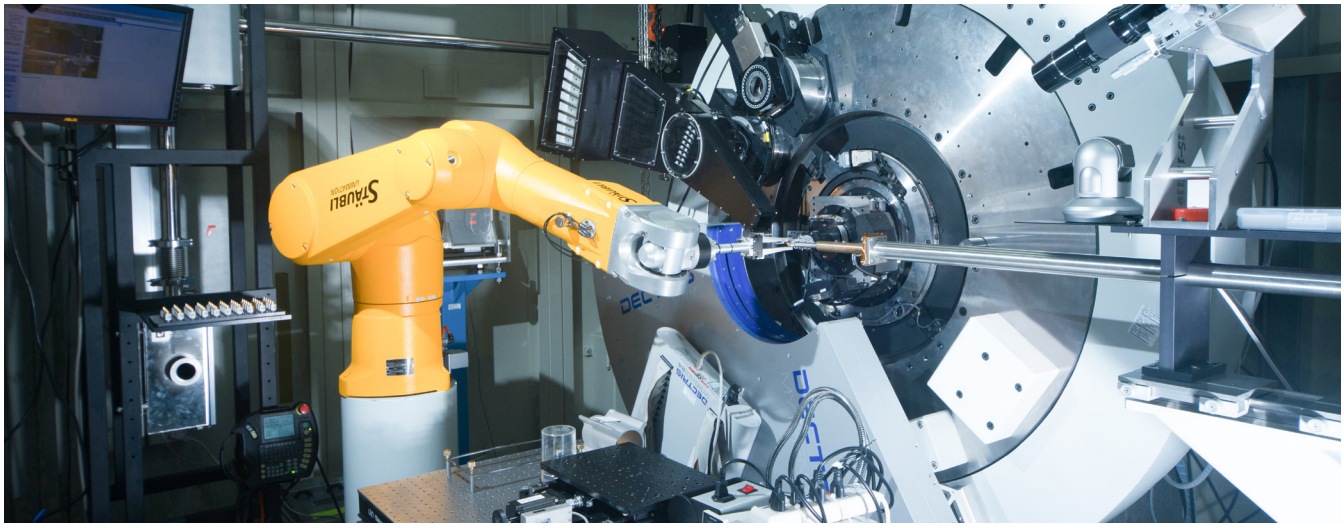
References

1. I. Katsounaros, S. Cherevko, A. R. Zeradjanin, and K. J. J. Mayrhofer, Angew. Chem. Int. Ed. **53**, 102 (2014).
2. S. C. Lin, C. S. Hsu, S. Y. Chiu, T. Y. Liao, and H. M. Chen, J. Am. Chem. Soc. **139**, 2224 (2017).



TPS 09A: High-resolution PXRD by multi-crystal analyzer detector.

Photo-Enhanced Ferromagnetism in K–Ni–Cr Prussian Blue Analogues

Researchers have succeeded to discover a large enhancement of the Ni and Cr ferromagnetic moments under UV light irradiation on K–Ni–Cr Prussian blue analogues.

Prussian blue analogues (PBAs) demonstrate many fascinating magnetic behaviors. In this study Wen-Hsien Li (National Central University) and his co-workers examine PBAs, with the general chemical formula of $A_xM[M'(CN)_6]_y{\cdot}nH_2O$ (A–M–M'), where M and M' indicate divalent or trivalent transition metal ions and A indicates monovalent alkali ions that are accommodated in the voids enclosed by the MN_6 and $M'C_6$ octahedra. It has been shown that a significant reduction in magnetization occurs as a consequence of light irradiation in layered Rb–Ni–Cr/Rb–Co–Fe/Rb–Ni–Cr heterostructures comprised of a photo-sensitive Rb–Co–Fe film sandwiched between two pressure-sensitive Rb–Ni–Cr films.[1,2] No photo-induced magnetism has been identified in isolated K–Ni–Cr, but light irradiation leads to a noticeable reduction (~8%) of the magnetization when this material is coated on a Rb–Co–Fe nano-cube.[3] This work aims to develop K–Ni–Cr PBAs, where light irradiation will enhance the magnetic strength of the compound. Li's group demonstrates that K–Ni–Cr can become photoactive in the high K^+-containing compound.

They detected significant increases of the Ni as well as Cr magnetic moments upon UV light irradiation in a 55 nm thick high K^+-containing K–Ni–Cr shell coated on a 240 nm Rb–Co–Fe cube. Surprisingly, the photo-enhancement of the magnetic moments for the $K_{0.98}$–Ni–$Cr_{0.70}$ phase was as large as that for the $Rb_{0.76}$–Co–$Fe_{0.74}$ phase.

The neutron diffraction measurements were conducted at the Bragg Institute, ANSTO, Australia, using the high-intensity powder diffractometer Wombat, employing an incident wavelength of $\lambda = 2.41$ Å defined by Ge (113) crystals. For these measurements, ~1 g of the sample was loosely loaded into a cylindrical aluminum holder (9 mm in diameter and 30 mm long) with a shiny inner surface. The device was equipped with a quartz tube (5 mm in diameter) located along the central axis of the holder to facilitate light irradiation. The PBA powder was loosely packed 2 mm thick in the quartz tube allowing 35% light transmission, which, combined with the shiny inner face of the Al holder that acted a light reflector, allowed the light to

bounce back and forth inside the holder for uniform illumination of the PBA sample.

X-ray diffraction measurements were first used to construct the backbone of the crystalline structure. Neutron diffraction was then used to identify the atomic positions and the stoichiometric amounts of the transition metal ions and H_2O molecules within the compound. The diffraction patterns were analyzed using the Rietveld method,[4] employing the GSAS program.[5] The observed and calculated X-ray and neutron diffraction patterns at 80 K are shown in **Fig. 1(a)**. The chemical compositions obtained for the two phases after final refinement were $Rb_{0.76}Co[Fe(CN)_6]_{0.74}[(H_2O)_6]_{0.26}\cdot 0.56H_2O$ with a cubic lattice constant of a = 9.943(2) Å and $K_{0.98}Ni[Cr(CN)_6]_{0.70}[(H_2O)_6]_{0.30}\cdot 0.11H_2O$ with a = 10.337(4) Å at 80 K. The proposed crystalline structure of the Rb–Co–Fe in the core and the K–Ni–Cr shell is shown in **Fig. 1(b)**.

Two magnetic transitions, labeled T_{m1} and T_{m2}, are clearly revealed in the isofield dc magnetization M(T) and ac magnetic susceptibility χ'(T) curves (**Fig. 2(a)**).

There is a large increase in the magnetization upon cooling below T_{m1} = 72 K, which is linked to the magnetic ordering of the Ni and Cr ions in the K–Ni–Cr phase on the shell. At 30 K, the Ni spins together with the Cr spins developed a ferromagnetic arrangement with magnetic moments of $\langle\mu_Z\rangle_{Ni}$ = 0.93(9) μ_B and $\langle\mu_Z\rangle_{Cr}$ = 1.50(9) μ_B pointing along the [111] crystallographic direction at 30 K (**Fig. 2(b)**). This magnetic diffraction pattern is indicative of the additional intensity that developed upon cooling from 80 to 30 K. It is analyzed employing the GSAS program, assuming the same spatial symmetry of the crystalline structure for the magnetic structure.

It is remarkable to see that the magnetic moments of both the K–Ni–Cr and Rb–Co–Fe phases increase significantly upon continuous irradiation with 365 nm UV light at 2.5 mW during the measurement, as revealed by the large increases of the neutron magnetic intensities associated with both phases (**Fig. 3**). Surprisingly, the magnetic phase of K–Ni–Cr is more sensitive to light irradiation than that of Rb–Co–Fe, as reflected by the increase in the representative (200)

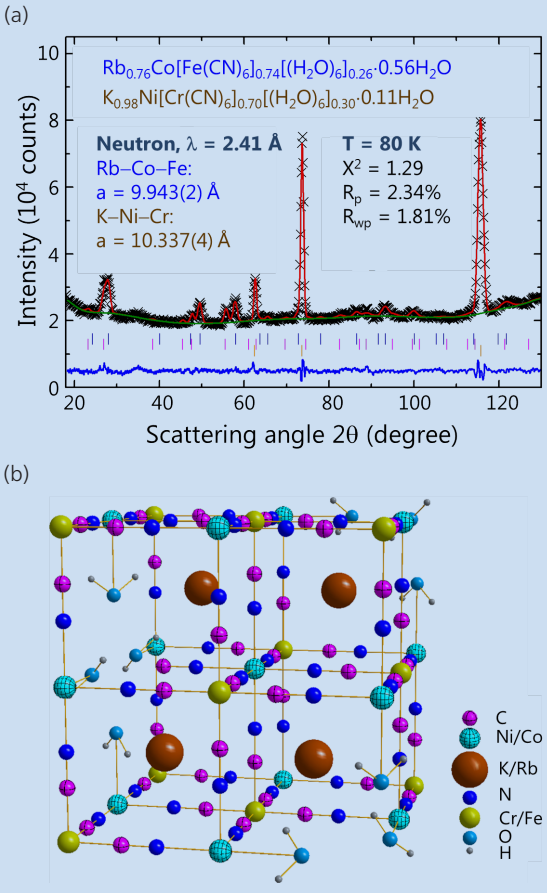


Fig. 1: (a) Observed (crosses) and fitted (solid lines) neutron powder diffraction patterns taken at 80 K. (b) Schematic drawing of the proposed crystalline structure of the Rb–C–Fe in the core and the K–Ni–Cr shell. [Reproduced from Ref. 1]

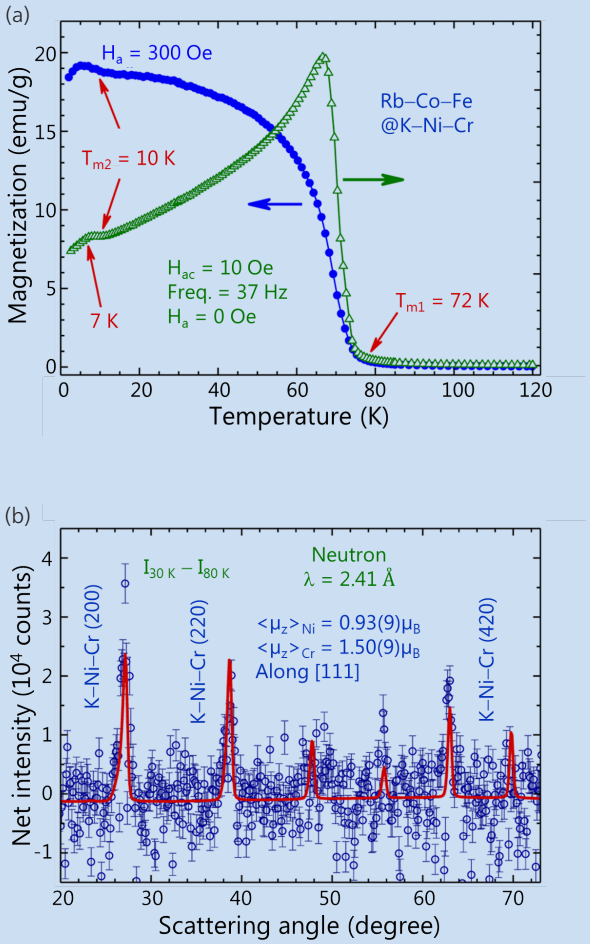


Fig. 2: (a) Temperature dependence of the magnetization M and the in-phase component χ' of the ac magnetic susceptibility of the PBA assembly. (b) Magnetic intensities observed at 30 K, where the neutron diffraction intensities observed at 80 K. [Reproduced from Ref. 1]

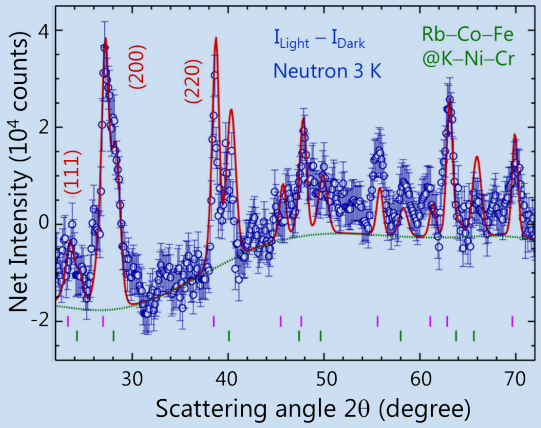


Fig. 3: Difference intensities between the neutron diffraction patterns taken with and without UV light irradiation at 3 K. [Reproduced from Ref. 1]

magnetic intensity of the K–Ni–Cr phase which is 1.7 times larger than that of the Rb–Co–Fe phase. It is the magnitude of the magnetic moment that develops upon light irradiation which gives rise to the increase in the magnetic intensities. The magnetic moments of the Ni and Cr ions increase by 0.23 μ_B and 0.32 μ_B, respectively, upon irradiation with 365 nm UV light at 2.5 mW. Correspondingly, magnetic moments of 0.26(1) μ_B for the Co ions and 0.19(2) μ_B for the Fe ions are found to develop. Photo-irradiation drives the Cr ions from in the S = 1 to S = 3/2 magnetic state and the Ni ions from in the S = 1/2 to S = 1. The increases in the magnetic moments of Cr and Ni ions corresponds to 32% of the Cr ions being photo-active, with only 0.23/0.32 = 72% of the electron transfer reaching the Ni ions.

In summary, a large enhancement of the Ni and Cr ferromagnetic moments under UV light irradiation was detected in 55 nm thick $K_{0.98}Ni[Cr(CN)_6]_{0.70}[(H_2O)_6]_{0.30}\cdot 0.11H_2O$ Prussian blue analogues. (Reported by Chi-Huang Lee, National Central University)

This report features the work of Wen-Hsien Li and his co-workers published in ACS Omega ***2****, 4227 (2017).*

ANSTO-TG1 WOMBAT – High-intensity Powder Diffractometer

- ENS
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References

1. C.-H. Lee, M.-Y. Wang, E. Batsaikhan, C.-M. Wu, C.-W. Wang, and W.-H. Li, ACS Omega **2**, 4227 (2017).
2. D. M. Pajerowski, M. J. Andrus, J. E. Gardner, E. S. Knowles, M. W. Meisel, and D. R. Talham, J. Am. Chem. Soc. **132**, 4058 (2010).
3. D. M. Pajerowski, J. E. Gardner, F. A. Frye, M. J. Andrus, M. F. Dumont, E. S. Knowles, M. W. Meisel, and D. R. Talham, Chem. Mater. **23**, 3045 (2011).
4 Matthieu F. Dumont, E. S. Knowles, A. Guiet, D. M. Pajerowski, A. Gomez, S. W. Kycia, M. W. Meisel, and D. R. Talham, Inorg. Chem. **50**, 4295 (2011).
5. H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).
6. A. C. Larson, and R. B. Von Dreele, LANL Report **LA-UR-86-748**, (1990).