Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Luminescence 119–120 (2006) 361–369
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Synchrotron radiation study of photo-induced spin-crossover transitions: Microscopic origin of nonlinear phase transition

H. Oyanagi[a,*], T. Tayagaki[b,1], K. Tanaka[b]

[a]National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
[b]Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

Available online 9 February 2006

Abstract

In situ X-ray absorption spectroscopy (XAS) using synchrotron radiation was used to probe the local structure of photo-induced phase transition of Fe (II) spin-crossover complex. We demonstrate that the local structure of spin-converted metastable phase can be probed by XAS using a novel pixel array detector using less than 1 mg of specimen. We find that the arrangement of nearest neighbors, i.e., the FeN_6 cluster does not change its symmetry upon the diamagnetic ($S = 0$) $\leftrightarrow$paramagnetic ($S = 2$) transformation under laser light (532 nm) excitation below 50 K. The intermediate-range structure (next-nearest neighbor correlation) shows that ligand molecules in the photo-induced high spin phase is distorted. The results suggest that the essential difference between the photo-induced and thermally induced high spin phases is the absence of intermediate-range order in the former. We propose that quenched disorder (inhomogeneity) in the intermediate-range structure is the microscopic origin of nonlinear nature of photo-induced phase transition (crippled cooperativity). It is demonstrated that in situ XAS using synchrotron radiation and state-of-the-art X-ray detector can provide detailed information on the local structure of metastable states trapped at low temperature.

PACS: 61.10.Lx; 64.60.My; 78.90.+t

Keywords: Synchrotron radiation; X-ray absorption spectroscopy; Local structure; Photo-induced spin-crossover transition

1. Introduction

Recently, photo-induced phase transition attracts much attention as a novel means of nanotechnology where multistability of a ground state gives rise to a variety of nanoscale modifications of local structure [1]. Photo-induced phase transitions such

*Corresponding author. Tel.: +81 298 61 5394; fax: +81 298 61 5085.
E-mail address: h.oyanagi@aist.go.jp (H. Oyanagi).
[1]Present address: Department of Applied Physics, University of Tokyo.

0022-2313/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2006.01.017

as ionic-neutral phase transitions in organic charge transfer (CT) crystals [2], magnetic phase transitions in spin-crossover complexes [3,4] and photo-induced charge, spin and orbital order/disorder transitions in perovskite manganites [5,6] form rich class of multistable ground state materials where photo-stimulation eventually results in a global phase transition with pronounced changes in macroscopic physical properties. Photo excitation induces a cooperative spin-crossover phase transition which shows a clear distinction with that of conventional thermally induced phase transitions [7,8]. [Fe (II)(2-pic)$_3$]Cl$_2$EtOH (2-pic = 2-amino-methyl-pyridine) (hereafter abbreviated as Fe-*pic*) is a typical spin-crossover complex which shows a thermally induced phase transition from low-spin (^{1}A$_1$, $S = 0$) to high spin (^{5}T$_2$, $S = 2$) state. Photo-induced magnetic transitions show non-linear characteristics such as threshold light intensity, incubation period and phase separation [9]. Photo-induced phase transitions are often discussed in terms of trapping of metastable spin state, i.e., light-induced excited spin state trapping (LIESST) [10]. In this viewpoint, the photo-induced phase is essentially the high-temperature phase quenched to low temperature having the same structure except the magnitude of thermal disorder. It was pointed out that a structural relaxation in an excited state may proceed with symmetric and non-symmetric normal coordinates and therefore symmetry breaking could happen. Even if the excited state is trapped by a metastable phase, it may further relax to another "false" ground state which may not be the same with the original one. Tayagaki et al., recently investigated the symmetry of photo-induced phase by Raman spectroscopy and observed broken symmetry in the photo-induced phase which is absent in the thermally induced phase [11]. Photo-induced phase transitions of materials with multistable ground states are expected to give novel phases [12,13]. The information on the local structure is essential to understand the nature of photo-induced high spin phases, for which X-ray absorption spectroscopy (XAS) is useful (Fig. 1). Here, we report the in situ XAS study of spin-crossover complex under light irradiation taking Fe-*pic* as a model system.

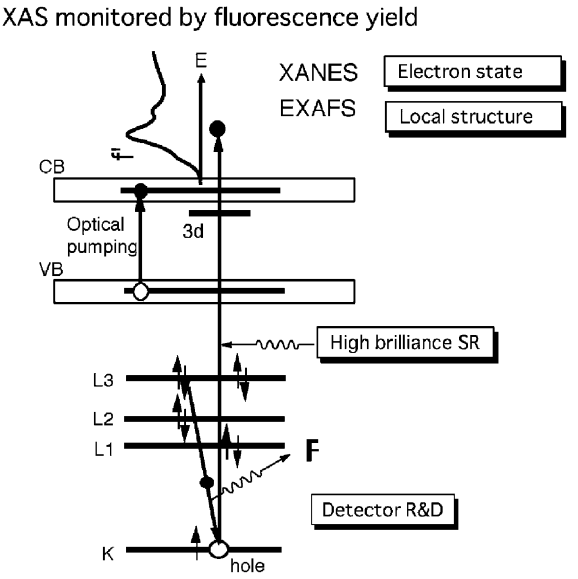

Fig. 1. Schematic diagram of XAS monitored by fluorescence yield for probing local structures under photo excitation. High brilliance X-ray from synchrotron radiation and high efficiency X-ray detector are essential to record fluorescence detected XAS from photo-excited specimen.

2. Experimental methods

In situ synchrotron radiation (SR) techniques provide real-time observation of atomic arrangements with high spatial sensitivity and precision. A major advantage of SR is that it covers a wide range of wavelengths continuously from infrared to gamma rays. This feature is attractive for spectroscopy since a wealth of detailed information on the electronic and structural properties of materials can be obtained by optimizing the wavelength of the radiation. Since the establishment of "first generation" facilities in the early 1970s, the X-ray emittance from synchrotron storage rings, where electrons traveling at almost relativistic speeds are constrained by magnetic fields to follow curved trajectories, has shown dramatic improvements. For "third generation" SR facilities such as ESRF, APS and SPring-8 that have ultralow extraneous emittance (<10 nmrad), insertion devices can produce coherent brilliant beams by undulating electrons in a periodic magnetic field. Such a device provides a quasi-monochromatic X-ray beam with