A structural phase transition coupled to the Fe^{3+} spin-state crossover in anhydrous $RbMn[Fe(CN)_6]$

A. I. Rykov · J. Wang · T. Zhang · K. Nomura

Abstract Linkage isomerism is the coexistence of iso-compositional molecules or solids differing by connectivity of the metal to a ligand. In a crystalline solid state, the rotation is possible for asymmetric ligands, e.g., for cyanide ligand. Here we report on our observation of a phase transition in anhydrous $RbMn[Fe(CN)_6]$ (nearly stoichiometric) and on the effect of linkage isomerism ensuing our interpretation of the results of Mössbauer study in which we observe the iron spin state crossover among two phases involved into this transition. The anhydrous $RbMn[Fe(CN)_6]$ can be prepared via prolonged thermal treatment (1 week at at 80 °C) of the as-synthesized hydrated $RbMn[Fe(CN)_6] \cdot H_2O$. The latter compound famous for its charge-transfer phase transition is a precursor in our case. As the temperature is raising above 80 °C (remaining below 100 °C) we observe $RbMn[Fe(CN)_6]$ that inherited its F-43 m symmetry from $RbMn[Fe(CN)_6] \cdot H_2O$ transforming to a phase of the Fm-3 m symmetry. In the latter, more than half of Fe^{3+} ions are in high-spin state. We suggest a plausible way to explain the spin-crossover that is to allow the linkage isomerism by rotation of the cyanide ligands.

Keywords Hexacyanoferrate · Spin crossover · Linkage isomerism · Mössbauer spectra

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1 Introduction

Cyanide is a nonsymmetric ligand, therefore, the phenomenon of linkage isomerization can be observed in the systems based on the cyanide ligand. Iron hexacyanomanganate was a system reported to be particularly susceptible to linkage isomerism [1]. On the other hand, manganese hexacyanoferrates, such as $RbMn[Fe(CN)_6]$, are known to exist in multiple valence-tautomeric forms owing to fast electron transfer within the pairs $Fe^{III}(S = 1/2)$–$Mn^{II}(S = 5/2)$ and $Fe^{II}(S = 0)$–$Mn^{III}(S = 2)$ [2]. The valence tautomery manifests itself as a hysteretic structural phase transition between low-temperature tetragonal (Fe^{II}-Mn^{III}) and high-temperature cubic (Fe^{II}-Mn^{III}) phases [3]. We report in this system another phase transition (cubic-to-cubic) which we interpret as the manifestation of the linkage isomerization at elevated temperatures (80 °C to 100 °C).

2 Experimental

The hexacyanoferrate $Mn_{1.07}Rb_{0.86}[Fe(CN)_6]\cdot H_2O$ was synthesized at 39 °C via adding to the 0.16 M solution of $K_3Fe(CN)_6$ the 0.167 M solution of $Mn(NO_3)_2\cdot 10H_2O$ premixed with RbCl in large (6-fold) excess of the latter. Single-phase samples of the insoluble brown-coloured precipitates were extracted through double washing the products in pure water. Next, adding 3 % of $^{57}Fe^{3+}$ to the solution of $Mn(NO_3)_2\cdot 10H_2O$ a similar synthesis was done that has resulted in the formula $Mn_{1.1}Fe_{0.03}Rb_{0.74}[Fe(CN)_6]\cdot H_2O$. The cationic composition of the washed products was determined by Rietveld analysis (FULLPROF program) of the x-ray diffraction (XRD) patterns. Mössbauer spectra were measured using a Wissel GMBH furnace on Topologic 500A spectrometer in the range 25 °C to 105 °C with the typical step of 5°. The isomer shifts relative to α-Fe are given.

3 Results and discussion

In the hydrated phase of $RbMn[Fe(CN)_6]H_2O$ the ions of Rb^+ and H_2O molecules occupy similar sites. These are the interstitials of the negatively charged metal-organic framework formed by Mn^{2+} cations and $[Fe(CN)_6]^{3-}$ complex anions. The sublattice of interstitials of the metal-organic framework is split into two sub-sublattices owing to the symmetry model F-43 m, in which each of the Mn^{2+} and H_2O species populates its own site. This kind of ordered superstructure is out of line with the majority of Prussian Blue analogues. The most part of Prussian Blues exhibits the randomly occupied interstitials by the equal shares of alkali cations and water molecules. The disordered structure is characterized by the symmetry group Fm-3 m. It is this structure that we observe the formation at heating the anhydrous rubidium-manganese hexacyanoferrate (Fig. 1).

As-synthesized samples can be characterized by the order parameter Δ defined as the difference of occupancies of Rb and water sublattices (Wyckoff sites 4c and 4d of the F-43 m group) by Rb and water, respectively. For the two samples whose syntheses are described above the Rietveld refinements gave the formulas $Mn_{1.07}Rb_{0.76}^{4c}Rb_{0.1}^{4d}[Fe(CN)_6]\cdot H_2O$ and $Mn_{1.1}Fe_{0.03}Rb_{0.5}^{4c}Rb_{0.24}^{4d}[Fe(CN)_6]\cdot H_2O$

Fig. 1 Cu K_α X-ray diffraction patterns of the anhydrous sample of $Mn_{1.07}Rb_{0.86}[Fe(CN)_6]$ before and after in-situ Mössbauer cycling the temperature up to 100 °C
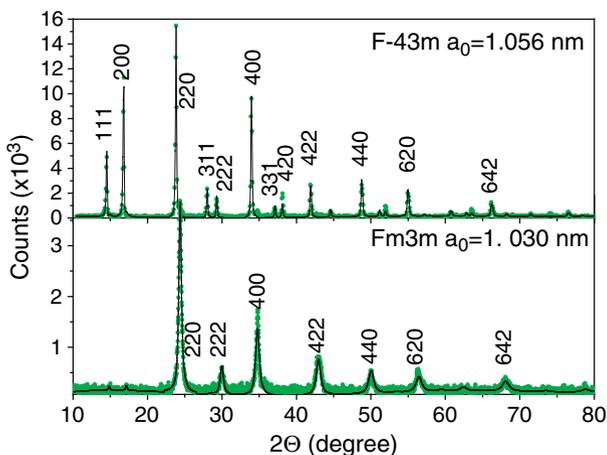
Table 1 Mössbauer spectra parameters in $Mn_{1.07}Rb_{0.86}[Fe(CN)_6] \cdot xH_2O$

Spectrum	Site	δ (mm/s)	Δ (mm/s)	%
As-synthesized	Singlet	−0.15(1)	−	50
T = 20 °C	Doublet	−0.16(1)	0.33(3)	50
As-synthesized	Singlet	−0.22(1)	−	20
T = 100 °C	Doublet	−0.23(1)	0.44(2)	80
Heated at 80 °C	Singlet	−0.18(1)	−	25
(1week) T = 100 °C	Doublet	−0.23(1)	0.33(1)	75
Heated at 80 °C	Singlet	−0.08(1)	−	42
(1week) T = 20 °C	Doublet	0.34(1)	0.93(1)	58

and the order parameters $\Delta = 0.66$ and $\Delta = 0.26$, respectively. Corresponding cubic lattice parameters were 1.056 and 1.055 nm. The as-synthesized samples retain their F-43 m structure either after prolonged (1 week) treatment at 80 °C or after short (4 h) treatment at 100 °C. However, when the prolonged (80 °C) and short (100 °C) thermal treatments were applied sequentially the transformation from F-43 m to Fm-3 m was observed as shown in Fig. 1. Therefore, the first treatment was understood to form the metastable anhydrous hexacyanoferrate. In this preliminary step, it is hard to detect in the XRD patterns the withdrawal of zeolitic water molecules. Because of the long duration (1 week) of this step, the thermogravimetric measurement at 80 °C could not be completed; therefore, the water content change was estimated in a rapid heating-cooling cycle to higher temperature (140 °C), at which the anhydrous F-43 m phase could not be preserved.

Mössbauer spectra of the original as-synthesized samples consist of a doublet of low-spin Fe^{3+} and its tautomeric low-spin Fe^{2+} singlet form [2] with similar chemical shifts (Table 1). With heating the singlet starts to die-off at 80 °C and the doublet form prevails in the range 90–100 °C. In this range, the sample remained for 4 h, however, the singlet spectra were restored at cooling the sample. In the XRD patterns, no difference with respect to the as-synthesized sample was seen. This reversible interconversion between room-temperature singlet and hot doublet can be explained as the behaviour intrinsic of the hydrated phase.
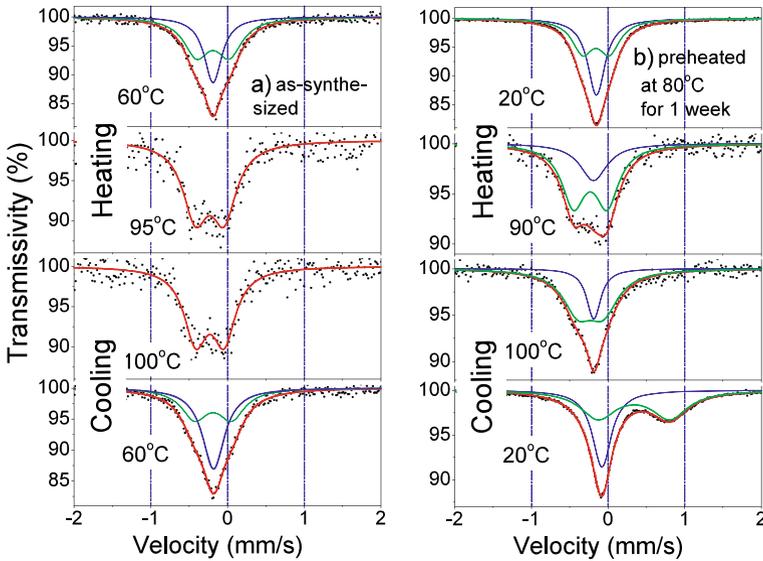
Fig. 2 Mössbauer spectra in two samples of $Mn_{1.07}Rb_{0.86}[Fe(CN)_6]$ recorded in-situ during the cycle of heating (to 100 °C) and cooling
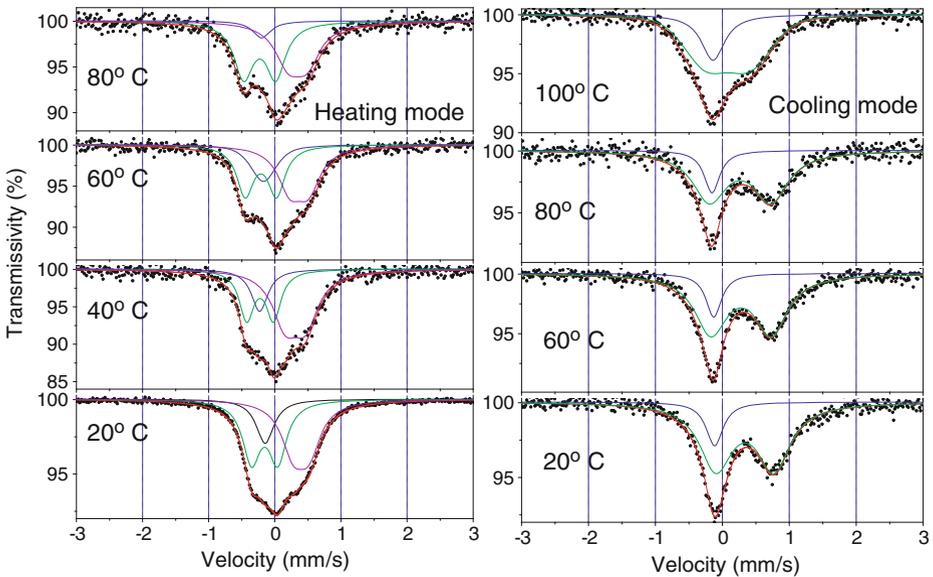
Fig. 3 Mössbauer spectra of the sample of $Mn_{1.1}Rb^{57}_{0.76}Fe_{0.03}[Fe(CN)_6]$ recorded in-situ during the cycle of heating (to 101 °C) and cooling

An aliquote of this sample preheated for one week at 80 °C showed a distinct behaviour (Fig. 2). The spectra measured in cooling mode reveal the large abundance (58 %) of the high-spin Fe^{3+} species. Could the Fe^{3+} ions migrate and exchange

Table 2 Mössbauer spectra parameters in $Mn_{1.1}Rb_{0.76}{}^{57}Fe_{0.03}[Fe(CN)_6]$

Spectrum	Site	δ (mm/s)	Δ (mm/s)	%
As-synthesized	Singlet	−0.15(1)	−	17
T = 20 °C	Doublet	−0.16(1)	0.33(3)	41
	Doublet	0.33(1)	0.21(4)	42
Heating mode,	Singlet	−0.21(1)	−	6
T = 80 °C	Doublet	−0.22(1)	0.44(2)	45
	Doublet	0.25(1)	0.23(4)	49
Cooling mode	Singlet	−0.14(1)	−	23
T = 100 °C	Doublet	0.09 (1)	0.67(1)	77
Cooled down	Singlet	−0.12(1)	−	15
T = 20 °C	Doublet	0.34(1)	0.86(1)	85

their positions with Mn^{2+} below 100 °C? It is rather conceivable that the cyanide ligands were rotated thus stabilizing the high-spin state of iron ions in nitrogen environments and low-spin state of manganese ions in carbon environments. The second subspectrum (single line) retains close to initial negative value of the isomer shift of −0.08 mm/s, associated with low-spin Fe(III).

In an additional experiment, we have measured the sample, in which we substituted 3 % of Mn with ^{57}Fe. In the heating mode, the ^{57}Fe doped into Mn(II)-sublattice shows a very small quadrupole splitting (Fig. 3). However, in the cooling mode, large percentage of the high-spin Fe^{3+} species (upto 85 %) appears, having the isomer shift of 0.33 mm/s and quadrupole splitting of 0.93 mm/s (Table 2). Clearly, a half of this subspectrum area originates from the ^{57}Fe species that we substituted into the Mn(II)-sublattice. The increase of their quadrupole splitting can be explained by the environment change at the F-43 m to Fm-3 m phase transition. The fact that the abundance of the high-spin $^{57}Fe^{3+}$ species has increased twice after the heating-cooling cycle implies that one half of them has experienced a transition from low-spin to high-spin state. But again, Mn^{2+} and Fe^{3+} do not exchange among their sites at 100°. That is why we explain these observations by linkage isomerism. More proofs to our interpretation of the observed phenomena are planned to be obtained by measuring the low-temperature Mössbauer spectra and magnetization of the disordered phase.

References

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