



	Experiment title: Anomalous thermal expansion in the alkali-free $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ compound	Experiment number: HE-2346
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Report:

The purpose of HE-2346 experiment was to investigate thermal expansion in different Co-Fe cyanides: $\text{Co}^{\text{II}}_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ and $\text{Rb}_2\text{Zn}^{\text{II}}_4[\text{Fe}^{\text{III}}(\text{CN})_6]_{3.3} \cdot 16\text{H}_2\text{O}$ or $\text{Rb}_2\text{Co}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_{3.3} \cdot 10\text{H}_2\text{O}$ and $\text{Cs}_2\text{Co}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_{3.3} \cdot 13\text{H}_2\text{O}$, representative of the $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ and $\text{Co}^{\text{III}}\text{-Fe}^{\text{II}}$ valence state configurations respectively.

The crystal structure of Prussian blue was first described by Buser *et al.*¹ and many studies were undertaken on its Co-Fe analogues since a photomagnetic effect was observed in 1996 implying a dia to ferrimagnetic transition under red light irradiation. This transition was attributed to an optically-induced $\text{Co}^{\text{III}}(\text{LS})\text{-Fe}^{\text{II}}(\text{LS}) \rightarrow \text{Co}^{\text{II}}(\text{HS})\text{-Fe}^{\text{III}}(\text{LS})$ electron transfer, accompanied by a spin state change of the Co ions.² Such a photomagnetic effect would open the way to applications in memory devices and magneto-optical switching. The crystal structure consists of $[\text{CoN}_6]$ and $[\text{Fe}(\text{CN})_6]$ polyhedral units connected in 3D through bridging CN groups. The alkali metal cations and the water molecules are located in the sub-octants of the face-centered cubic structure. To identify the parameters which control the electron transfer and the Co spin transition (ligand field strength,³ displacive transition involving the alkali metal ions⁴ similarly to ferroelectric BaTiO_3 , bending of the Co-NC-Fe dihedral angle⁴...), we have carried out structural investigations of reference compounds for the $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ and $\text{Co}^{\text{III}}\text{-Fe}^{\text{II}}$ valence state configurations.

During preliminary experiments (HE-1721 and HE-1956), we have observed a very large thermal expansion for the alkali-free compound $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$, indicative of a “soft” crystal structure. However, these data have also shown a strongly hysteretic behaviour of the lattice constant which could be

attributed to kinetics-dependent (de)hydration or else to some dynamics involving either the zeolitic water molecules or the Co-NC-Fe backbone. In an alkali-doped cobalt hexacyanoferrate, the freezing of the H₂O dynamics has been evidenced at the vicinity of the spin transition by MAS D NMR.⁵ However, it would be important to check whether this effect is mainly related to the large volume contraction ($\Delta V/V \sim 9\%$) or if it is systematic in this class of materials.

We have used the standard diffraction set-up of BM1A, with the image plate detection system for fast powder data acquisition as a function of temperature (90-300K) using an Oxford Cryostream N₂ blower.

Preliminary results

According to preliminary LeBail analyses of the 4 reference compounds, all show an hysteretic behaviour of the unit cell parameter, in the 225-300K range, which is strongly dependent on kinetics down to 0.5K.min⁻¹ (an exemple is given in Fig. 2). The Co^{II}-Fe^{III} based compounds show a very large thermal expansion coefficient while the Co^{III}-Fe^{II} phases display a much smaller variation of the lattice constant with temperature. This report is focused on the Rietveld analysis of the Rb₂Co₄[Fe(CN)₆]_{3.3}.10H₂O derivative (named RbCoFe in the following). This compound does not exhibit a spontaneous (or thermal) spin transition. It is mainly composed of Co^{III}-Fe^{II} diamagnetic pairs, thus allowing a combined X-ray diffraction and ¹H NMR study. The *Fullprof* suite of programs was used to refine the powder X-ray diffraction patterns. An example of calculated curve is given in Fig. 1. Chemical occupancies were fixed on the basis of the results of elemental analyses. It is worth mentioning that the water content was assumed to be constant in the 90-300K range. Indeed, thermogravimetric analyses on this sample did not reveal any significant weight loss below 340K. The structural model proposed for Prussian blue was used as a starting point (*Fm3m* space group). Co atoms were placed in (0,0,0) and Fe atoms in (1/2,1/2,1/2) (*4a* and *4b* Wyckoff positions, respectively). The crystal structure contains 0.7 [Fe(CN)₆] vacancy per unit cell, each of them being replaced by a cluster of 6 H₂O molecules. The missing nitrogen atoms were replaced by oxygen atoms of type 1 (O(1)) to complete the coordination sphere of Co. C, N and O(1) atoms were placed at position 24*e*. Rb atoms were located at position 8*c* (1/4,1/4,1/4). The zeolitic water molecules (O atoms of type 2, O(2)) may be linked to a neighbouring H₂O(1) molecules by hydrogen bonds. This binding leads to a slight off-centering of the H₂O(2) molecules (from position 8*c* to 32*f*). Even though we should take into account O(2) atoms both in (1/4,1/4,1/4) and in (*x,x,x*) positions, we only considered the latter ones in order to decrease the number of refined parameters. The major consequence will be to artificially increase the thermal factor of O(2) to account for the static positional disorder.

The temperature displacement factors, *U*(Co) and *U*(Fe) were refined independently. As we assume the C≡N bond as rigid, the *U*(C), *U*(N) and *U*(O₁) parameters were constrained to be equal (O(1) atoms actually contribute very little to the diffracted intensity). We also used the constraint *U*(Rb)= *U*(O₂). An attempt was made to decorrelate *U*(Rb) and *U*(O₂) but it led to divergence for the studied *Q*-range, as well as an attempt to displace the Rb atoms to position 32*f*. The influence of this constraint on the final results will be discussed in the following.

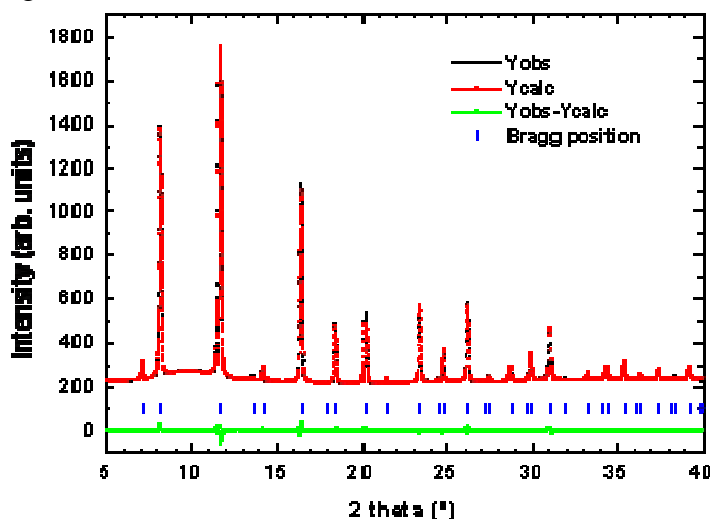


Fig. 1: Observed (red curve) and calculated (dark curve) powder X-ray diffraction patterns at 300 K for the RbCoFe sample ($\lambda = 0.7183\text{\AA}$)
 $R_p = 5.97\%$ and $R_{wp} = 4.67\%$.

The lattice parameter value plotted as a function of temperature shows the expected lattice contraction on cooling but presents an hysteretic behaviour on warming, between 250K and 300K (see Fig. 2). The computation of the various distances shows that d(Fe-C) displays a quasi-linear and reversible change with temperature, while the Co-N distance varies very little (see Fig. 4 and 5). This result would confort the hypothesis of rigid [Fe(CN)₆] units. Only the position of the O(2) atoms is significantly modified and displays an hysteresis similar to that observed for the lattice constant (Fig.3).

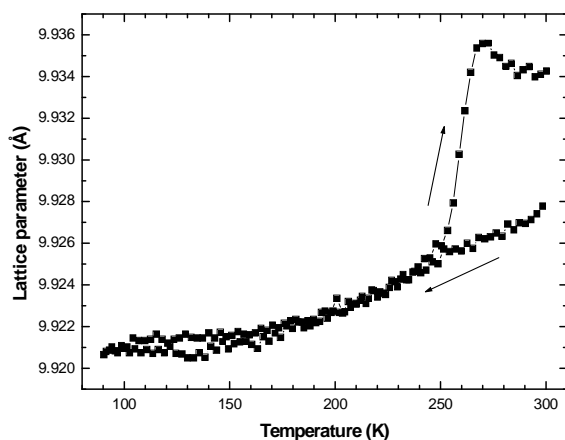


Fig. 2: Lattice parameter as a function of temperature, on cooling from 300 K to 90 K, and on warming from 90 K to 300 K.

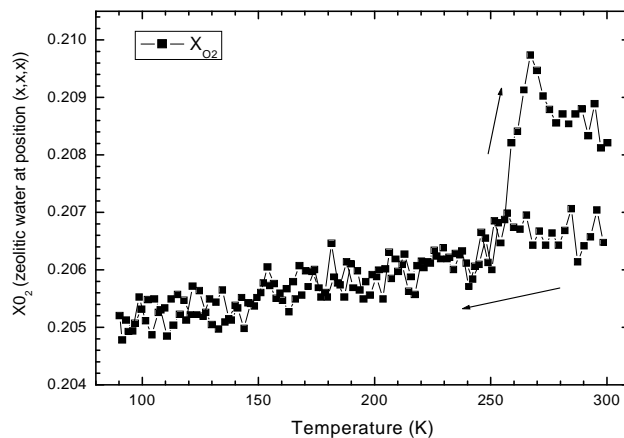


Fig. 3: Position of the zeolitic water molecules (O(2)) as a function of temperature, 90-300K.

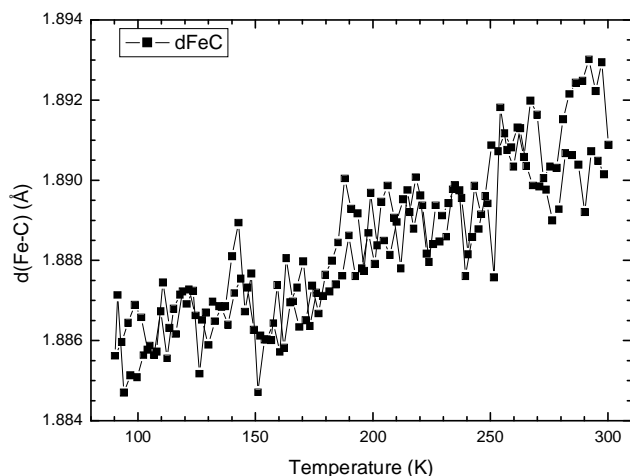


Fig. 4: Distance Fe-C as a function of temperature, 90-300K.

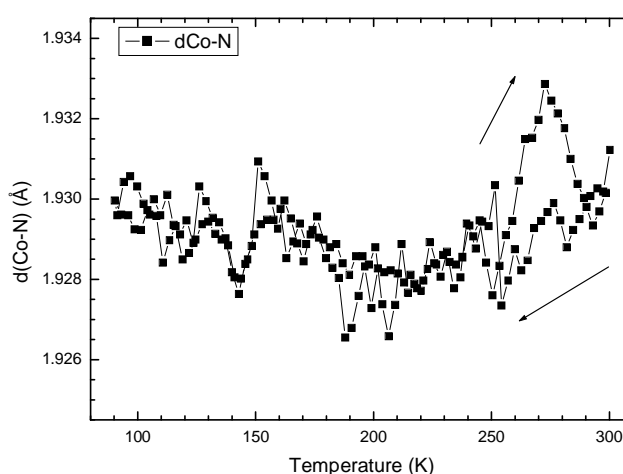


Fig. 5: Distance Co-N as a function of temperature, 90-300K.

It is important to note that the temperature displacement parameter, U of all atoms exhibits a linear and fully reversible change with temperature. The motion of the zeolitic water molecules (O(2)) would therefore be responsible for the hysteretic behaviour of the lattice expansion between 250 and 300K. This movement has been confirmed at room temperature by ¹H NMR experiments. However, because of the constraint $U(\text{Rb}) = U(\text{O}_2)$ used in the refinement procedure, the change in the position of O(2) could either reflect an off-centering of the zeolitic water molecules in the *fcc* sub-octants or else a change in their dynamics. NMR experiments at variable temperature would help to discriminate between these two hypotheses.

Rietveld analyses for the Co^{II}-Fe^{III} based phases are in progress to understand the origin of their large expansion coefficient.

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- [2] Sato *et al.*, *Science* **1996**, 272, 704.
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Paper associated to work performed during this experiment:

When local deformations trigger lattice instability: Flow diagram investigations for photoinduced and quenched metastable states in a Prussian blue analog

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Abstract: The structural aspects of the metastable states for $\text{K}_{0.32}\text{Co}[\text{Fe}(\text{CN})_6]_{0.76} \cdot 3\text{H}_2\text{O}$ have been investigated by synchrotron x-ray powder diffraction. The title compound exhibits nonequilibrium high spin (HS) states of Co-II($S = 3/2$)-Fe-III($S = 1/2$) configuration, induced by rapid cooling or photoexcitation from the low-temperature (LT) phase. By introducing a new local order parameter of tilting angle between cyanide-bridged Fe and Co-based octahedra, we discovered the existence of a precursor phenomenon triggering the collective instability during the thermal relaxation of the photoexcited (PX) state. Moreover, we introduced a methodology, based on the flow diagram studies, which allowed us to clearly distinguish the obtained metastable states through their strength of spin-lattice coupling, leading to various pathways in the phase space during the combined electroelastic relaxation process.