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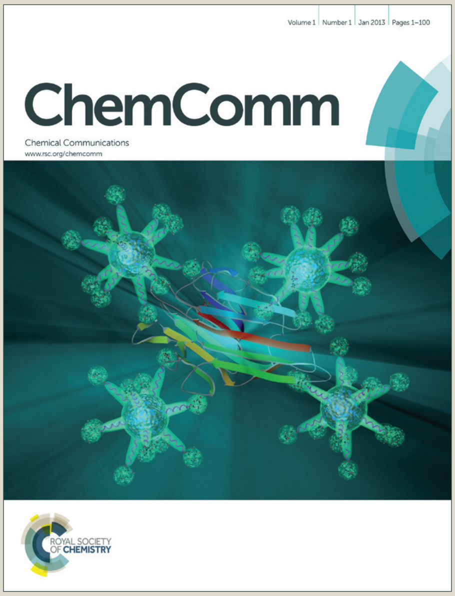

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High Pressure Induced Charge Transfer in 3*d*-4*f* Bimetallic Photomagnetic Materials

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Pressure-induced crystal color change of photo-magnetic materials $[Ln(DMF)_4(H_2O)_3(\mu\text{-}CN)M(CN)_5]\cdot H_2O$, Ln=Y, M=Fe (1), Ln=Y, M=Co (2), Ln=Nd, M=Fe (3) (DMF=N,N-dimethyl formamide) are investigated using variable pressure X-ray Absorption Near-Edge Structure (XANES) spectroscopy and X-ray diffraction. For 1 the effect is caused by ligand-to-metal charge transfer (LMCT) on the iron site.

Photo-induced magnetization is an attractive property for potential use in technological applications such as switches or memory devices. Materials of this type include spin-crossover systems, Prussian blue analogs (PBA) and *d-f* bimetallic complexes,[1] and in these systems the magnetic properties can be altered by light irradiation. The photo-magnetic properties are sometimes accompanied by structural changes,[2-4] spin-transition,[5] charge transfer,[6] or linkage isomerization.[7, 8] The change in magnetic properties typically can be induced by illumination using UV-VIS light sources at very low temperatures (usually ~10 K), but in some cases also by application of an external pressure at room temperature.[5, 9, 10] Since pressurization is able to perturb systems on the same energy scale as visible light, it offers a different route to unveiling interesting physical properties. One prominent example of this is the change of the spin state exhibited by iron(II) complexes,[5] which can be initiated either by cooling, by photo-activation at low temperatures (usually less than 50 K) or by high pressure at room temperature. Similar behavior has been observed for the compound, $CsCo(3\text{-}CNpy)_2W(CN)_8\cdot H_2O$.[10] An abrupt spin-transition with a large hysteresis loop in temperature (~50 K) has been characterized by IR[11] and X-ray absorption spectroscopy,[12] and it was explained as charge transfer through a cyanide-bridging ligand between the Co and W metal ions: $W^{V}(S=1/2)\text{–}CN\text{–}Co^{II}_{HS}$ (S=3/2) ↔ $W^{IV}(S=0)\text{–}CN\text{–}Co^{III}_{LS}$ (S=0). Varying both pressure and temperature enable a change in the magnetic properties of this compound below 0.5 GPa.[10] The hysteresis loop shifts to higher temperature and becomes narrower with increasing pressure, and finally disappears when the pressure reaches 0.5 GPa. The crystal color is observed to change from red to green near 0.4 GPa at room temperature, and this has been explained by charge transfer between the Co and W atoms.

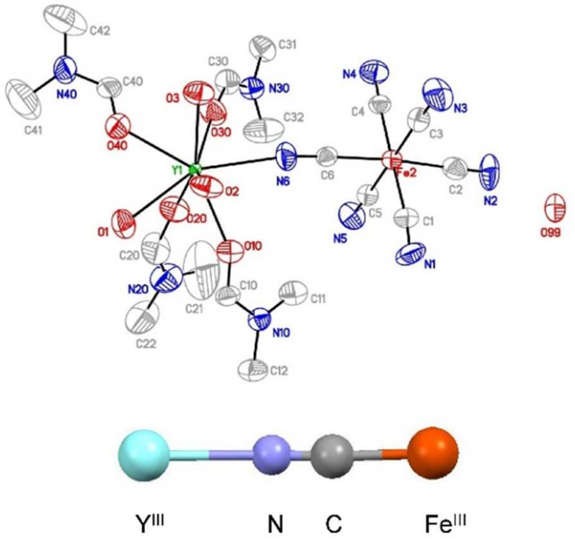

Fig. 1. Molecular structure of **1** at ambient pressure.

In the present communication, we report studies of the cyanide-bridged 3*d*-4*f* hetero-bimetallic family, $[Ln(DMF)_4(H_2O)_3(\mu\text{-}CN)M(CN)_5]\cdot H_2O$ where Ln=Y, M=Fe (1), Ln=Y, M=Co (2), Ln=Nd, M=Fe (3). $[\{Nd(DMF)_4(H_2O)_3\}(\mu\text{-}CN)\{M(CN)_5H_2O\}]$ with M = Fe or Co previously has been shownto have increased magnetization when illuminated by UV (M = Fe) or visible (M = Co) light at temperatures below 50 K.[13, 14] The light-induced increase in magnetization disappears for temperatures above 50 K. Mössbauer spectroscopy on the M = Fe compound, **3**, before and after UV illumination at 10 K indicated that the oxidation state of iron is unchanged.[13, 14] On the other hand, UV and IR spectroscopy indicate that the magnetic phenomenon may be caused by LMCT.[13] IR spectroscopy studies of the M = Co compound, **2**, indicate that the mechanism may be charge transfer and/or polarization from Nd^{3+} to Co^{3+}.[14] Svendsen *et al.* carried out photo-crystallographic studies on a wide range of similar materials,[3, 4] and these data indicate LMCT on the Fe site under irradiation with a laser at 15 K. This explanation was also supported by ab-initio calculations.[4]

The synthesis procedures of compounds **1**-**3** are identical to the literature.[3] $K_3[Fe(CN)_6]$ (415.5 mg ~1 mmol) were dissolved in 20 ml water and added into the bottom of a tube. $[Y(NO_3)_3]$ (362.9 mg ~1 mmol) or $[Nd(NO_3)_3]$ were dissolved by 10 ml DMF and then added very slowly along the side of the tube in order to keep the DMF layer on top of the water layer. Yellow crystals of **1** and **3** appeared after a few days. Compound **2** was grown by the same procedures using $K_3[Co(CN)_6]$ and $[Y(NO_3)_3]$ as precursors, and colorless crystals were obtained in a few days.

High Pressure XANES experiments were carried out at the Fe and Y K-edges in transmission mode at the GeoSoilEnviroCARS beamline ID-13-E, Advanced Photon Source, Argonne National Laboratory.[15] Compound **1** was placed in the Be gasket hole with a ruby chip using a symmetric DAC. In order to induce the color change of **1**, paratone-N oil was used as pressure transmitting medium (PTM). The synchrotron radiation beam was focused down to 10×10 μm². The radiation passed through the Be gasket and was measured by an ion chamber. The XANES signal at the Fe and Y K-edges were measured at each pressure point. One ambient pressure dataset and six high pressure datasets were taken. Except for the spectrum at ambient pressure (P0), the other data were measured using the DAC. The synchrotron radiation energy at the Y and Fe K-edges were calibrated by Y and Fe foil, respectively. Reference compounds containing iron or yttrium ions ($K_3Fe(CN)_6$, $K_4Fe(CN)_6$, Y_2O_3, $Y(NO)_3$) were also collected at ambient pressure (See Electronic Supplementary Information, ESI).

Ambient pressure single crystal X-ray diffraction data was collected on Bruker APEXII diffractometer for **1** and on Agilent SuperNOVA diffractometer equipped with micro-focus Mo X-ray source for **2** and **3**. All crystals crystallize in the monoclinic system.[16] High pressure single crystal X-ray Diffraction data were collected on all three systems on an Agilent SuperNOVA diffractometer. A Boehler-Almax plate DAC equipped with a pair of Type Ia Boehler Almax Design 600-μm-culet diamonds was used. The structures were refined with keywords DELU, SIMU, RIGU and SADI. The chosen crystals were of good crystal quality with average mosaicity 0.6–0.7. The high pressure structure data were collected at several pressure points for each compound using Paratone-N oil (now called Parabar 10312) as PTM. High pressure data of **1** was also collected at several pressure points using a 1:1 mixture of iso- and n-pentane as PTM.[17] However, only some structures of all the three compounds can be determined reliably. Further crystallographic and refinement details are given in Tables S1-S3 of ESI. The pressure was measured using the fluorescence R1 peak of Ruby chip in every experiment and the pressure values are estimated from the equation of state of ruby chips which was calibrated in advance of the experiments.[18]

The molecular structure of **1** is shown in Fig. 1. In a previous study,[19] external pressure was demonstrated to induce a reversible color change in **1** from yellow to red when the pressure was increased to around 4.5 GPa. Here we present additional HP studies on **2** and **3** showing that external pressure also can induce color change in **3** (from yellow to deep orange) when the pressure is above 3 GPa. On the other hand, the Co containing compound, **2**, remains colorless even when pressurized to 10 GPa, as shown in Fig. 2 (see also ESI). The crystallographic data of **1**-**3** are shown in the ESI (Tables S1-S3). The pressures, at which successful structure determination was possible, were only up to 0.70(5) GPa for **1**, 2.40(4) GPa for **2** and 0.34(6) GPa for **3** when using paratone-N oil as PTM. These pressures are much lower than the pressures required for LMCT. The hydrostatic mixed iso- and n-pentane was also tested for **1** but structure determination was only reliable up to 1.30(3) GPa. Numerous attempts to determine the structure above 4 GPa in the red crystal state of **1** were carried out, but they were all unsuccessful. One reason for this may be the loss of crystallinity when the crystal is pressurized. The lower degree of structural order causes visible peak broadening. A non-hydrostatic PTM[20, 21] can induce crystal strain causing peak broadening and peak shifts and lead to pressure shifts in phase transitions. The present HP structural data show that the effect of pressure on the molecular structure is different than the effect of UV light excitation. When excited by UV light the Y–O bond distances increase whereas pressure leads to a decrease. The pressure-dependence of unit cell parameters and key bond lengths are shown in the ESI.

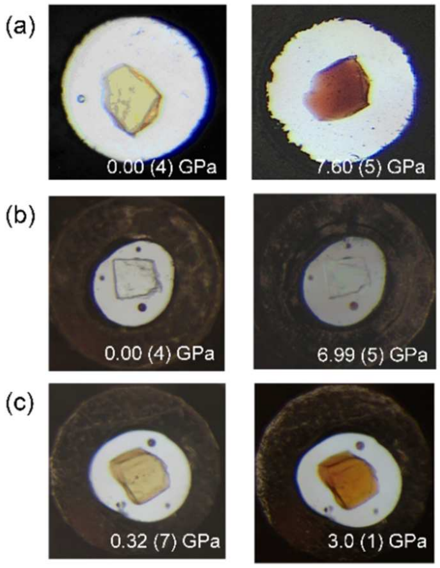

Fig. 2. Optical imaging in diamond anvil cells showing the color of compound **1** (a), **2** (b) and **3** (c) at ambient (left) and high pressures (right).

There are (at least) four possible causes for the color changes: (a) metal-ligand charge transfer (MLCT), (b) LMCT, (c) spin crossover, or (d) linkage isomerization of cyanide. The first two possibilities require changes in the number of *d*-electrons on the metal site, and in the atomic charges of the involved atoms. They may also be associated with a spin state transition. X-ray absorption near-edge structure (XANES) analysis is a very sensitive technique to characterize changes in the local atomic electronic environment such as atomic charge, spin state, *d*-orbital population, local symmetry or bond distance.[6, 22, 23-25] Hence, a variable-pressure XANES study of **1** has been performed at the K-edges of yttrium and iron in order to investigate the mechanism of the pressure-induced color changes. In **1**, the nominal atomic charges of both metal ions are +3. The electronic configuration of iron(III) is $[Ar]3d^5$ and the electronic configuration of yttrium(III) is [Kr].

The *in-situ* variable-pressure XANES data of iron(III) and yttrium(III) are shown in Fig. 3. The most significant changes on the iron site are at pressures between 3.62(5) (P2) and 4.66(7) (P3) GPa, which is concurrent with the observation of color change. Energy red-shifts are observed in the absorption edge region (E) and of the absorption white line (A) by -3.2 and -0.6 eV, respectively. The red-shift of the iron K-edge implies reduction of the iron ion. However, the onset of the energy shift of the absorption peak (A) is observed at a pressure of 2.71(4) GPa (P1), which is lower than the pressure for the onset of the color change (~4.0 GPa). It is also noted that the intensity of peak A changes dramatically as the color changes from yellow to red. The absorption peak position (A) has been used as a fingerprint of the atomic charge in a series of CoFe PBA compounds.[6, 23] However, some studies have shown that the peak position (A) can be influenced by multiple scattering resonances due to changes in the metal-ligand bond distance.[26] It is therefore hard to assign a single cause to this shift.

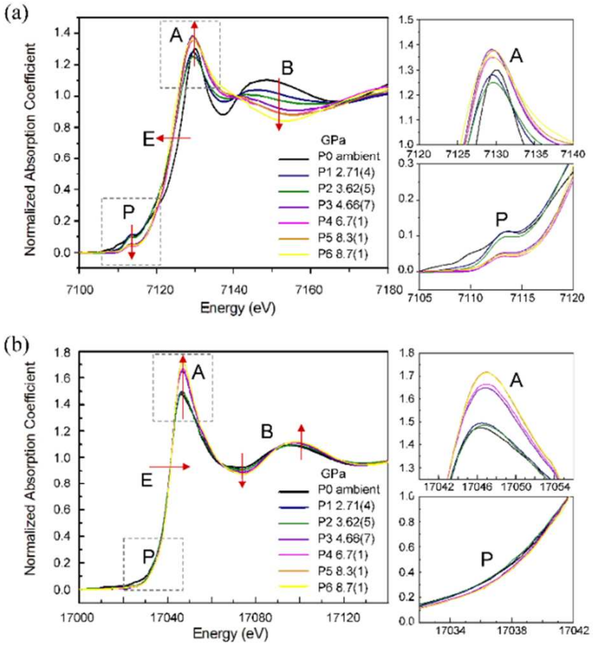

Fig. 3. Pressure-dependent XANES of **1** on (a) Fe and (b) Y sites. The pre-edge (P) and absorption white-line (A) of both sites are enlarged in the right column.

The intensity of the pre-edge peak (P) as well as its shape are closely related to the number of 3*d* electrons, atomic charge, coordination number, absorber site symmetry and geometrical distortion.[24, 25] The pre-edge features of the iron ion is due to a 1*s*→3*d* transition, a dipole forbidden but quadruple allowed transition due to *p*-*d* orbital mixing. The pre-edge absorption peak thus contains information about the *d*-orbital population of Fe. In compound **1**, the Fe site symmetry is close to a regular octahedron.

Iron(III) in **1** is expected to be low spin because of the strong field cyanide ligands, $[Fe(CN)_6]^{3-}$. Therefore, two 1*s*→3*d* (e_g and t_{2g}) transitions are expected while only one 1*s*→3*d* (e_g) transition is expected for an iron(II) in low spin state.[24] Accordingly, a symmetric peak (one peak) is expected for low spin iron(II) and an asymmetric peak or two peaks are expected for low spin iron(III). In Fig. 3a, it is hard to see the difference below and above 4 GPa, but two peaks (7110 and 7113 eV) are observed at ambient pressure. Furthermore, a red-shift of -0.5 eV is observed for the pre-edge peak. The red-shift of the spectra and the peak shape of pre-edge of iron reveal a charge transfer on the iron site, which appears to happen before 2.71 GPa.

The K-edge spectra of yttrium are shown in Fig. 3b and also show several pressure-dependent changes. Small blue-shifts are observed at the absorption edge (+0.43 eV) and at the white line absorption peak (1*s*→5*p*) (+0.65 eV). A small blue-shift is observed in the B region as well. Although the 4*d* orbital is empty, no pre-edge peak (1*s*→4*d*) is observed.[27] The intensity of peak A increases dramatically at pressures above 4.0 GPa which agrees with the observations of the iron K-edge. As mentioned before, the small energy shifts for E, A and B can be caused by multiple scattering resonances due to changes in the Y-ligand bond distance.[26] However, the mechanism of metal-to-metal charge transfer seems unlikely, because one electron has to be removed from the fully occupied 4*p* orbital, Y^{III} ($4p^6$)→Y^{IV} ($4p^5$) in order for the oxidation of yttrium(III) to happen.

The results of the iron and yttrium XANES thus imply that the charge transfer takes place at the iron site. Moreover, a continuous decrease of intensity in the multiple scattering region (B) of the iron site was observed. The intensity in the multiple scattering region (B) of $[Fe(CN)_6]^{2-}$ and $[Fe(CN)_6]^{3-}$ should not change much when electron transfer takes place, e.g. as observed in CoFe PBA materials,[23] even as the material is pressurized to 1.5 GPa.[9] The multiple scattering resonances are strongly related to the bond distance from the absorber to the atoms of the 1^{st} and 2^{nd} coordination shells and also to the spin state of the absorber. In the spin crossover compound[28] $Fe[HB(3,5\text{-}CH_3)_2pz]_3]_2$, which was pressurized up to 9 GPa, the spin state was observed to change from high spin to low spin, resulting in a blue-shift of the white line peak of 3–5 eV accompanied by a substantial change in the relative intensity in the multiple scattering region (relate spin state change to bond distance change). The decreased intensity in the multiple scattering region (B) may thus be explained by Fe–C or C–N bond distance changes due to a LMCT.

Interestingly, the pressure-induced color change is only observed when using paratone-N oil, a non-hydrostatic pressure transmitting medium (PTM). The most popular quasi-hydrostatic PTM, such as 16:3:1 methanol-ethanol-water and 4:1 methanol-ethanol mixtures, are not suitable because they dissolve the compound. A quasi-hydrostatic PTM, 1:1 mixed iso- and n-pentane (hydrostatic limit ~7.0 GPa[17, 29]), was tested but the color change of **1** was not observed in this PTM, even for pressures up to 7 GPa. Therefore, this pressure-induced color change, or LMCT, must be caused by the non-hydrostatic effects of the PTM.[21] The studied compounds are quite soft (poor crystallinity under pressure), and the non-hydrostatic PTM may cause uneven changes of intermolecular interactions and ligand field which may induce the LMCT on the iron site.

Further pressurization/depressurization tests on compound **1**-**3** have been performed. The results of these color change tests are shown in supporting information (Figure S1-S3). The color of compound **1** at ambient pressure is yellow, becomes orange within 2–4 GPa, then turns red at 4–7 GPa, before losing its color (becoming clear/colorless) when pressure is between 7 (P9) and 10 GPa. The color change becomes irreversible when **1** is pressurized above roughly 7 GPa. Similar observations are found for compound **3**. However, compound **2** remains colorless up to 10 GPa, the highest pressure studied.

Conclusions

External stimuli such as temperature, pressure and illumination can cause the magnetization of a material to change. The physical origin of such phenomena may be (a) spin crossover or spin state changes, (b) linkage isomerization, and (c) electron transfer. In the present study of **1**, clear reduction of the iron ion and significant multiple scattering changes at the Fe K-edge were observed, and oxidation at the Y site was excluded. Linkage isomerization has been observed in $K_{0.4}Fe_4[Cr(CN)_6]_{2.8}\cdot16H_2O$[8] but the atomic charge does not change in this compound. Therefore, linkage isomerism can be excluded as well. Accordingly, the mechanism of color change under pressure of **1** and **3** is concluded to originate from a pressure-induced LMCT at the iron site. Although pressure does not induce a color change in **2** this does not exclude that external pressure affects the bond distance or ligand field in compound **2**, and LMCT in **2** may take place in the non-visible range.

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Notes and references

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[c] ChemMatCARS beam line, The University of Chicago, Advanced Photon Source, Argonne, IL, 60439 (USA).

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Electronic Supplementary Information (ESI) available: Crystallographic tables, additional crystal photos, unit cell parameters and bond lengths, XANES standard data. See DOI:10.1039/c000000x/

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