Chapter 3

Single Crystalline Mn-Fe Prussian Blue Analogues

Single crystals of the Prussian Blue analog RbMn[Fe(CN)₆]·H₂O have been obtained by a slow diffusion method. The obtained X-ray diffraction data at room temperature are best described by the cubic space group F43m with lattice constant \( a = 10.521 \) Å. The corresponding Fe - C and Mn - N distances of 1.929 Å and 2.205 Å, respectively, are indicative for low-spin Fe³⁺ and high-spin Mn²⁺ constituents, in agreement with polycrystalline data. As evidenced by SQUID, \(^{57}\text{Fe} \) Mössbauer and Raman data, these single crystals exhibit the fascinating charge transfer transition from high-spin Mn²⁺ and low-spin Fe³⁺ to high-spin Mn³⁺ and low-spin Fe²⁺ both under the influence of visible light and temperature. In contrast to the polycrystalline MnFe PBA materials, only 50% of the metal centers in the material undergo charge transfer, a feature which appears inherent to the crystalline structure. This partial switching of the compound is argued to be related to the existence of different Fe sites within the crystal, brought about by an ordered Rb/H₂O distribution over the interstitial sites. This notion is confirmed by the \(^{57}\text{Fe} \) Mössbauer data, which reveal the presence of two different Fe sites in both the high and low temperature phase. Concurrently, as was observed in the polycrystalline material, the single crystals also exhibit a photo-induced LT-to-HT transition at low temperatures. The cooperative nature of the system manifests itself through the occurrence of an excitation power density threshold, only above which full optical conversion is attained.

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3.1 Introduction

Photomagnetic materials form a unique and fascinating field in contemporary physics, as they couple the traditionally unrelated disciplines of optics and magnetism. Moreover, that very same coupling makes them particularly interesting from technological, application-oriented point of view [1]. Among materials displaying photo-induced spin-crossover [2, 3, 4, 5, 6] and valence tautomerism [7, 8, 9, 10, 11], an important subclass is formed by the so-called Prussian Blue Analogues (PBAs) introduced in the preceding chapter. PBAs, of the generic formula $A_xM'[M(CN)_6]_y\cdot zH_2O$ (where $A$ is an alkali cation or $NR_4^+$ while $M$ and $M'$ are metal ions), are extremely versatile with respect to their physical properties upon variation of their constituents and stoichiometry, in particular with respect to the choice of metal ions [12, 13]. Their merits were recognized already at a very early stage, when it was discovered that favorable electronic transitions or electron transfer between the metallic constituents facilitated their use as pigments [14] and as components for batteries [15]. More recently, the observed changes in several physical properties of PBAs, induced by various types of external stimuli, was anticipated to enable their implementation in molecular scale (nano-)devices [16, 17]. Of particular interest in this respect are PBA magnets with two compensation temperatures [18, 19] or the temperature dependent dual magnetic properties that are combined within mixed ferro-ferrimagnets [18, 20]. These physical phenomena may be coupled to other unique properties such as negative thermal expansion [21, 22, 23] and porosity [24, 25, 26, 27, 28, 29, 30, 31]. The latter offers a further parameter for tuning the magneto-optical behavior through solvatochromism [24, 25, 26, 27], as well as providing reversible storage capability for, e.g., $N_2$ [28] or $H_2$ [29, 30, 31].

Unique in PBAs, is the extended range of light-induced phenomena, such as magnetic pole inversion [18, 32, 33], (de)magnetization [34, 35, 36, 37], spin crossover of Fe$^{II}$ [38], and charge transfer [37, 39, 40, 41, 42]. For instance, in the MnFe PBA (RbMn[Fe(CN)$_6$]), a 532 nm pulse at 3 K induces a charge transfer (CT) from low-spin Fe$^{II}$ and high-spin Mn$^{III}$ to low-spin Fe$^{III}$ and high-spin Mn$^{II}$, much like the photo-induced charge transfer around 90 K discussed in Chapter 2 [43]. The occurrence of the effect at these temperatures makes the phenomenon even more interesting, since here the Fe$^{II}$Mn$^{III}$ ground state is ferromagnetic, while the induced metastable Fe$^{III}$Mn$^{II}$ state is not. Thus, the potential for optical control of a macroscopic sample magnetization can be explored at these temperatures.

Arguably, many current and forthcoming application appear feasible for this class of three-dimensional inorganic materials. A further development of the field would strongly benefit from an extended knowledge of the relationship between structural features and the material’s physical properties, which would ideally require functional single crystals. Nevertheless, at present the number of known PBA crystal structures with a $A_xM'[M(CN)_6]_y\cdot zH_2O$ stoichiometry is very small.
Moreover, those structures that have been determined correspond to specific compounds that do not exhibit physical properties interesting from an applications point of view [44, 45, 46]. The unavailability of structural data also applies to the MnFe PBA, of which only very recently microscopic single crystals have been synthesized [47]. These single crystals, however, do not exhibit the charge transfer transition characteristic for MnFe PBA systems (See Chapter 2). It is well established for these materials, that there is a strong coupling between the specific system stoichiometry and its physical properties [48, 49, 50]. The charge transfer inactivity of these single crystals is presumably due to unbalanced redox potentials of the individual metal sites, which in turn is a consequence of the unfavorable stoichiometry (Rb\(_{0.61}\)Mn\([\text{Fe(CN)}_6]\)\(_{0.87}\)·1.7 H\(_2\)O) of these specific crystals. As was explained in the introduction of Chapter 2, MnFe PBA systems often suffer from such a nonstoichiometry, which is a consequence of the inherent charge disproportionality of the constituent building blocks. Consequently, the materials often contain varying amounts of [Fe(CN)\(_6\)]\(^-\) vacancies and a corresponding number of water molecules [48]. In this chapter the physical properties of RbMn[Fe(CN)\(_6\)] single crystals obtained through an alternative method are investigated. These millimeter-sized cubic crystals do exhibit both the light- and temperature-induced charge transfer transition. SQUID magnetometry, \(^{57}\)Fe Mössbauer and Raman spectroscopy are employed to probe the crystals' properties, and reveal that 50% of the metal ions in the system participate in the charge transfer transitions.

### 3.2 Experimental Methods

#### 3.2.1 Sample synthesis

Synthesis and initial characterization of the single crystals studied in this chapter was performed by Esther Vertelman in the Inorganic Chemistry group of the Zernike Institute for Advanced Materials (Groningen). All used chemical reagents were purchased at Sigma Aldrich and used without further purification. Cube-shaped, dark brown crystals of RbMn[Fe(CN)\(_6\)]·H\(_2\)O have been synthesized through a modified version of the crystallization method developed by Kepert et al. [51] For the synthesis, a 10 mL vial was placed within a 100 mL jar with a screw cap, as sketched in Figure 3.1. The jar was filled with an aqueous solution of 0.5 M RbCl at room temperature (the 'buffer' solution), up to a level approximately 0.5 cm above the top of the vial. 2 mL of an aqueous solution of 1 M MnCl\(_2\)·4 H\(_2\)O) (cooled on ice) was injected at the bottom of the vial using a syringe while 2 mL of an aqueous solution of 1 M K\(_3\)[Fe(CN)\(_6\)] (also cooled on ice) was injected at the bottom of the large jar. Next, the jar was closed with the screw cap and placed in a temperature stabilized water bath of 45°C for 48 hours. Through slow diffusion of the constituents, the MnFe PBA product is formed in a controlled manner at the top edge of the small vial, the interface where the reagents meet. After 2 days dark brown cubic crystals had been formed. These were filtrated, washed with
Figure 3.1: Schematic illustration sketching the slow diffusion method used to obtain single crystalline MnFe PBA. The reagents, separately injected at the bottom of the vial and jar, respectively, slowly diffuse through the common 'buffer' solution to meet atop the small vial and form the PBA product at a controlled rate.

water and 96% ethanol of room temperature, and allowed to dry in air for 24 hours, affording RbMn[Fe(CN)₆]·H₂O crystals in a 47% yield. Analytically calculated elemental weight percentages for a RbMn[Fe(CN)₆]·H₂O stoichiometry: C 19.46 %, N 22.69 %, H 0.54 %. Experimentally found percentages: C 19.41 %, N 22.75 % and H 0.59 %.

3.2.2 Instrumentation and measurement

Crystallography

All crystallography experiments described in this chapter were performed by Auke Meetsma at the Zernike Institute for Advanced Materials in Groningen. A crystal with dimensions of 0.31 x 0.28 x 0.21 mm was mounted on top of a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer (Platform with a full three-circle goniometer) [52]. The diffractometer was equipped with a 4K CCD detector, which was set at a distance of 60.0 mm from the crystal. The sample temperature during the measurement was 293 K. Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). The corresponding generator was set at 50 kV/40 mA. Preliminary determination of the unit cell constants and data collection control were performed using SMART. The intensities of reflections on a hemisphere were collected through a combination of 3 sets of exposures (frames). Each set had a different angle φ for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time of 10.0 seconds per frame. Data integration and global cell refinement was per-
3.2 Experimental Methods

formed using the SAINT software \[52\]. The final unit cell was obtained from the $xyz$ centroids of 1705 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption; a multi scan absorption correction was applied, based on the intensities of symmetry related reflections measured at different angular settings (SADABS \[53\]), and reduced to $F_o^2$. The program suite SAINTPLUS was used for space group determination (XPREP) \[52\].

All refinement calculations and graphics were performed on a HP XW6200 (Intel XEON 3.2 GHz)/Debian-Linux computer at the University of Groningen with the program package SHELXL (least square refinements) \[54\], a locally modified version of the program PLUTO (preparation of illustrations) \[55\] and the PLATON package \[56, 57\] (checking the final results for missed symmetry with the MISSYM option, solvent accessible voids with the SOLV option, calculation of geometric data and the ORTEP illustrations \[54\]). Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography \[58\]. Extensive details on the crystallographic data collection and structure refinement can be found elsewhere \[59\].

SQUID magnetometry

Magnetic measurements were performed by Esther Vertelman in the Inorganic Chemistry group of the Zernike Institute for Advanced Materials (Groningen), on a Quantum Design MPMS magnetometer with a superconducting quantum interference device. Samples were prepared by putting 8-10 mg of crystalline RbMn[Fe(CN)$_6$]·H$_2$O (accurately weighed) between two pieces of cotton wool in a gelcap. In the magnetic susceptibility measurements, the sample was slowly cooled from room temperature to 5 K under a field of 0.1 T. Measurements were taken while keeping the field constant and varying the temperature from 5 K to 330 K and back to 150 K.

\textsuperscript{57}Fe Mössbauer spectroscopy

\textsuperscript{57}Fe Mössbauer spectra were recorded by Gabor Molnár at the Centre National de la Recherche Scientifique in Toulouse, using a conventional constant-acceleration type spectrometer equipped with a 50 mCi \textsuperscript{57}Co source and a flow-type liquid Helium cryostat. Spectra of the crystals (30 mg) were recorded between 50 K and 293 K. Prior to measuring the room temperature spectrum the sample was warmed to 350 K to ensure complete conversion to the HT phase. Least square fittings of the Mössbauer spectra were carried out under the assumption of Lorentzian line shapes, using the Recoil software package \[60\]. For an extensive description of the technique, see Chapter 6.
Raman spectroscopy

Inelastic light scattering experiments in the CN stretching region were performed in a 180° backscattering configuration, using a triple grating micro-Raman spectrometer (T64000-Jobin Yvon), equipped with a liquid nitrogen cooled CCD detector. The frequency resolution was better than 2 cm$^{-1}$ for the spectral region considered. The samples were placed in a liquid Helium cooled optical flow-cryostat (Oxford Instruments). The temperature was stabilized with an accuracy better than 0.1 K throughout the whole temperature range. A fraction of the second harmonic output of a Nd:YVO$_4$ laser (532.6 nm, Verdi-Coherent) was focused on the sample using a 50x microscope objective (Olympus). All spectra reported in this chapter were recorded in parallel polarization mode, with a total integration time of 15 minutes, unless stated otherwise.

3.3 Results and Discussion

3.3.1 Crystallography

The initial atomic coordinates for refinement of the crystal structure were taken from a refined powder structure [61, 62]. The positional and anisotropic displacement parameters for the crystal structure were refined. Crystal data and selected details on data collection and refinement are given in Table 3.1. The obtained final fractional atomic coordinates and equivalent displacement parameters for the atoms are given in Table 3.2. Thus, the structural unit cell [63] was identified as cubic. Space group $F\bar{4}3m$ was derived from the systematic extinctions and discriminated from other candidate space groups, which comply with the same extinction conditions, during the structure determination process. Though examination of the final atomic coordinates of the structure (see Table 3.2) yielded an additional inversion center, refinement with corresponding space group $F\bar{m}3m$ did not lead to chemically reasonable Fe-C and Mn-N distances (i.e. distances consistent with the room temperature low-spin Fe$^{III}$ and high-spin Mn$^{II}$ state).

Table 3.1: Crystal data and selected details of the structure determination at 293 K.

<table>
<thead>
<tr>
<th>a. Crystal data and details of the structure determination.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moiety formula</td>
</tr>
<tr>
<td>Formula weight (g·mol$^{-1}$)</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group, no.</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
</tr>
</tbody>
</table>

Continued on Next Page...
3.3 Results and Discussion

| V, (Å³) | 1164.6(4) |
| Θ range: min.-max.(deg.); # reflections | 3.35 - 29.76 ; 1705 |
| Formula Z | 4 |
| Space group Z | 96 |
| Approx. crystal dimensions (mm) | 0.31x0.28x0.21 |

### b. Data collection.

- Radiation type; λ Å: Mo Kα, 0.71073
- Temperature (K): 293(1)
- Measurement method: σ- and ω-scans
- Index ranges: \(h, k: -12 \rightarrow 14; l: -13 \rightarrow 14\)
- X-ray exposure time (h): 7.8

### c. Refinement.

- Number of reflections: 181
- Number of refined parameters: 16
- Final agreement factors:
  \[ wR(F^2) = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}} \]
  0.1004
- Residual electron density in final Difference Fourier map, (e/Å³): -0.9, 0.8(2)

A schematic ORTEP drawing of the best structural model for single crystalline MnFe PBA at 293 K, based on the cubic space group \(F\bar{4}3m\) (\(a = 10.521(2)\) Å), is depicted in Figure 3.2. The Fe ion is in an octahedral environment formed by the 6 C atoms of the cyano ligands that bridge the Fe and Mn ions. Similarly, Mn is in an octahedral environment formed by 6 N atoms. Rb and O (from \(H_2O\)) are stoichiometrically present and located in the fully occupied interstitial sites. Rb is distributed over two positions (4c, standard occupancy factor (s.o.f.) 0.7512(4) and 4d, s.o.f. 0.2488(4)). The oxygen (of the interstitial \(H_2O\) molecules) is located on the same symmetry positions as Rb (4c & 4d) and is disordered correspondingly. The interatomic distances of 1.929(4) Å for Fe-C and 2.205(5) Å for Mn-N are indicative for low-spin (LS) \(\text{Fe}^{III}\) and high-spin (HS) \(\text{Mn}^{II}\), respectively [37, 46, 64], corresponding to the high-temperature (HT) configuration of the material [65]. Despite numerous efforts, the low temperature structure of the material could not be elucidated. The data recorded at 100 K yielded an inconclusive structural model, as the corresponding diffraction measurements revealed a multitude of diffuse spots that prevented the determination of a realistic unit cell. Further details on the attempted structure determination at 100 K can be found elsewhere [59].
Figure 3.2: Room temperature structure of single crystalline RbMn[Fe(CN)₆]·H₂O. (a) Perspective ORTEP drawing of metal coordination clusters (50% probability level). (b) Unit cell representation, space group $F\bar{4}3m$.

Table 3.2: Final fractional atomic coordinates and equivalent isotropic displacement parameters with s.u.’s in parentheses, for single crystalline RbMn[Fe(CN)₆]·H₂O.

<table>
<thead>
<tr>
<th>Atoms of the Asymmetric Unit.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq.}(\text{Å}^2)$</th>
<th>s.o.f.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.0(-)</td>
<td>0.0(-)</td>
<td>0.0(-)</td>
<td>0.0170(3)</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.0(-)</td>
<td>0.0(-)</td>
<td>0.5(-)</td>
<td>0.0149(3)</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.0(-)</td>
<td>0.0(-)</td>
<td>0.2904(5)</td>
<td>0.0463(11)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.0(-)</td>
<td>0.0(-)</td>
<td>0.1828(4)</td>
<td>0.0281(9)</td>
<td></td>
</tr>
<tr>
<td>Rb1†</td>
<td>0.25000(-)</td>
<td>0.25000(-)</td>
<td>0.25000(-)</td>
<td>0.1340(12)</td>
<td>0.7512(4)</td>
</tr>
<tr>
<td>Rb2‡</td>
<td>0.75000(-)</td>
<td>0.75000(-)</td>
<td>0.75000(-)</td>
<td>0.210(5)</td>
<td>0.2488(4)</td>
</tr>
<tr>
<td>O1†</td>
<td>0.25000(-)</td>
<td>0.25000(-)</td>
<td>0.25000(-)</td>
<td>0.1340(12)</td>
<td></td>
</tr>
<tr>
<td>O2†</td>
<td>0.75000(-)</td>
<td>0.75000(-)</td>
<td>0.75000(-)</td>
<td>0.210(5)</td>
<td></td>
</tr>
</tbody>
</table>

$U_{eq.} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

†Indicates a s.o.f. (standard occupancy factor) of 0.7512(4)
‡Indicates a s.o.f. of 0.2488(4)

3.3.2 SQUID magnetometry
The temperature dependence of $\chi_M T$ of single crystalline RbMn[Fe(CN)₆]·H₂O, where $\chi_M$ is the molar magnetic susceptibility per formula unit and $T$ the temperature, is depicted in the left panel of Figure 3.3. The room temperature (295 K)
3.3 Results and Discussion

Figure 3.3: Temperature dependent magnetic properties of single crystalline RbMn[Fe(CN)₆]·H₂O. Left panel: Temperature dependence of χₘT versus T. Dashed arrows indicate the temperature dependence of the data as measured in successive heating and cooling runs, while vertical dashed lines indicate the corresponding transition temperatures. Right panel: Magnetization (M) at low temperatures. At Tₑ = 12 K, the MnFe system becomes ferromagnetic.

χₘT value is 4.7 cm³ K mol⁻¹, which corresponds well to the χₘT value of 4.8 cm³ K mol⁻¹ expected for a weakly coupled paramagnetic \{S₁;S₂\} = \{5/2;1/2\} material (expected HT values are calculated assuming a 100% HT configuration of the material [66]). Upon cooling, χₘT decreases around 250 K until it reaches a value of 4.0 cm³ K mol⁻¹ at 150 K. T₁/₂↓ (defined as the temperature at which 50% of the CT transition has occurred in the cooling run) is found to be 237 K for this process. For a paramagnetic \{S₁;S₂\} = \{2;0\} material (high spin MnIII and low spin FeII, in the case of a 100 % low-temperature (LT) configuration of the material), a χₘT value of 3.0 cm³ K mol⁻¹ would be expected, which is lower than the experimentally observed value of 4.0 cm³ K mol⁻¹. If exactly 50% of the material is assumed to switch from the HT to the LT configuration across the CT transition, however, the expected low temperature χₘT value would be 3.9 cm³ K mol⁻¹, which is very close to the experimental value. It therefore seems feasible that approximately 50% of the MnFe pairs have undergone charge transfer and adopt the LT configuration on cooling. Such a partial transition is intriguing considering that microcrystalline samples of comparable stoichiometry exhibit a virtually complete conversion [48], as was found in Chapter 2.

The reverse charge transfer process occurs at a temperature of T₁/₂↑ = 292 K in a heating run. The broad hysteresis of the transition (55 K) reflects the cooperativity of the charge transfer process. As shown in the right panel of Figure 3.3, the LT phase of the material undergoes magnetic ordering at Tₑ = 12 K. This ordering, and thus also the steep increase of χₘT at these temperatures, has been proposed to arise from a mechanism of mixed-valence electron delocalization of the
Mn ions, similar to the mechanism involving the Fe$^{III}$ ions in parent compound Prussian Blue Fe$_4^{III}$[Fe$^{II}$(CN)$_6^{III}$]$_3$·14H$_2$O [65, 67]. At 4 K, the magnetization value amounts to approximately 1800 emu mol$^{-1}$, which corresponds to about half of the molar magnetization found for polycrystalline samples [59]. The latter further supports the proposed 50 % charge transfer conversion in the single crystals, as it is well established that only the LT configuration of the material orders ferromagnetically.

3.3.3 $^{57}$Fe Mössbauer spectroscopy

$^{57}$Fe Mössbauer spectra of the RbMn[Fe(CN)$_6$]-H$_2$O single crystals at 293 K and 50 K are shown in Figure 3.4. The corresponding hyperfine parameters (isomer shift ($\delta$), quadrupole splitting ($\Delta$) and half width at half maximum ($\Gamma/2$)) that were obtained from a least square fitting procedure are given in Table 3.3. For a concise account of the basic principles of Mössbauer spectroscopy, the reader is referred to the introduction of Chapter 6. For the 50 K and 293 K spectra, a two-component fit to the Mössbauer spectrum yields satisfactorily results; in both cases, the spectrum consists of a singlet and a quadrupolar doublet, with area ratios 51(6)/49(6) for 50 K and 43(7)/57(7) for 293 K, respectively (See Fig. 3.4). Based on the hyperfine parameters (Table 3.3) and the strong temperature
3.3 Results and Discussion

Figure 3.5: Left panel: Spectral weight of Fe sites in $^{57}$Fe Mössbauer spectra as a function of temperature. Data are obtained from least square fits to corresponding spectra (see text). Right panel: Temperature dependence of normalized spectral weight difference w.r.t the 50 K spectrum. The legend holds for both panels, solid lines are guides to the eye.

dependence of the quadrupole splitting, both the high temperature (HT) and the low temperature (LT) doublet can be assigned to a low spin (LS) Fe$^{III}$ species in a slightly distorted (cubic) environment [68]. The HT singlet can be assigned either to LS Fe$^{II}$ or LS Fe$^{III}$ in a local cubic symmetry. These two species cannot be distinguished solely on the basis of the corresponding isomer shift [68]. However, based on Raman data which show only two bands at 295 K (ascribed to CN-stretching between HS Mn$^{II}$ and LS Fe$^{III}$, vide infra), this singlet is assigned to LS Fe$^{III}$ here. Singlets arising from LS Fe$^{III}$ in $^{57}$Fe Mössbauer spectra have been reported before [69, 70].

As was the case for the HT singlet, the LT singlet in the 50 K spectrum can be assigned to either LS Fe$^{II}$ or LS Fe$^{III}$ in a local cubic symmetry. However, as was revealed by the magnetic measurements, upon lowering the temperature the material undergoes a (partial) charge transfer transition at $T_{1/2\downarrow} = 237$ K, where about half of the Fe ions become bivalent. Thus, the LT singlet must correspond to LS Fe$^{II}$ ions. Thus, the HT $^{57}$Fe Mössbauer spectrum is comprised of a LS Fe$^{III}$ doublet and a LS Fe$^{III}$ singlet, of approximately equal spectral weight (site 1, $\delta = -0.138(2)$ mm s$^{-1}$, $\Delta = 0$ mm s$^{-1}$, 43(7)%; site 2, $\delta = -0.150(2)$ mm s$^{-1}$, $\Delta = 0.43(1)$ mm s$^{-1}$, 57(7) %). Similarly, the low temperature spectrum consists of LS Fe$^{III}$ and LS Fe$^{II}$ components, also of approximately equal spectral weight (site 1, $\delta = -0.033(4)$ mm s$^{-1}$, $\Delta = 0$ mm s$^{-1}$, 51(6)%; site 2, $\delta = -0.067(5)$ mm s$^{-1}$, $\Delta = 0.78(2)$ mm s$^{-1}$, 49(6) %). Overall, these data suggest that in the HT phase two distinct LS Fe$^{III}$ sites are present, only one of which (that giving rise to a singlet) switches valence across the temperature-induced charge transfer
transition. Such a partial switching can be explained by a possible distinction between iron sites in terms of their charge transfer capability, which is a result of their differing local environment. This notion is corroborated by the relative area ratios of the singlet and doublet components in the $^{57}$Fe Mössbauer spectra.

To further investigate the possible existence of two distinct Fe sites, a series of $^{57}$Fe Mössbauer spectra was recorded in a cooling run, across the charge transfer transition. The corresponding spectra were all fitted using three contributions; a singlet for both LS Fe$^{II}$ and LS Fe$^{III}$ in a perfect cubic environment, and a quadrupole doublet. The two singlets represent the electron transfer active Fe ions in the LT and the HT phase respectively, and the doublet accounts for the CT-inactive ions present in both phases. In the fitting procedure, the chemical isomer shift ($\delta$), the widths ($\Gamma$), quadrupole splitting ($\Delta$) and area fractions ($A/A_{tot.}$) of the individual contributions were allowed to vary; results are summarized in table 3.3. Figure 3.5 depicts the temperature dependence of the corresponding fitted area fractions. As is clear from both graphs, the area fraction (spectral weight) of the doublet stays more or less constant around 50 % throughout the temperature region, indicating that about half of the Fe sites does not undergo charge transfer upon cooling. The area fraction of the LT singlet (LS Fe$^{II}$) increases across the charge transfer transition, while simultaneously the area fraction of the HT singlet (LS Fe$^{III}$) decreases correspondingly. This behavior is in line with the proposed distinction between the iron sites in terms of their charge transfer capability.

Table 3.3: Hyperfine parameters extracted from fits to $^{57}$Fe Mössbauer spectra of the RbMn[Fe(CN)$_6$]·H$_2$O crystals.

<table>
<thead>
<tr>
<th>Quadrupole Doublet</th>
<th>$T$ (K)</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>$\Gamma/2$ (mm/s)</th>
<th>$A/A_{tot.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>-0.150(2)</td>
<td>0.43(1)</td>
<td>0.145(7)</td>
<td>57(7) %</td>
<td></td>
</tr>
<tr>
<td>255</td>
<td>-0.1444(6)</td>
<td>0.46(5)</td>
<td>0.16(3)</td>
<td>62(30) %</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>-0.117(8)</td>
<td>0.55(5)</td>
<td>0.18(3)</td>
<td>59(22) %</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-0.087(9)</td>
<td>0.64(4)</td>
<td>0.18(3)</td>
<td>45(15) %</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>-0.084(10)</td>
<td>0.71(3)</td>
<td>0.17(3)</td>
<td>34(12) %</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-0.067(5)</td>
<td>0.78(2)</td>
<td>0.20(1)</td>
<td>49(6) %</td>
<td></td>
</tr>
</tbody>
</table>

Singlet (HT)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>$\Gamma/2$ (mm/s)</th>
<th>$A/A_{tot.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>-0.138(2)</td>
<td>0.0</td>
<td>0.16(2)</td>
<td>43(7) %</td>
</tr>
<tr>
<td>255</td>
<td>-0.134(7)</td>
<td>0.0</td>
<td>0.17(8)</td>
<td>38(32) %</td>
</tr>
<tr>
<td>200</td>
<td>-0.112(6)</td>
<td>0.0</td>
<td>0.18(22)</td>
<td>15(29) %</td>
</tr>
<tr>
<td>150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0 %</td>
</tr>
<tr>
<td>125</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0 %</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0 %</td>
</tr>
</tbody>
</table>

*Continued on Next Page...*
In short, the $^{57}$Fe Mössbauer data are consistent with the magnetic measurements in that about half of the MnFe pairs in the materials undergo charge transfer upon cooling. Additionally, the data suggest this partial switching is related to the presence of two distinct Fe sites within the crystal structure.

### 3.3.4 Raman Spectroscopy

As was done for the polycrystalline samples in Chapter 2, inelastic light scattering (Raman scattering) is employed in order to indirectly determine the electronic and magnetic properties of the materials. This is done by exploiting the sensitivity of the vibrational stretching mode of CN-moieties to their local surroundings [71]. The stretching frequency of the cyano-bridge is known to be characteristic of the type, valence and coordination number of the metal ions it connects. A general rule of thumb hereby is that as the oxidation state of either one of the metal centers increases, so does the vibrational frequency and vice versa. Table 3.4 lists the expected frequency ranges of CN-moieties in different bimetallic bridges possibly occurring in the RbMn[Fe(CN)$_6$]-H$_2$O single crystals. A more extensive list can be found in Table 2.2 (p. 37). Data in both tables are estimates based on literature and experimental data of materials containing the specific or closely related CN-environments [48, 65, 71, 72, 73, 74].
Table 3.4: Expected frequency ranges for CN stretching modes, $\nu_{CN}$ of CN-moieties in various types of bimetallic cyano bridges (M = 3d metal ion).

<table>
<thead>
<tr>
<th>Cyano bridge</th>
<th>Frequency range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{II}$-CN-M$</em>{III}$</td>
<td>2065-2100 [71, 72, 73, 74]</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{II}$-CN-M$</em>{II}$</td>
<td>2090-2140 [48, 65, 71, 73]</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{III}$-CN-M$</em>{II}$</td>
<td>2146-2185 [48, 65, 71, 72, 74, 73]</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{III}$-CN-M$</em>{III}$</td>
<td>2180-2210 [71, 72]</td>
<td></td>
</tr>
</tbody>
</table>

**Temperature dependence**

Figure 3.6 shows the evolution of the 532 nm excited Raman spectrum of the CN stretch vibrations in single crystalline RbMn[Fe(CN)$_6$]-H$_2$O upon cooling. The crystal was heated to 330 K (above the hysteresis loop, see Fig. 3.3) prior to measurements to ensure the samples started out in their HT phase. Like for the polycrystalline samples (Chapter 2), group theory analysis predicts a split-up of the vibrational CN stretching mode into an $A_1$, an $E$ and a $T_2$ normal mode (the CN moiety is placed on the $C_2v$ site of the $F\bar{4}3m$ ($T_2^d$) HT space group [48, 61, 62, 75]). Only the $A_1$ and $E$ normal modes are expected to be observed in the parallel polarization spectra of Figure 3.6 (due to their non-zero diagonal Raman tensor components). Assuming a 100% HT configuration (LS Fe$_{III}$ and HS Mn$_{II}$) of the material at high temperatures, only one type of direct environment occurs for the CN moieties; the system consists of only Fe$_{III}$-CN-Mn$_{II}$ cyano bridges. Indeed, the 295 K spectrum in Fig. 3.6 shows only two lines (red lines at 2155 and 2164 cm$^{-1}$), which occur in the expected frequency range and are thus ascribed to the $A_1$ and $E$ normal modes of the Fe$_{III}$-CN-Mn$_{II}$ cyano bridge, in agreement with previous assignments [41, 48, 49].

The above magnetic measurements and $^{57}$Fe Mössbauer spectroscopy indicate a partial intervalence charge transfer of only 50% in the crystals upon cooling. As a result, the situation at lower temperatures is such, that four types of distinct 3d metal centers are present: LS Fe$_{III}$ (inactive), HS Mn$_{II}$, LS Fe$_{II}$ (active) and HS Mn$_{III}$, as was already sketched in Figure 2.10 (page 41) of the preceding chapter. Consequently, at temperatures below the CT transition, four types of cyano bridges occur within the material, of which Fe$_{III}$-CN-Mn$_{II}$ and Fe$_{II}$-CN-Mn$_{III}$ correspond to the respective HT and LT configurations of the material. However, the transition being only partial results in the presence of Fe$_{III}$-CN-Mn$_{III}$ and Fe$_{III}$-CN-Mn$_{III}$ bridges as well. Thus, in the LT phase of the crystalline material, we expect to see peaks arising from all these different cyano bridges. In addition,
Figure 3.6: Raman scattering spectra (black squares) of single crystalline RbMn[Fe(CN)₆]-H₂O at various temperatures. Multiple lorentzian lineshapes (filled) were combined to obtain a fit. The red and blue filled peaks represent vibrations characteristic for the HT and LT configuration, respectively. The spectra are normalized with respect to the integrated intensity of the HT lines and are shown with an offset for clarity. P indicates the excitation density on the sample.
each of these vibrational modes are expected to split into multiple normal modes due to the crystallographic symmetry, which further complicates the vibrational spectrum. In fact, assuming that the LT phase has a lower symmetry, as compared to the HT phase, the vibrational modes for each type of cyano bridge are expected to split up even more than is the case for the one cyano bridge in the HT phase. Indeed, across the CT phase transition, several new spectral features appear in the Raman spectrum, at the cost of the HT lines. These features, occurring mostly at lower energies, evolve into several new peaks at 2086, 2091, 2110, 2130, and 2202 cm$^{-1}$ as the material crosses into its LT phase (blue lines in Fig. 3.6). Since the vibrational frequencies of Fe$^{II}$-CN-Mn$^{II}$ and Fe$^{II}$-CN-Mn$^{III}$ moieties are expected at these lower frequencies, i.e. in the overlapping 2065-2110 cm$^{-1}$ and 2095-2140 cm$^{-1}$ ranges, respectively, the 2086, 2091, 2110, and 2130 cm$^{-1}$ modes are assigned to these CN bridges. Unfortunately, considering the large number of overlapping expected and observed lines, it is virtually impossible to give an accurate full assignment of the observed LT phase modes at this point. Still, the observed lower frequency lines are considered as markers of the LT phase, since they are only expected to be observed below the (partial) CT transition temperature. Moreover, similar modes were previously observed and assigned correspondingly in the polycrystalline material (Chapter 2) [49]. The new line observed at higher frequency (2202 cm$^{-1}$) can be regarded as another such marker, since it reveals the presence of an Fe$^{III}$-CN-Mn$^{III}$ bridge (the only anticipated bridge in this system consistent with a higher frequency vibration). The combined presence of this band and the lines corresponding to the HT phase (Fe$^{III}$-CN-Mn$^{II}$) in the LT Raman spectra (below 150 K) underline once more the incomplete CT transition as they are expected only if the compound has contributions of both the LT and HT configuration.

Another, even more obvious indication of the occurrence of the CT transition is the associated color change. As was the case for the polycrystalline material in the previous chapter, the single crystals also exhibit a rather pronounced color change across the CT transition, going from a lighter appearance in the HT phase, to a dark appearance in the LT phase. Figure 3.7 shows the visual monitoring of a single crystal surface in its LT phase, at 220 K (prior to the experiment, the sample was cooled to 50 K to ensure positioning in the heating part of the magnetic hysteresis loop, see Fig. 3.3). Using the c.w. (continuous wave) 532 nm laser beam also used as the Raman probe (power density $\simeq 2000$ W cm$^{-2}$), the sample can be heated locally, upon which it assumes the HT state and changes to the corresponding lighter color. As the equilibrium temperature is within the hysteresis loop, the heating-induced CT transition is stable and a pattern can be 'written' on the sample surface in a controlled fashion. Panels 1-4 of Fig. 3.7 show the chronological, stepwise writing of a face-like shape of HT material within the (LT phase) crystal surface. Panel 5 is taken after irradiating the sample with an increased power density of $\simeq 10^4$ W cm$^{-2}$. As the converted sample area is much larger than the beam focus in this case, the effect is attributed to indirect
Figure 3.7: Local, laser-induced heating of a MnFe PBA single crystal through the CT transition, demonstrating the accompanying color change. Lighter areas correspond to the material in its LT phase, while darker areas correspond to the HT phase. Prior to the experiment, the sample was cooled to 50 K and subsequently heated to 220 K, to ensure the sample was in its LT phase. Panels 1-4 show the chronological, stepwise sketching of a 'face' of HT material on the sample surface, where a focused laser beam (532 nm, continuous wave (c.w.)) is used to locally heat the crystal, inducing the LT to HT transition and the associated color change, thus 'writing' the pattern. In panels 1-3, dotted shapes indicate the surface area that is heated during the interval between that and the next frame. Between panel 4 and 5, the incident laser power is increased by 400 %, which results in the LT to HT transition occurring in an area larger than the laser spot size, demonstrating the indirect heating- rather than photo-induced nature of the effect. Panels a and b are zoom-out pictures of the crystal surface taken after frames 3 and 5, respectively.
laser-induced heating rather than due to direct photo-excitation. Although the latter could in principle also be responsible considering the cooperative interactions in the system, at these temperatures the incident power dependence does not exhibit a marked threshold behavior, as one would expect in that case (vide infra). Panels a and b are corresponding zoom-outs of the same sample, showing the the face-like shape and other HT phase patterns laser-written on the crystal surface.

**Photoactivity**

Comparing the temperature evolution of the Raman spectrum with the magnetic measurements, it appears that the phase transition is 'lagging' in the Raman data, meaning that the transition seems to start above 200 K, being 'completed' only around 100 K. This can be explained by considering the photo-activity of the material. As discussed in Chapter 2, the material is known to be photo-excited to the HT configuration by 532 nm light when in the LT configuration [41, 76]. Moreover, due to the increased resistance to photo-damage of the crystalline material, a higher excitation power density was used in this case, which increases the local heating contribution of the laser probe. Consequently, the Raman spectrum at temperatures where this photo-excitation occurs is the combined result of the temperature-induced HT-LT conversion, these light-induced effects and local sample heating. The efficiency of the photo-conversion is temperature dependent and seems to be high in temperature regions of bistability of the HT and LT configurations, e.g. near the hysteresis loop in the magnetic data, as well as around 90 K (See Chapter 2). When combined, these effects can explain the apparent temperature downshift of the CT transition as seen in the Raman data. In line with expectation, the photo-excitation of the crystals is also reflected in their optical properties; the excited 'HT-like' material appears a substantially lighter brown w.r.t the LT phase material (the inverse color change is observed upon cooling through the CT transition). Similar color changes (to varying degree) of the sample surface upon irradiation (of equal power density) have been observed at 150, 100 and 80 K, reflecting the broad temperature range of the photo-activity of the material. Whether the color changes at these temperatures are mainly due to indirect laser heating or direct photo-excitation to the HT (-like) phase cannot be assuredly distinguished at this point. However, a laser-induced heating effect seems the more likely, considering the fact that at 50 K, in contrast, the color change is hardly observed. This indicates there is little to no photo-induced conversion (direct or indirect) to the HT configuration at this temperature. Thus, the 50 K Raman spectrum is considered the only spectrum reflecting the 'pure' low temperature phase of the material, showing the presence of both HT and LT configurations.

The characteristic photo-activity of the material is also dramatically reflected in the 4 K spectrum recorded with an excitation density of 3000 W cm$^{-2}$. In these conditions, the Raman spectrum exhibits lines originating from the HT
3.3 Results and Discussion

Figure 3.8: Left panel: Excitation power density dependence of the Raman spectrum of single crystalline RbMn[Fe(CN)₆]·H₂O at 4 K. The spectra are normalized with respect to the total integrated intensity and are shown with an offset for clarity. P indicates the excitation density on the sample. Spectra were recorded with a total integration time of 7 minutes. Right panel: Ratio between integrated intensity of LT and HT lines versus excitation power density.

configuration only. In contrast, by only reducing the excitation density to 1275 W cm⁻², the corresponding spectrum consists of both LT and HT lines. Due to the cooperative nature of the CT transition, it is possible to switch the material to a metastable HT configuration, above a certain excitation power density [43]. In other words, if the amount of photo-excited MnFe pairs exceeds a certain density, the associated volume changes stabilize the excited state overall (an energy barrier w.r.t. relaxation to the ground state is introduced), making it metastable and leaving the system in the full HT configuration at low temperatures. In line with expectation and observation in the polycrystalline samples (Chapter 2), the striking color change (the excited state appearing lighter) is also observed upon photo-conversion to the metastable HT configuration at 4 K. Also for these crystalline samples, the photo-excited state was visually monitored in a slow heating process, and found to relax to the darker LT ground state at a temperature of ~125 K, consistent with the literature value (120 K) [43] and the relaxation temperature found for polycrystalline material in the previous Chapter (123 K). This simultaneously proves the direct photo-induced nature of the effect at these temperatures, as an indirect heating-induced HT-phase would neither be metastable, nor would it relax to the LT-phase upon heating.

The power density dependence of the Raman spectrum at 4 K, depicted in the left panel of Figure 3.8, confirms the threshold behavior expected in a cooperative system. As the laser power incident on the sample is increased, the spectral weight ratio of the LT and HT lines (right panel of Fig. 3.8) suddenly decreases
between 1275 and 1700 W cm$^{-2}$. In addition to being a feature of cooperative behavior, the excitation density threshold also confirms that the transition is indeed of optically induced nature at this temperature, rather than being the result of laser-induced sample heating.

Overall, the Raman data are in good agreement with the magnetic measurements and the $^{57}$Fe Mössbauer results. Temperature dependent spectra in the spectral region of cyano vibrations support the conclusion that only part of the Fe-CN-Mn bridges are converted to the LT configuration. Additionally, the data, in particular the 4 K spectra, demonstrate the photo-activity of the material. Specifically, at 4K complete optical LT to HT switching is observed using 532 nm light excitation above a threshold excitation power density. The latter property is particularly interesting, as below 12 K the material is ferromagnetic in its LT phase (See Fig. 3.3), while it is (expected to be) paramagnetic in the photo-induced metastable HT phase. The c.w. (continuous wave) power density threshold for complete switching of MnFe single crystals at 4 K is found to be approximately 1500 W cm$^{-2}$ for 532 nm light.

3.4 Discussion

Based on the results presented above, one can conclude that the temperature-induced charge transfer transition involves only about 50 % of the MnFe pairs in single crystalline RbMn[Fe(CN)$_6$]·H$_2$O. There are several reasons to infer that this observed partial switching is an intrinsic property of the single crystals. Firstly, magnetic susceptibility data recorded for independently prepared single crystalline samples confirm the 50 % switching ratio. Secondly, the $^{57}$Fe Mössbauer data reveal the presence of at least two different iron sites within the material both above and below the CT transition, also in an approximate 50:50 ratio. (Fig. 3.4). Indeed, the temperature dependent $^{57}$Fe Mössbauer data confirm that only one of these iron sites switches valence across the CT transition (Fig. 3.5). Lastly, the concept of intrinsic partial switching is also verified by Raman spectroscopy, which is crucial and very conclusive regarding this point, as spectra recorded on different individual crystals evidence a reproducible extent of partial switching. The incomplete CT transition can be rationalized by assuming a distinction between these different iron sites, occurring in a 1:1 ratio, in terms of their charge transfer capability. Naturally, the next issue then becomes determining the origin of these two distinct iron sites.

3.4.1 Tentative model

As mentioned above, the incomplete charge transfer transition can originate from a distinction between different iron sites in terms of charge transfer capability. Here one of the models that could explain the intrinsic presence of two different
Figure 3.9: (a) The two types of unit cells, A and B. Spheres indicate the Rb positions; the interstitial sites without a sphere contain water molecules. Solid lines represent the cubic rock salt structure formed by the Fe and Mn ions and the CN ligands. The corresponding atoms are omitted for clarity. (b) Two different iron sites. Darker spheres originate from unit cell A, while lighter spheres originate from unit cell B; interstitial sites without a sphere contain water molecules. Solid lines represent the cubic rock salt structure formed by the Fe and Mn ions and the CN ligands. The corresponding atoms are omitted for clarity.
Fe (and Mn) sites is discussed.

The distinction in charge transfer capability of the different iron sites can be explained by differing local environments, more specifically, by differences in the second coordination sphere around the iron ions (and likely also the manganese ions). In order to further substantiate this notion, the crystallographic data of RbMn[Fe(CN)₆]·H₂O are revisited. From there, the only structural variable ambiguity found in the material is the distribution of the Rb⁺ ion and O (from H₂O) over the interstitial lattice sites. Both Rb and O are stoichiometrically present and both interstitial sites (4c and 4d in the F43m space group, respectively) are fully occupied (see Table 3.2). The variability is in the distribution of both Rb and O over these interstitial sites; the Rb ions (water molecules) occupy the 4c and 4d sites in a 3:1 (1:3) ratio. As a result, there is a distribution of two different types of unit cells, types A and B (Figure 3.9), which are related by a center of inversion. Thus, the inequivalent Fe and Mn environments may be generated by a particular pattern in the distribution of the different unit cells, which in turn originates from the disorder of the Rb ions (and water molecules) over the two interstitial sites. For example, the local environment of an Fe atom sandwiched in between neighboring unit cells of the same type (See I, Figure 3.9) is different from that of one in between unit cells of types A and B (II, Figure 3.9).

Considering a non-random distribution of unit cells A and B in the material, one can think of a 'super unit cell' which incorporates this higher order. In the case of the super unit cell represented in Figure 3.10a, constructed from 8 building blocks that correspond to either unit cell A or B, careful evaluation of the Fe (and Mn) environments in this 'super cell' reveals three distinct iron (and manganese) sites in a 2:1:1 ratio (Figure 3.10b). Assuming that only certain types of iron environments will allow for valence tautomerism and thus charge transfer, such a super cell structure can account for the observed 50% switching in the single crystalline material. Unfortunately, with the current crystallographic data, it is not possible to resolve such a presumed higher ordering of different unit cells.

A random ordering of unit cells A and B would result in a large, random variety of iron and manganese sites, each of which will have different charge transfer properties. Consequently, assuming such a non-ordered distribution, one would also expect a variation in the charge transfer conversion ratio from individual crystal to crystal, as the metal site statistics would vary randomly in that case. Given the fact that our experimental results consistently reveal a 50% CT conversion ratio for different individual crystals prepared in independent synthesis batches, it is unlikely that such a mere random distribution accounts for the observed 50% conversion fraction. Though the above super cell is not the only possible model, the general concept - a distinction in CT capability of iron sites through differing Rb/H₂O orderings on the interstitial sites - is believed to be the origin of the partial charge transfer in these crystals. Unfortunately, despite numerous attempts, such a superstructural ordering on the interstitial sites could not be resolved using conventional x-ray diffraction methods to date; synchrotron based diffraction experiments may provide the answer in the future.
Figure 3.10: (a) Distribution of the two types of unit cells, A (white box) and B (black box) in a proposed 'super unit cell', indicated by the dotted grey line. (b) Three different local environments of the iron (and manganese) sites, as they occur in the 'super unit cell' in a 2:1:1 ratio (from top to bottom). Darker spheres originate from unit cell A (75% of the cells), while lighter spheres originate from unit cell B (25% of the cells). Interstitial sites without a sphere contain water molecules. Solid lines represent the cubic rock salt structure formed by the Fe and Mn ions and the CN ligands. The corresponding atoms are omitted for clarity.
3.5 Conclusions

Summarizing, this chapter discussed the determination of the single crystal structure of the Prussian Blue analog RbMn[Fe(CN)_6]·H_2O. The single crystalline material is shown to undergo the temperature-induced reversible valence transfer between the HS Mn^{II} and LS Fe^{III} ions upon cooling, which leads to the presence of HS Mn^{III} and LS Fe^{II} ions in the low temperature phase. In contrast to the polycrystalline materials discussed in Chapter 2 however, the charge transfer transition is found to be only partial in the crystals, in which the conversion percentage appears to be limited to approximately 50%. This consistently observed partial switching is argued to be an intrinsic property of the crystals based on several arguments. Firstly, the 50% conversion fraction is confirmed by SQUID magnetometry data for several independently prepared single crystals. Secondly, ^{57}Fe Mössbauer data reveal the presence of at least two different iron sites within the material, also in an approximate 1:1 ratio, of which only one switches valence across the CT transition. Finally, Raman spectra recorded on different individual crystals reveal a similar extent of partial switching in all crystals.

Additionally, Raman spectroscopy also discloses a transition from the LT to the HT configuration upon visible light irradiation (532 nm) in single crystals, as was observed for the polycrystalline material. At 4 K, the material is shown to be photo-converted to a metastable HT configuration (Fe^{III}Mn^{II}) in its entirety, provided the continuous wave excitation power density exceeds the threshold value, which is found to be \( \approx 1500 \text{ W cm}^{-2} \) for 532 nm light. The occurrence of the light-induced CT transition at 4 K is particularly interesting, as there the LT ground state (Fe^{II}Mn^{III}) is ferromagnetic, while the induced metastable HT state (Fe^{III}Mn^{II}) is not. Thus, potential optical control over a macroscopic sample magnetization may be explored at these temperatures.

The incomplete charge transfer transition found in the RbMn[Fe(CN)_6] crystals is assigned to the presence of multiple distinct Fe sites in the material, which differ in terms of charge transfer capability. This distinction in CT capability is argued to be brought about by a non-random distribution of Rb ions and H_2O molecules over the interstitial sites.
Bibliography


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The theoretical $C$ values were calculated using the formula $C = \frac{N_A \mu_B^2 g^2}{3k_B} \sum_i c_i S_i (S_i + 1)$, where $N_A$ is Avogadro’s number, $\mu_B$ is the Bohr magneton, $g$ is the g-factor, taken as 2, $S_i$ is the spin of the various transition metal ions in the sample, $c_i$ is the corresponding stoichiometry coefficient of those ions (as given by the elemental analysis) and $k_B$ is Boltzmann’s constant.


