

Pump and probe X-ray absorption fine structure using high-brilliance photon sources

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Pump and probe X-ray absorption fine structure (XAFS) is used as a local probe of excited atoms, which can provide direct information on lattice distortion, relaxation and atomic rearrangements associated with electronic excitations. *In situ* XAFS experiments during optical excitation are reported. Utilizing a grazing-incidence fluorescence excitation, which minimizes the mismatch between the probing depths of X-ray excitation and optical pumping, it is found that the dominant photoinduced defect state in amorphous selenium at low temperature is a pair of threefold neutral C_3^0 states: $2C_2^* \rightarrow (C_3^0 - C_3^0)$, where C_2^* denotes the twofold excited lone-pair state. The results indicate that optical pumping of chalcogen atoms at low temperature leads to locally over-coordinated defect pairs similar to those in the liquid state. The origin of reversible photostructural changes, such as photodarkening or photoinduced fluidity, is attributed to the structural disorder caused by the formation and annihilation of dynamical interchain bonds during optical melting.

Keywords: pump and probe; XAFS; photostructural changes; optical melting; amorphous Se; X-ray undulators.

1. Introduction

Pump and probe experiments in X-ray absorption fine structure (XAFS) allow one to study the local and dynamical atomic arrangements around optically excited atoms within $\sim 8 \text{ \AA}$ (Kolobov *et al.*, 1996). Most of the previous optical pumping experiments have been aimed at the photodissociation of ligands in haemeproteins; structural studies on CO-binding in myoglobin have been reported (Chance *et al.*, 1983; Powers *et al.*, 1987; Mills *et al.*, 1984; Bianconi *et al.*, 1994). Here we discuss the application of pump and probe XAFS to solid-state physics as a promising means of snapshot measurement of local lattice distortion, relaxation and, in some cases, bond alternation as a result of optical excitation of valence electrons. The mismatch between the optical pumping and X-ray excitation can be reconciled by introducing a surface-sensitive fluorescence excitation. Using a grazing-incidence geometry, a high-brilliance photon source and a densely packed solid-state detector array, one can study the local structure of optically excited states in a thin film.

Upon irradiation with photons having an energy larger than a bandgap, chalcogenide glasses show photostructural changes such as an optical absorption-edge shift or photodarkening (Tanaka, 1975). The origin of the photoinduced phenomena has been

discussed in relation to various defect coordinations but direct experimental information has been missing since most experiments were performed *ex situ*, although photoinduced metastable states are easily transformed to the ground states above the glass transition temperature, T_g . In this paper, we demonstrate that *in situ* XAFS can provide the local structure of excited states. Efforts have been taken to achieve a high precision in structural parameters, in particular the coordination number, since over-coordinated or under-coordinated defect states are observed as a small change of a site-averaged coordination number. High signal statistics are obtained by a combination of a multipole wiggler and a Ge detector array (Oyanagi *et al.*, 1995). Taking the non-irradiated initial state as a reference, a relative change in coordination upon irradiation as small as a few percent has been successfully detected and analyzed. The *in situ* EXAFS measurements on amorphous (*a*-) Se at low temperature revealed the light-induced reversible change in the first coordination sphere (Kolobov *et al.*, 1996).

2. Pump and probe XAFS

Fig. 1 shows the principle of pump and probe XAFS experiments. In this experiment, a 0.1 \mu m -thick thin film was used for an efficient optical excitation while a grazing-incidence fluorescence excitation was used for minimizing the mismatch in optical and X-ray excitations. An *a*-Se sample was mounted on an aluminium holder of a cryostat equipped with X-ray and optical windows, *i.e.* a Kapton window for introducing the incident X-ray beam and observing the fluorescent X-rays and a Mylar window for *in situ* light irradiation. A closed-cycle He refrigerator with a cooling power of $\sim 9 \text{ W}$ at 20 K was used. In the initial experiment, a 500 W Xe lamp with an IR-cut filter was used as an inducing light source, the light intensity on the surface of the sample being about 250 mW cm^{-2} . The experimental set-up for irradiation at low temperature and a grazing-incidence fluorescence excitation is shown schematically in Fig. 2. After cooling the sample to 30 K , the Se *K*-edge absorption spectrum for the starting film was measured. Our *a*-Se samples were thin films (0.1 \mu m thick) prepared by thermal evaporation of bulk selenium onto silica glass substrates kept at room temperature in a vacuum of $\sim 10^{-5}$ torr.

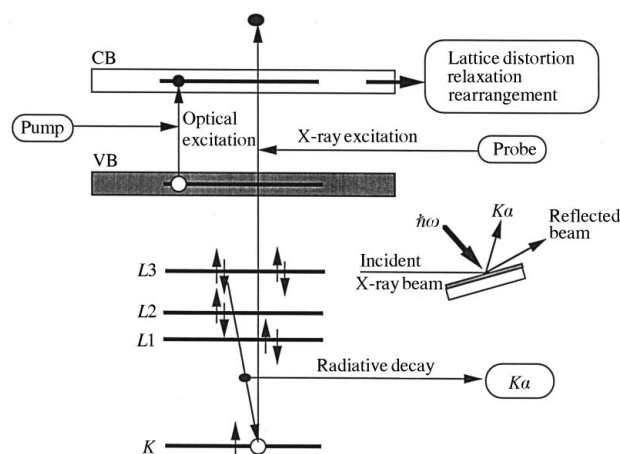


Figure 1
Principle of pump and probe X-ray absorption fine structure (XAFS). VB: valence band; CB: conduction band.

The EXAFS measurements were performed in a fluorescence mode at station BL13B at the Photon Factory using a 27-pole wiggler. A directly water-cooled Si(111) double-crystal monochromator provided an intense X-ray beam with a photon flux more than a magnitude higher than normal bending-magnet radiation with an energy resolution of ~ 2 eV at 9 keV. An array of 19 Ge detectors (Oyanagi *et al.*, 1997) was used to record the fluorescence signal. The packing ratio of the detector array is 57% and a total count rate of 3.8 MHz is obtained with an energy resolution of ~ 240 eV (5.9 keV) using a shaping time of 0.5 μ s. The sample was irradiated in the cryostat for several hours and the data for the irradiated film under light irradiation were measured. Immediately after this measurement, the lamp was switched off and the post-irradiation data followed. In order to check reversibility, the irradiated sample was heated to 300 K and kept at this temperature for 2 h to remove photodarkening (Averyanov *et al.*, 1980), and then cooled to 30 K, at which the measurement was repeated.

3. Photoinduced local structure change

The EXAFS oscillations for *a*-Se and *c*-Se extracted from the Se K_{α} fluorescence spectra taken at 30 K were analyzed. The first-shell EXAFS oscillations $k\chi(k)$ extending from 4.5 to 15 \AA^{-1} were curve-fitted by a single-scattering formula and the structural parameters, such as bond length, coordination number and mean-square relative displacement (MSRD), were obtained after analyzing the correlation between these parameters. In Fig. 3, variations in the normalized coordination number and MSRD associated with sequences of sample treatment are summarized. The coordination number increases reversibly in the sample kept under irradiation by about 4–7% depending on the light intensity and exposure time. The MSRD also increases under light irradiation. After illumination, the original coordination number is restored while the light-enhanced structural disorder remains. The observed structural change, averaged over all sites, indicates locally increased coordination, such as threefold-coordinated sites. Annealing of the irradiated sample at 300 K (near T_g) resulted in recovery of the initial values for both the coordination number and the disorder parameter. These changes were not observed in the data of *c*-Se, confirming that they are not related to thermal effects upon irradiation.

The observation of a larger coordination number than two in *a*-Se is interpreted as experimental evidence of threefold-coordinated sites: $2C_2^* \rightarrow (C_3^0 - C_3^0)$, where C_2^* denotes twofold excited lone-pair states. Photoinduced effects in chalcogenides have been intensively discussed based on the valence-alternation-pairs (VAP) model (Kastner *et al.*, 1976), which assumed that dangling bonds are transformed pairs of positively charged threefold-coordinated and negatively charged singly-coordinated sites: $2C_2^0 \rightarrow (C_3^+ - C_1^-)$. Although energetically favoured because of Coulombic interaction, such a configuration is not formed since the average coordination for charged defect pairs would be constant.

4. Optical melting

Recent molecular-dynamics calculations for *a*-Se showed that the average coordination number exceeds 2.0 (2.17 at 350 K), *i.e.* the threefold-coordinated sites dominate over monocoordinated sites (Hohl & Jones, 1991). This implies that neutral threefold defect pairs serving as interchain covalent bonds are formed by either thermal or optical excitation instead of charged defect pairs. Under light irradiation, electrons from the top of the valence band, formed by lone-pair electrons, are excited into the conduction band leaving one electron in the former lone-pair orbital, as illustrated in Fig. 4. When the two excited lone-pair states C_2^* are created within an interchain distance, they would form a dynamical covalent bond linking the two chains and decrease the Coulombic repulsion between lone pairs. The formation of these new interchain bonds (optical melting) introduces a local distortion observed as an increase in the MSRD in spite of a free rotation of the dihedral angle.

Here we consider the role of threefold defect pairs in the photoinduced effects, *i.e.* photodarkening (Tanaka, 1975) and photoinduced fluidity (Hisakuni & Tanaka, 1995). Switching off the light, the defect pairs immediately split away because of the repulsive force between lone-pair electrons. However, the atoms trapped in metastable potential pockets cannot move at low temperature and the structural disorder is quenched even after switching off the light since the energy barrier between the potential minima corresponding to different configurations is higher than kT (Pfeifer *et al.*, 1989). The quenched structural disorder observed as broadening in bond length distribution

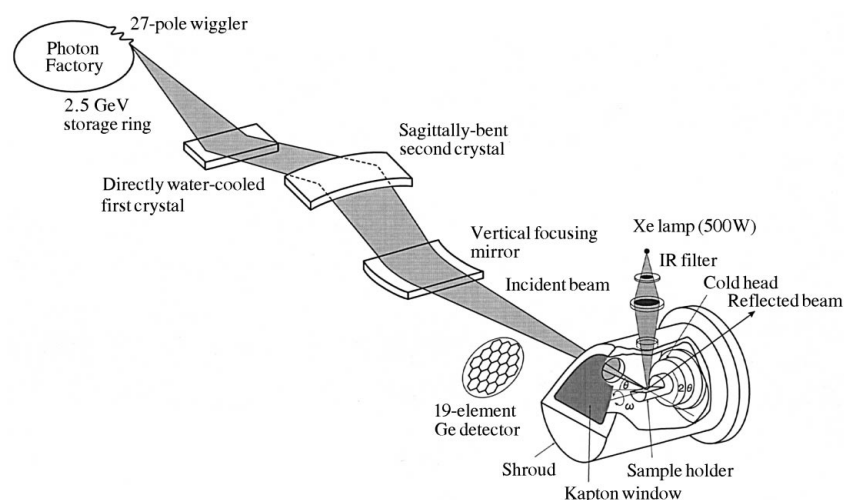


Figure 2
Experimental set-up for *in situ* XAFS during illumination.

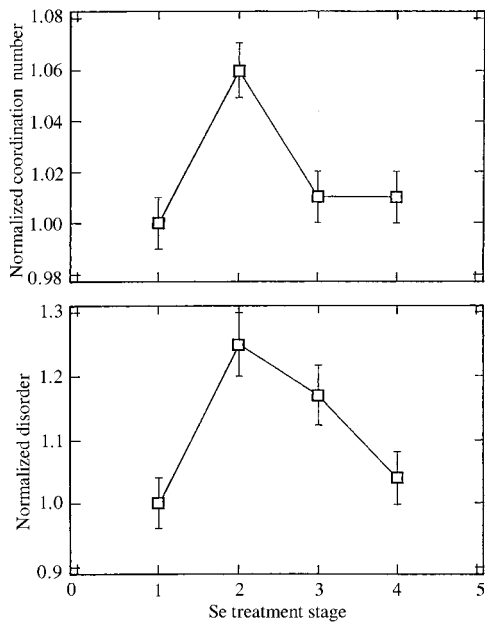


Figure 3

Results of a least-squares-curve fit analysis of the Se *K*-EXAFS data for *a*-Se plotted against the treatment stage (1: as-prepared; 2: under illumination; 3: after illumination; 4: after annealing at 300 K). The figures show the normalized coordination number (top) and the normalized mean-square relative displacement (bottom). The error bar indicates the range of systematic error in the normalized values evaluated from the repeated measurements.

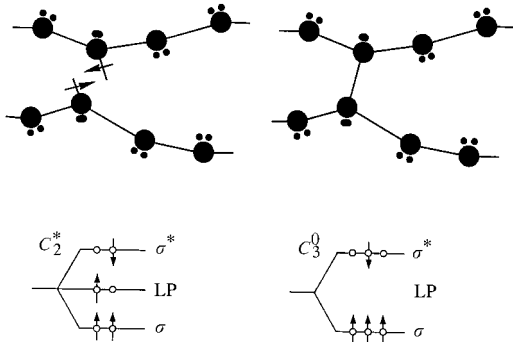


Figure 4

Schematic diagram of the threefold defect pair formed by the optical excitation of lone pair (LP) electrons on adjacent chalcogen atoms: $2C_2^* \rightarrow (C_3^0 - C_3^0)$, where C_2^* denotes twofold excited lone-pair states.

decreases the conduction band tail leading to the photo-darkening. During the photoexcitation, interchain links are formed sequentially, competing with the relaxation process. The fluidity of chain molecules is suppressed by static interchain links.

However, the interchain linkage in the present case is a dynamical one. Such a spatially extended defect coordination would increase fluidity during the illumination.

5. Summary

Despite numerous studies of photoinduced changes in amorphous chalcogenides, the mechanism remains unclear since the nature of changes is local and dynamical, which cannot be probed by spatially and time-averaged techniques, although previous *ex situ* XAFS measurements were unable to detect any change in the first coordination sphere (Frumar *et al.*, 1984; Yang *et al.*, 1987; Gladden *et al.*, 1987). This is the first direct evidence for the photoinduced formation of over-coordinated sites; our *in situ* pump and probe measurements at low temperature successfully observed a significant reversible change in coordination number and relative displacement of Se atoms correlated to photoexcitation. We propose that the optical excitation of lone pairs in a disordered system at low temperature leads to local melting inducing neutral threefold defect pairs, and the quenched structural disorder is the origin of photostructural change in chalcogenide glasses.

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