

Electronic states and local structures of photomagnetic CuMo cyanides

Xiao-Dong Ma¹, Toshihiko Yokoyama*^{1,2},

Toshiya Hozumi³, Kazuhito Hashimoto³, Shin-ichi Ohkoshi³

¹Dept. Structural Molecular Science, Grad. Univ. of Adv. Studies (Sokendai), Okazaki 444-8585, Japan

²Institute for Molecular Sciences, Myodaiji-cho, Okazaki 444-8585, Japan

³Dept. Chem., Grad. School Sci., Nagoya University, Chikusa-ku, Nagoya 464-8602, Japan

Introduction

Prussian-blue analogues often exhibit noble magnetic properties such as photoinduced magnetization and high Curie temperature. In this work, we have investigated the local structures and the electronic states mainly of the photoinduced phases of these two CuMo cyanides of $\text{Cu}_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$ (**1**) [1] and $\text{Cs}_{0.5}\text{Cu}_{1.75}\text{Mo}(\text{CN})_8 \cdot 1.5\text{H}_2\text{O}$ (**2**) [2] by means of XAFS. Usually, the photoinduced phase at low temperature (LT) is considered to be structurally identical to that of the corresponding high-temperature phase. The photoinduced phase is however an essentially new state for these compounds because the CuMo cyanides are in the LT phase even at room temperature and are likely to decompose with the temperature rise.

Experimental

The XAFS measurements were performed at BL10B (transmission) and 12C (fluorescence). Fluorescence XAFS spectra were taken for Cu and Mo *K* edges of (**1**) and (**2**) at 30 K. In order to measure the reliable spectra of the photoinduced phase, fluorescence detection was essential because the penetration depth of the visible light is much smaller than that of the x rays.

Results and discussion

Figure 1 shows the Cu *K*-edge XANES spectra of samples (**1**) and (**2**) before and after photoirradiation, together with the reference spectra of Cu_2O and CuO . As illustrated in the spectra of Cu_2O and CuO , monovalent Cu compounds show a typical resonance peak at ~8984 eV, while divalent Cu gives a weak $1s \rightarrow 3d$ dipole-forbidden absorption at ~8981 eV and a shoulder at ~8990 eV. From Fig. 1, one can immediately conclude that the Cu atoms in samples (**1**) and (**2**) are divalent before photoirradiation, and monovalent Cu appears after photoirradiation.

Figure 2 shows the Mo and Cu *K*-edge EXAFS $k^3\chi(k)$ and their Fourier transforms of sample (**2**). Overall, one can find that the features of the initial LT and photoinduced phases are almost identical. The interatomic distances are almost the same between the initial and the photoinduced phases. Differences between the low-temperature and the photoinduced phases can however be detected in the amplitude in the EXAFS oscillation. From the curve-fitting results, the coordination numbers of the Mo-N, Mo-Cu, and Cu-Mo shells are found to be reduced, while those of the Mo-C, Cu-N, and Cu-C shells as well as the first-nearest

neighbor Mo-C and Cu-N shells are kept constant. The latter implies enhancement of the static Debye-Waller factors instead of the reduction of the coordination number. The reduction of the coordination numbers for the Mo-N, Mo-Cu, and Cu-Mo shells may be ascribed not to the bond breaking but to the bond bending. One can qualitatively conclude that due to the photoirradiation the Mo-CN bond is bent, while Cu-NC is kept rather collinear.

References

- [1] S. Ohkoshi et al. *Synthetic Metals*, 122, 523 (2001).
 [2] T. Hozumi et al. *J. Am. Chem. Soc.* 127, 3864 (2005).
 * yokoyama@ims.ac.jp

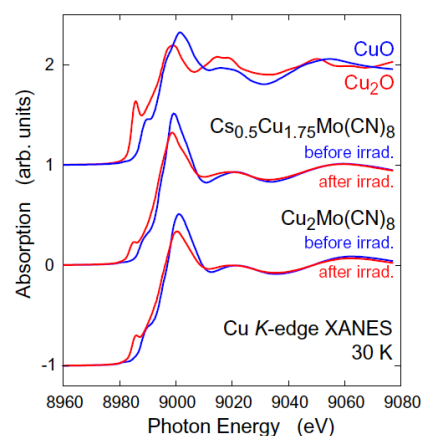


Fig. 1: Cu *K*-edge XANES spectra of samples (**1**) (middle) and (**2**) (bottom), together with Cu_2O and CuO .

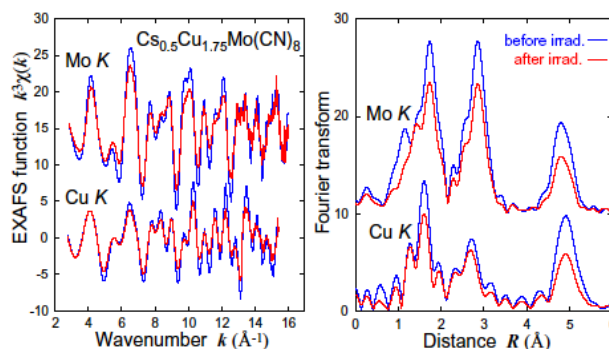


Fig. 2: Mo and Cu *K*-edge EXAFS $k^3\chi(k)$ and their Fourier transforms of sample (**2**) before and after laser irradiation.