X-ray two-photon absorption spectroscopy

Successful lasing at SACLA has opened up a new frontier of nonlinear optics, i.e., X-ray nonlinear optics. Up to now, various nonlinear optical phenomena [1], such as two- and multiphoton absorption, saturable absorption, second harmonic generation, superradiance, stimulated emission, and sum-frequency generation, have been observed in the hard X-ray region.

Since nonlinear optical processes originate from different mechanisms from linear processes, they can access different information of materials. For example, the selection rule of direct two-photon absorption (TPA) is the opposite of one-photon absorption. As a result, direct TPA can use the $1s$-$3d$ transition, whereas the conventional X-ray absorption spectroscopy relies on the $1s$-$4p$ transition [2]. The $3d$ electrons play important roles in the $3d$ transition metal compounds, which include valuable functional materials, such as high-temperature superconductors. The ability of direct TPA to access the $3d$ orbital may provide a better understanding of the physical properties.

However, none of the X-ray nonlinear optical phenomena have been applied to novel spectroscopic and diffractive techniques. One reason is the need for intense X-rays. In fact, we employed intense X-rays with peak intensities beyond 10^{19} W/cm^2 to observe direct TPA and found that the electronic state of the sample changes within the femtosecond pulse duration [3]. Therefore, we cannot measure the sample as it is, i.e., in the ground state, when we use high intensity X-rays.

In this study [4], we determined the threshold above which a change in electronic state appears in the absorption spectrum and measured the direct TPA spectrum of metallic copper around the threshold at SACLA **BL3**. This is the first application of an X-ray nonlinear optical process to nonlinear spectroscopy.

First, we discuss the threshold. Figure 1 shows the absorption spectra (XANES, X-ray absorption near-edge structure) of copper measured with intense X-rays in transmission geometry. The pulse energies range from 0.5 to 20 μJ. The peak intensity is estimated to be around 10^{15} W/cm^2 from the focus size of 1.5×1.6 μm^2 and the pulse duration of 8 fs. The spectrum starts to change in the vicinity of the absorption edge. At higher pulse energies, the absorption edge shifts toward the higher photon-energy side. We consider that the spectral change is caused by impact ionization, where a fast photoelectron created by X-ray absorption ionizes the surrounding atoms. Simultaneous X-ray absorption within the small focal spot quickly creates a number of energetic free electrons, which change the absorption coefficient and spectrum.

The analysis of the pulse energy dependence of XANES is not straightforward because the X-ray intensity decreases as the beam propagates in the sample. X-ray absorption with different absorption coefficients contributes to the measured transmittance. Detailed analysis [4] gives the threshold for measuring the unchanged spectrum to be an energy density of 0.02 μJ/μm^3 (1.5 eV/atom). It is interesting to compare this threshold with the energy density of melting, which is 0.3 eV/atom for copper and is five times lower than the threshold. The melt limit may give a rough estimation of the threshold.
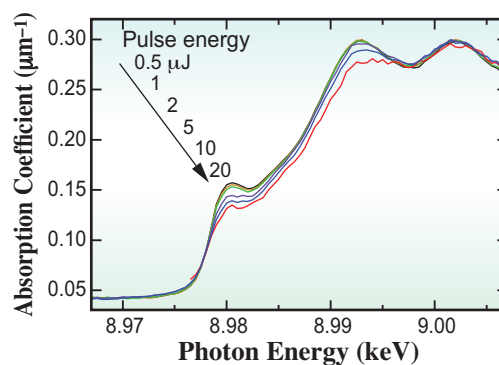

Fig. 1. Pulse energy dependence of XANES of metallic copper.

Now, we consider the experimental difficulties caused by the low threshold. The peak intensity, which can be used to measure the TPA signal, becomes much lower than that in the previous observation [3]. Since the contribution of TPA to the total absorption is negligible, we measure the weak X-ray fluorescence from the excited state by TPA as the signal. Thus, it is crucial to suppress the background sources, such as the elastic scattering, the Compton scattering, and the fluorescence due to higher harmonics. The scattering can be suppressed by measuring the TPA fluorescence signal at a right angle to the incidence within the polarization plane. It is more important to eliminate the higher harmonics, because they can produce a strong fluorescence by the linear absorption. The third-harmonic radiation was reduced by using cutoff mirrors. The second harmonic was eliminated by the forbidden 222 reflection of a double channel-cut Si 111 monochromator.

Figure 2 shows the TPA spectrum, which is the photon energy dependence of the TPA cross section. The cross section is deduced from the pulse energy dependence of the TPA fluorescence count at each photon energy. The TPA spectrum is considerably different from the one-photon absorption (XANES). The absorption edge in the TPA spectrum is lower than that in XANES. The shift of the absorption edge is consistent with the fact that the $1s$-$3d$ transition is allowed for TPA. The $3d$ orbital is closer to the nucleus than the $4p$ orbital and is subjected to a stronger potential. The creation of a K-shell core hole increases the binding energy of the $3d$ orbital and moves the TPA edge toward the lower-photon-energy side. Unfortunately, there is no quantitative theory to interpret the TPA spectrum. However, divergence toward the edge can be explained by the Anderson orthogonality catastrophe in metals with an incomplete shell [2].

In summary, we determined the threshold above which the intrinsic absorption spectrum cannot be measured owing to impact ionization. The threshold is found to be an absorbed energy density of 0.02 $\mu J/\mu m^3$ for metallic copper, which may be reached under typical experimental conditions with X-ray free-electron lasers. Thus, an extended survey of the threshold in various materials is needed to design experimental conditions. We successfully measured the direct TPA spectrum of metallic copper around the threshold, in spite of four-orders-of-magnitude lower peak intensities than those used for the direct TPA experiment. Our achievement is expected to encourage further investigation of the X-ray nonlinear optical process for novel application to nonlinear spectroscopy.
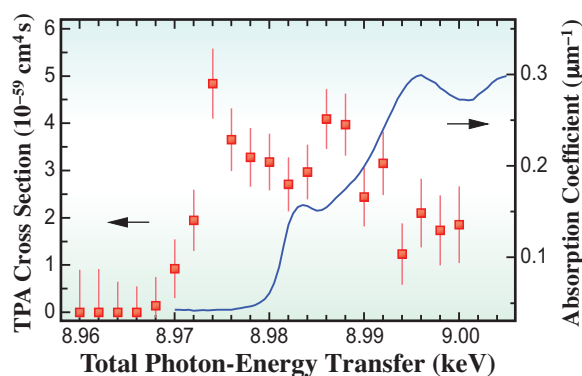

Fig. 2. Direct TPA spectrum (filled squares) and XANES (solid line) of metallic copper. Vertical bars represent the fitting error.

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References
[1] R.W. Boyd: Nonlinear Optics (Academic Press, London, 2003).
[2] F. de Groot and A. Kotani: Core Level Spectroscopy of Solids (CRC Press, New York, 2008).
[3] K. Tamasaku *et al.*: Nat. Photon. **8** (2014) 313.
[4] *K. Tamasaku, E. Shigemasa, Y. Inubushi, I. Inoue, T. Osaka, T. Katayama, M. Yabashi, A. Koide, T. Yokoyama and T. Ishikawa: Phys. Rev. Lett. **121** (2018) 083901.*