Development of light-modulated XAFS spectroscopy (2)

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Structural and electronic changes upon photo-excitation have been studied by various methods. In the case of materials with no long-range ordering, XAFS is one of the most useful tools to obtain direct information on local structures and electronic properties. However, it is quite difficult to observe dynamic behaviours by the conventional XAFS method. The purpose of this study is to apply the light-modulation method, which is widely used for Raman, IR, and UV-vis spectroscopies, to x-ray absorption spectroscopy. Previously, we reported the detection of light-modulated XANES and EXAFS spectra using a Xe-arc lamp as the visible light source [1]. However, the possibility of heating effect upon light irradiation should be eliminated. Thus, we performed similar experiments using a low-power laser.

All measurements were carried out in the fluorescence mode at BL-9A and 12C with double-crystal Si(111) monochromators detuned by ~40%. The incident x-rays were detected by an ionization chamber filled with N_2 and fluorescent x-rays by a Lytle detector filled with Ar. Experimental setup is shown in our previous report. A focused Xe lamp (supplied power of 300 W, 350-700 nm) and a Nd-YAG laser (50 mW, 532 nm, spot diameter of 3~4 mm at the sample position) were used as the light sources. To avoid noises caused by the signal fluctuations after moving the monochromator, the signal counter was controlled by an external timer circuit and waited before counting for ~15 seconds. To avoid vibration, the Lytle detector was set on silicone rubber insulators. Acquisition time was 10 or 20 seconds for each data point. A light-induced spin-crossover complex $Fe(pic)_3Cl_2 \cdot C_2H_5OH$ (pic=2-aminomethylpyridine) (**1**) powders were dispersed on Scotch tapes and used as the sample. All spectra were normalized to the edge jumps, and outputs of the lock-in amplifier were corrected to the original order.

Figure 1 shows light-modulated Fe *K*-edge XANES difference spectra of **1** at various temperatures. Under laser irradiation the difference is largest at 49 K and smaller at higher temperatures (Fig.1(a)). It is natural because the lifetime of the trapped state decays upon warming. However, under Xe-lamp irradiation, the order depends on light intensity. At BL-9A, the difference is smaller at higher temperatures (Fig.1(b)), while it is larger at BL-12C (Fig.1(c)), where geometrical limitation does not allow to collect enough light from the light source. The light-induced spin-crossover transition of **1** shows a threshold behavior upon light intensity [2]. This could be the origin of the strange temperature dependence seen in Fig.1(c): under weak light irradiation **1** cannot be excited by light effectively and the contribution of local heating increases, while using intense light over the threshold light excitation becomes the main contributor. A low-power laser is ideal as the light source because such a problem will not arise.

[1] K. Okamoto et al., PF Activity Report 18, 293 (2001).
[2] Y. Ogawa et al., Phys. Rev. Lett. 84 (2000) 3181.

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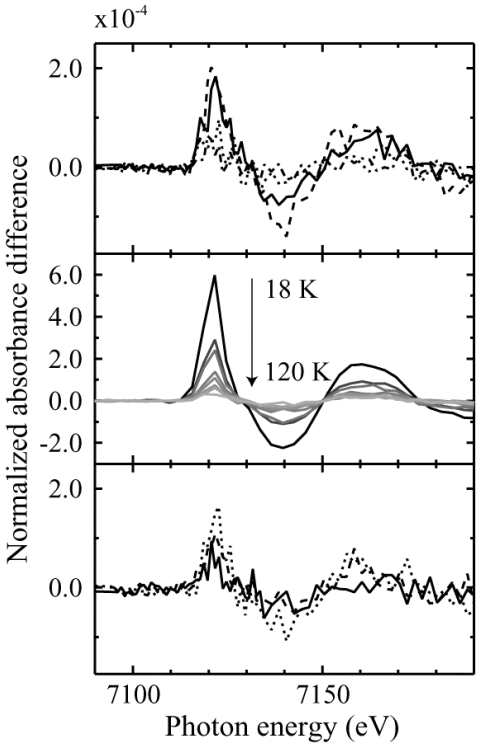

Fig. 1. Light-modulated Fe *K*-edge XANES difference spectra (a) under Nd-YAG laser irradiation at 30 K (solid line), 49 K (dashed line), 67 K (dotted line), and 96 K (dash-dotted line), (b) under intense Xe-lamp irradiation on warming process from 18 K to 120 K at BL-9A, and (c) under weak Xe-lamp irradiation at 29 K (solid line), 41 K (dashed line), and 61 K (dotted line) measured at BL-12C. The modulation frequency was 10 Hz for (a) and (c), and 5 Hz for (b). The differences on S/N ratios are mainly due to the difference of the amplifier risetime.