of obtaining a spin-density map of the entire unit cell by the usual *Fourier* transformation procedure is out of the question. Owing to the rapid decrease of the magnetic form factor with increasing *Bragg* angle, we concentrated our measurements on the low angle region. Moreover, only reflections with odd indices have intensities which depend on the spin transfer to Fe(II) (*cf.* eqn. (4)). The single well resolved peak that meets both these requirements is the 111 reflection. We therefore measured this reflection and the equally well resolved 200 and 400 reflections in 0.1° steps using long counting times in order to obtain a reliable scale factor. A portion of this data is shown in *Figure 2.*

Reduction and Evaluation of Data. - Because the nuclear structure is not known to sufficient accuracy it was not possible to make use of conventional flipping ratio measurements. The intensities for each spin state were measured and normalized point by point and fitted as *Gaussians* by a least-squares procedure (together with a 3-parameter background) by means of a computer program provided by *Wolfers* [11] which also gives standard deviations σ of the intensities. The σ's describing the deviation from a *Gaussian*-line shape computed by this program exceed the statistically determined standard deviations by a factor of about 4, but are considered to be a better estimate of the real uncertainties [11].

The left hand side of the *Table* shows the observed intensities $I^{\uparrow}$ and $I^{\downarrow}$ for the two directions of neutron polarization, normalized and corrected for multiplicity, together with their standard deviations. Allowing for incomplete magnetization, the intensities are given by

$$\begin{aligned} I^{\uparrow} &= F_N^2 + 2\,mPF_NF_M + \left(\frac{2}{3} + \frac{1}{3}m^2\right) F_M^2 \\ I^{\downarrow} &= F_N^2 + 2\,mP(1\text{-}2E)F_NF_M + \left(\frac{2}{3} + \frac{1}{3}m^2\right) F_M^2 \end{aligned} \tag{1}$$

where F_N and F_M are the observed nuclear and magnetic structure factors, respectively [6]. From eqn. (1) the relative nuclear and magnetic structure factors, shown with their standard deviations on the right hand side of the *Table,* may now be evaluated. Throughout these calculations the standard deviations of results were determined according to $\sigma_y(x_i) = \sqrt{\Sigma_i((\partial y/\partial x_i)\sigma_{x_i})^2}$.

To obtain the magnitude of the spin on the Fe(II), we note that neglecting the *Debye-Waller* factor the magnetic structure factor is given by

$$F_M^{hkl} = (e^2\gamma/mc^2)\Sigma_i \langle S_i \rangle\ f_i^{hkl} \exp\left[2\pi i\left(\frac{hx+ky+lz}{a}\right)\right] \tag{2}$$

where $\langle S_i \rangle$ is the expectation value of S_z at site i. In order to find $\langle S_{Fe(II)} \rangle$, we used the form factor for high-spin Fe(III) to describe the magnetic scattering from all the Fe-ions and neglected all orbital contributions. The magnetic form factors were determined graphically from tabulated literature values [12] as: (111) 0.936, (200) 0.918, (400) 0.732. The small amount of ferricyanide present was assumed to

Table. *Polarized neutron-diffraction intensities and structure factors for Prussian Blue at 3 K and 4.8 T* for m = 0.98 (σ is standard deviation)

	$I^{\uparrow}$	σ	$I^{\downarrow}$	σ	F_N	σ	F_M	σ
111	4.135	0.0797	0.675	0.0310	0.717	0.0320	1.410	0.0483
200	12.86	0.188	1.478	0.0545	2.286	0.0318	1.383	0.0354
400	103.6	3.25	66.0	1.50	9.13	0.133	1.14	0.102

occupy the same position in the crystal lattice as ferrocyanide, giving the following occupancies for the space group Fm3m: 4 high-spin Fe(III) on 4a, 3 low-spin Fe(II) and q low-spin Fe(III) on 4b; q as determined by chemical analysis was 0.07±0.005. It was further assumed that the spin of the low-spin Fe(III) was parallel to that on the 4a sites.

Excluding the ferricyanide the total spin in each unit cell is:

$$4\langle S_{Fe(III)}\rangle + 3\langle S_{Fe(II)}\rangle = 10. \tag{3}$$

Furthermore, the absolute values of the geometric parts of the structure factors are the same for all contributions (that of 4b to the odd peaks being negative) so the resulting magnetic structure factors for odd (ooo) and even (eee) peaks are

$$\begin{aligned} F_M^{ooo} &= (\text{constant})\,(10 - 6\langle S_{Fe(II)}\rangle - \tfrac{1}{2}q)\,f^{ooo} \\ F_M^{eee} &= (\text{constant})\,(10 + \tfrac{1}{2}q)\,f^{eee} \end{aligned} \tag{4}$$

The observed magnetic structure factors F_M were subjected to a least-squares refinement [13] using the scale factor and $\langle S_{Fe(II)}\rangle$ as parameters. The function minimized was $\Sigma w(|F_{obs.}| - |F_{cal.}|)^2$ where the weighting function was represented by $\sigma(F_{obs.})^{-2}$.

Results and Discussion. - The least-squares treatment of F_M for the 111, 200, and 400 reflections converges to a value of $\langle S_{Fe(II)}\rangle$ of -0.008 ± 0.028. The standard deviation of $\langle S_{Fe(II)}\rangle$ is disappointingly high. Nevertheless, we consider it to be realistic by taking into account various possible sources of errors, *e.g.* slight distortions in the geometry of the experiment from ideal alignment, deviations of the diffraction peaks from *Gaussian* shape, *etc.*

The magnitude of $\langle S_{Fe(II)}\rangle$ is very sensitive to the value of magnetization m. This dependence is most clearly illustrated by the same calculations but using $m = 0.975\pm0.01$ instead of $m = 0.98\pm0.01$. In this case the result is $\langle S_{Fe(II)}\rangle = 0.003\pm0.026$. It must be pointed out that a negative value of $\langle S_{Fe(II)}\rangle$ is physically unreasonable. A negative sign would imply that the spin on the 4b site is antiparallel to that on 4a. Since we know that the high-spin Fe(III)-spins are ferromagnetically aligned, each with a half-filled d-shell, only a spin antiparallel to the Fe(III)-spins can be transferred to them from the Fe(II), leaving behind an unpaired electron spin directed parallel to the uncompensated Fe(III).

It is worth noting that there is a simple connection between $\langle S_{Fe(II)}\rangle$ and the valence delocalization coefficient a. Let us write the ground state wavefunction as [14]

$$\psi_G = (1-a^2)^{1/2}\,\psi_o + a\,\psi_1 \tag{5}$$

where $\psi_o = [C^6N^{30}]$ symbolizes the zero order ground state in which a low-spin Fe(II) with six d-electrons at the site surrounded by six C-atoms has six high-spin Fe(III) neighbours, each with five d-electrons, at the nitrogen ends of the same cyanide groups. In the intervalence charge transfer excited state $\psi_1 = [C^5N^{31}]$ an electron has been transferred from the Fe(II) to an appropriate linear combination of the surrounding Fe(III). Full details of the symmetry arguments used to construct these wavefunctions are given in [14] but it is sufficient to point out here that in the zero order ground state $\langle\psi_o|S_{zFe(III)}|\psi_o\rangle = 5/2$ and $\langle\psi_o|S_{zFe(II)}|\psi_o\rangle = 0$, while in the intervalence charge transfer excited state, we have $\langle\psi_1|S_{zFe(III)}|\psi_1\rangle_{av} = 5/2 - 1/6\cdot 2$ and $\langle\psi_1|S_{zFe(II)}|\psi_1\rangle = 1/2$, where 'av' expresses an average over all six Fe(III) sites. Thus, for the true ground state ψ_G, we have $\langle\psi_G|S_{zFe(III)}|\psi_G\rangle = 5/2 - 1/12\,a^2$ and $\langle\psi_G|S_{zFe(II)}|\psi_G\rangle = 1/2\,a^2$, *i.e.* in the nomenclature used above $a^2 = 2\langle S_{Fe(II)}\rangle$.

The result of our polarized neutron diffraction on Prussian Blue gives a value for a^2 of -0.016 ± 0.056. The spin delocalization in the ground state corresponds to less than about 5% of an electron. This upper limit can be compared with the predictions of different models of valence delocalization in mixed valence compounds [14]. A perturbation model in which 'local' CN $(\pi) \rightarrow$ Fe(III) and Fe(II) $\rightarrow$ CN(π^*) states provide the means of mixing ψ_0 in (5) with ψ_1, gave a^2 as 0.011 [14]. The intensity of the intervalence transition of Prussian Blue has also been used to derive a value of 0.01 for a^2 [3]. Owing to the difficulties of reliably measuring the optical density of colloidal solutions and to analytical uncertainties, this value reflects only the order of magnitude of a^2. Both these figures lie within the standard deviation of our experiment. However, we cannot exclude the possibility that the theoretical predictions for a^2 are too high. The fact that we are looking for a very small amount of spin density at a particular site in a unit cell containing a large number, *i.e.* 20, of unpaired electrons is a severe limitation in the present application. It must be emphasized, however, that polarized neutron diffraction is the only method to directly determine spin delocalization. In contrast to a^2 values deduced from other experiments, our result does therefore not depend on approximations and assumptions of a particular theoretical model. We have demonstrated that it is possible, in principle, to determine spin transfer in a high symmetry lattice from polarized neutron diffraction of a powder. The high standard deviation of our result, on the other hand, clearly reveals the limitations of the method.

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