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Zero Thermal Expansion in a Prussian Blue Analogue

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Most materials exhibit positive thermal expansion coefficients, which lead to expanded lattices with increasing temperature due to the population of higher energy levels of anharmonic lattice vibrations. The occurrence of negative thermal expansion (NTE) (i.e., when the material contracts on heating over a certain temperature range) is relatively rare but has important technological applications.[1] Such behavior typically originates from the presence of low-energy transverse vibrations (in ice)[2] or volume-reducing cooperative rotations of rigid corner-sharing polyhedra (in β-quartz, ZrW_2O_8),[3,4] or from the occurrence of continuous electronic valence transitions (in $Sm_{1-x}Gd_xS$, $Sm_{2.75}C_{60}$).[5,6] Even rarer is the occurrence of zero thermal expansion (ZTE), whereupon the material neither expands nor contracts volumetrically over certain temperature ranges (Invar Fe−Ni alloys, YbGaGe).[7,8] Here we report the unexpected finding that isotropic nearly ZTE (i.e., negligible bulk change) in a large temperature range between 4.2 and 300 K is exhibited by a molecular-based system, namely the mixed-metal molecular polycyanide framework material (Prussian Blue analogue), $Fe[Co(CN)_6]$.

The structural properties of $Fe[Co(CN)_6]$ were studied as a function of temperature between 4.2 and 300 K by high-resolution synchrotron X-ray powder diffraction.[9] Inspection of the extended range diffraction dataset at 300 K did not reveal any reflections violating face-centered cubic (fcc) extinction rules, and the refinements were undertaken with the generic structural model (space group Fm-$3m$) of the Prussian blue family of mixed-metal polycyanides,[10] comprising a three-dimensional network of $Fe(NC)_6$ and $Co(CN)_6$ octahedra (inset in Figure 1) bridged by the cyanide ligands ($a = 10.19240(6)$ Å at 300 K). However, at the very high resolution of the present measurements, all diffraction peaks were observed to display a distinct asymmetry at lower angles. To model this, the Rietveld refinement was performed with a phenomenological two-phase model to incorporate an isostructural minority phase with a slightly expanded lattice size. The results of the final Rietveld refinement are shown in Figure 1, with the fitted parameters summarized in Table S1 (Supporting Information). The Fe−N and Co−C bond distances of the $Fe(NC)_6$ and $Co(CN)_6$ octahedra refine to 2.000(8) and 2.010(11) Å, respectively, consistent with the Fe^{III}−NC−Co^{III} assignment of the metal valence states.[11] No evidence of significant deviations from the ideal metal stoichiometry was found for either the majority or the minority phase. However, while the majority phase strictly consists of a three-dimensional network of Fe- and Co-centered octahedra bridged by the cyanide ligands with little evidence of occupation of the tetrahedral interstices of the framework structure, the minority phase incorporates a significant amount of disordered H_2O molecules in the interstitial space.
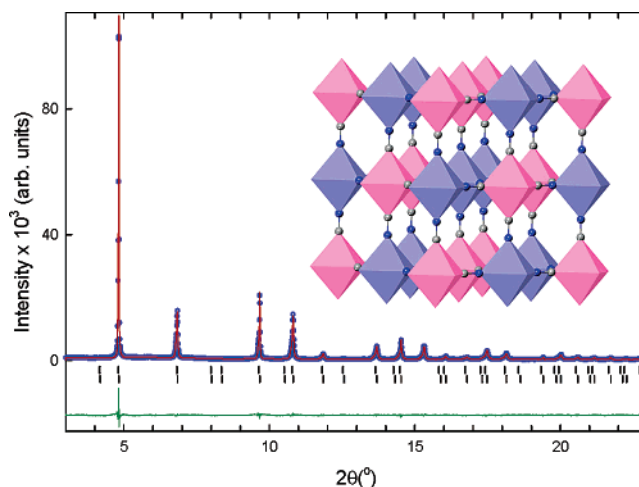
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Figure 1. Final observed (○) and calculated (—) synchrotron X-ray powder ($\lambda = 0.42966$ Å) diffraction profiles for $Fe[Co(CN)_6]$ at 300 K ($a = 10.19240(6)$ Å; space group Fm-$3m$; agreement factors of the Rietveld refinement: $R_{wp} = 5.66\%$, $R_{exp} = 1.39\%$, $R_{F2} = 4.90\%$). The lower solid line shows the difference profile, and the tic marks show the reflection positions. (Inset) Cubic framework structure of $Fe[Co(CN)_6]$. Alternating $Fe(NC)_6$ (red) and $Co(CN)_6$ (blue) octahedra are bridged by CN ligands.

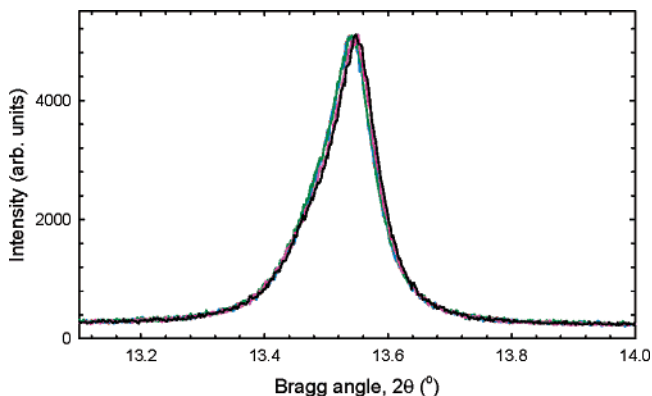**Figure 2.** Selected region of the synchrotron X-ray diffraction profiles ($\lambda = 0.85028$ Å) of $Fe[Co(CN)_6]$ showing the evolution of the cubic (220) Bragg reflection with temperature (4.2 K, blue; 150 K, green; 250 K, pink; 300 K, black line).

This is in accord with its slightly expanded lattice dimensions and accounts for the presence of H_2O revealed by the elemental analysis.[9]

A striking feature of the temperature dependence of the diffraction data is that, while the crystal structure remains strictly cubic down to 4.2 K, the angular position of the diffraction peaks shows essentially no shift with a change in temperature (Figure 2), implying an anomalous structural behavior whereby the variation in the dimensions of the material is nearly zero between 300 and 4.2 K. Extraction of reliable lattice constants was performed with
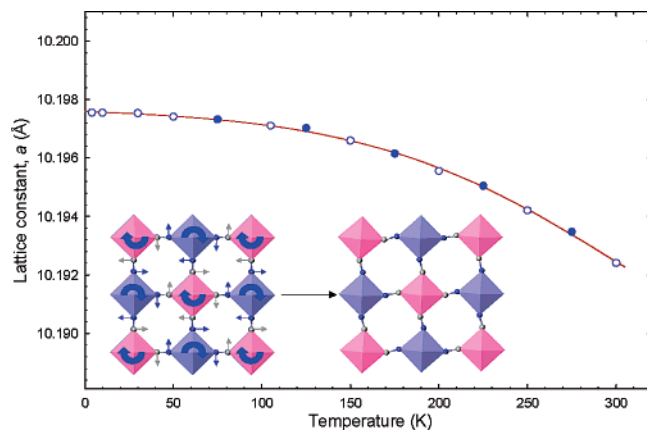
Figure 3. Temperature evolution of the cubic lattice constant of Fe[Co-(CN)$_6$] between 4.2 and 300 K. The open and filled blue symbols are data collected on cooling and heating, respectively. The estimated errors are smaller than the size of the symbols. The line is a guide to the eye. (Inset) Example of the postulated rigid unit (floppy) rotational modes supported by the polycyanide framework structure of Prussian blue analogues.

the LeBail pattern decomposition technique using the same two-phase structural model at all temperatures. The temperature evolution of the extracted cubic lattice constants is shown in Figure 3.[12] The thermal expansivity, α_a ($= d(\ln a)/dT$) remains extremely small and negative (average value $-1.47(1)$ ppm/K) throughout the temperature range, leading to an overall increase in lattice size of 0.05% on cooling from 300 to 4.2 K. This is considerably smaller than the large negative thermal expansion effect ($\alpha_a = -18$ ppm/K) reported for the open structure of Zn(CN)$_2$, which comprises interlinked disordered tetrahedral Zn(C,N)$_4$ units.[13]

The mechanism responsible for the anomalous thermal expansion behavior in Fe[Co(CN)$_6$] over a broad temperature range is, we believe, related to that documented for framework oxides and oxyfluorides such as ZrW$_2$O$_8$ ($\alpha_a = -9.1$ ppm/K) and TaO$_2$F ($\alpha_a = 0.6$ ppm/K).[1,4,14] In these flexible systems, NTE has been shown to derive from the presence of low-energy, highly anharmonic transverse thermal vibrations, which tend to contract the lattice on heating. Such vibrations have been termed rigid unit (or floppy) modes[3] and involve cooperative rotational motion of the rigid tetrahedral or octahedral building blocks of the structure. In a similar fashion, the Prussian blue architecture incorporates stiff octahedral units with strong metal–carbon and metal–nitrogen bonds joined linearly by the relatively loose cyanide bridges, which confer to the structure considerable flexibility. An example of the type of rigid unit (floppy) rotational modes which are supported by the polycyanide framework in the Prussian blue structural family and which may be responsible for the observed anomalous thermal behavior is shown in the inset of Figure 3. In the present system, the volume-reducing octahedral rotational modes appear to finely balance the usual effect of positive thermal expansion forces, thereby leading to an overall nearly zero thermal expansion. Invar has been quoted as having a thermal expansion coefficient of 0.07 ppm/K over a restricted temperature range of 278–303 K.[7]

The technological applications of ZTE and NTE materials (and their composites) principally derive from their ability to withstand heat dissipation or thermal shock without any damage. Prussian blue analogues, A$_x$M$_y$[M′(CN)$_6$]·nH$_2$O, are members of a diverse family of multifunctional molecular materials with electronically active metal sublattices studied widely for their unusual electronic and magnetic properties. In addition to having molecular-based ferromagnetic properties with Curie temperatures higher than room temperature,[15] they are ideal systems to explore switching phenomena at the molecular level, with potential applications in memory devices and magneto-optical switching.[16,17] Here we have demonstrated another important effect (namely ZTE) which adds to the palette of properties of this family of materials. The enormous flexibility in their structural and electronic properties could be exploited in the future to design other ZTE or variable NTE multifunctional materials through the suitable selection of other transition metal ions and/or interstitial units.

Supporting Information Available: Table of the extracted structural parameters of the Rietveld refinement of the synchrotron X-ray diffraction profile of Fe[Co(CN)$_6$] at 300 K and figure showing the temperature dependence of the magnetic susceptibility. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Fe[Co(CN)$_6$] was prepared as a light yellow solid by reaction of aqueous solutions of FeCl$_3$ (0.1 M) and K$_3$[Co(CN)$_6$] (0.1 M), and its stoichiometry was checked by elemental analysis (Fe:Co:H$_2$O = 1.07:1:1.4, K < 10 ppm). X-ray powder diffraction measurements with a STOE diffractometer were consistent with a single-phase material. For the synchrotron X-ray diffraction measurements, the sample was sealed in a thin-wall glass capillary 0.5 mm in diameter. With the sample inside a continuous-flow cryostat, synchrotron X-ray powder diffraction data ($\lambda = 0.85028$ Å, $2\theta = 5−35°$, step size = 0.002°) were collected at various temperatures between 300 and 4.2 K using the high-resolution powder X-ray diffraction beamline ID31 at the ESRF, Grenoble, France. Complementary higher-statistics diffraction data over a longer Q-range were also collected at 300 K using X-rays with $\lambda = 0.42966$ Å ($2\theta = 2.5−25°$, step size = 0.002°). Data analysis was performed with the GSAS suite of Rietveld analysis programs (Larsen, A. C.; von Dreele, R. B. GSAS software, LANL Report No. LAUR 86-748).
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