

Effect of core-to-valence resonant photoexcitation in an atom on the fluorescence X-ray emission from the neighboring atoms for multi-element material

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1 Introduction

XAFS (EXAFS, XANES) is a powerful method to determine electronic and geometrical structure around a specific atom in a multi-element material. In general fluorescence-XAFS, the intensity of fluorescence X-rays from the specific atom to be analyzed is plotted as a function of photon energy. As an example, let's consider a mica (phlogopite : $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) that is treated in this report. If we want to know the structure around a potassium atom in the mica, the intensity of potassium $K\alpha$ X-rays is plotted as a function of the incident X-ray energy. The typical results for X-ray fluorescence (XRF) spectrum and potassium K -edge XAFS spectrum for mica are shown in Fig. 1 (the details will be discussed in Section 3). A simple question may be raised as to whether the intensity of the fluorescence X-rays from elements other than potassium changes or not around the potassium K -edge? The answer may be "No", because the core-levels are localized in each atom even for a multi-element material, so the cross section of the core ionization is determined independently for each atom. However, in photoelectron spectroscopy, there have been some reports where a core-to-valence resonant photoexcitation affects the photoemission from the neighboring atoms, which is called "multi-atom resonance" [1]. In this reference, they excited Mn L_3 -edge in MnO, and observed that the O $1s$ intensity was enhanced at the core-to-valence resonance excitation at the Mn L_3 -edge. The present authors have investigated the similar phenomenon for SiO_2 . We found that the O $1s$ intensity was rather reduced at the core-to-valence resonance excitation at the Si K -edge [2]. Also, for X-ray fluorescence emission, the present authors have investigated the effect of core-to-valence resonance excitation on the X-ray emission from the neighboring atoms for simple binary compounds. For CaCl_2 , we found that the intensity of Cl $K\alpha$ X-rays was reduced at the core-to-valence resonance excitation at the Ca K -edge in solid CaCl_2 , but it was not changed in aqueous solution of CaCl_2 [3]. All the systems treated in the above reports were simple compounds composed of two kinds of elements. However, in order to clarify the effects of core-to-valence resonant photoexcitation on the neighboring atoms more clearly, it would be essential to

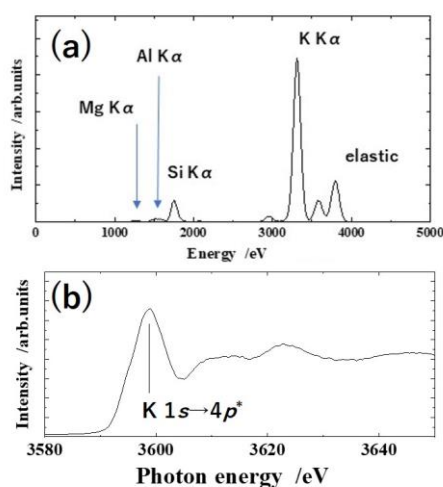


Fig. 1: (a) X-ray fluorescence (XRF) spectrum excited by 3800 eV X-rays, and (b) potassium K -edge XAFS spectrum for mica (phlogopite : $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$). In the XAFS spectrum, the intensity of the potassium $K\alpha$ peak in the XRF spectrum was plotted as a function of X-ray energy.

investigate compounds that are composed of multiple kinds of elements.

In the present study, we investigated the effects of resonant photoexcitation on the neighboring atoms for an artificially synthesized mica (phlogopite: $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) that has layered structure. This sample was chosen as a preliminary study of complex environmental samples such as clay and soil. We have excited potassium atoms at the core-to-valence resonance energy, and investigated whether the intensity of the characteristic X-rays from the other atoms changes or not.

2 Experiment

The sample investigated was a single crystal of artificially synthesized mica (phlogopite) of $20 \times 20 \times 1.0$ mm purchased from Itoh Kikoh Co., Ltd. The chemical composition of the mica was $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$.

The experiments were performed at the BL-27A soft X-ray station, Photon Factory. We used the specially

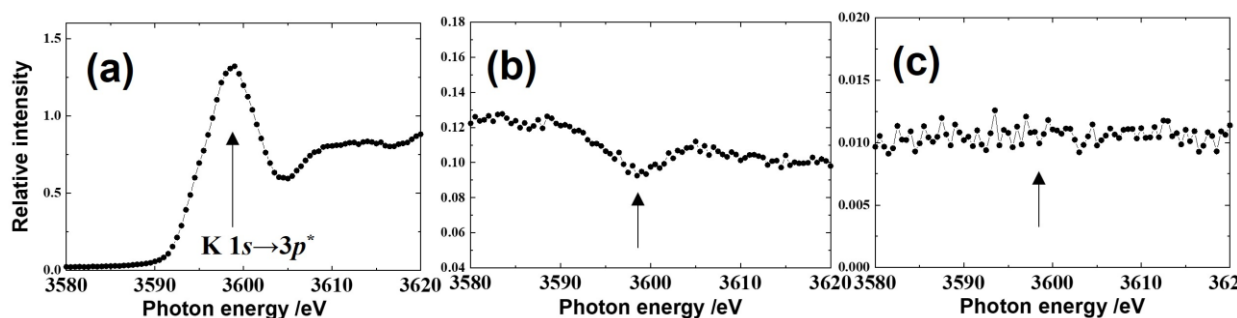


Fig. 2: Intensity of (a) potassium $K\alpha$ X-rays, (b) silicon $K\alpha$ X-rays, and (c) aluminum $K\alpha$ X-rays as a function of incident photon energy around the potassium K -edge for mica.

designed fluorescence XAFS system [4], in which XAFS spectra in soft X-ray region can be measured in helium atmosphere. The X-rays were irradiated from the bottom of the sample at the angle of 0.8° . The fluorescence X-ray was detected with Si drift detector (AMPTEK, X-123) that was located perpendicularly under the sample. The photon flux was normalized by the drain current of aluminium mesh in vacuum, located in front of the sample.

Before the measurements, the mica sample was cleaved to make thin film ($<10\ \mu\text{m}$) to avoid the self-absorption effects.

3 Results and Discussion

Fig. 1 (a) shows the X-ray fluorescence spectrum for mica excited by 3800 eV X-rays, which is above the potassium K -edge. Fig. 1 (b) presents the fluorescence XAFS spectrum at the potassium K -edge. In this measurement, the intensity of potassium $K\alpha$ X-rays shown in Fig. 1 (a) was plotted as a function of energy of the incident X-rays. The most intense peak around 3589 eV originates from the resonant excitation corresponding to the dipole-allowed potassium $1s\rightarrow 4p^*$ transition [5].

Fig. 2 shows the intensity of (a) potassium $K\alpha$, (b) silicon $K\alpha$, and (c) aluminum $K\alpha$ X-rays as a function of photon energy around the potassium K -edge. It was found that the intensity of silicon $K\alpha$ X-rays was reduced by about 11% at the potassium $1s\rightarrow 3p^*$ resonance energy (Fig. 2(b)). In the previous study, we found that the similar phenomena happened for CaCl_2 , where the intensity of Cl $K\alpha$ X-rays was reduced at the Ca $1s\rightarrow 3p^*$ resonance energy in solid state, but not reduced in aqueous solution [3]. Since Ca atom is directly bonded with Cl in solid, but not in aqueous solution, the observed phenomenon was interpreted by the perturbation of the photoionization cross section of an atom due to the resonantly excited electrons remaining in the valence unoccupied orbital [3]. The same phenomenon seems to have occurred in the present case, considering the crystal structure of mica, as follows.

The structure of mica is a monoclinic aluminosilicate, and a layer consists of Si/Al hexagons (Si/Al ratio is 3:1) which

are surrounded by oxygen tetrahedrons. Below this layer, there is another layer of Al atoms which is octahedrally surrounded by oxygen atoms. After another tetrahedrally surrounded Si/Al layer, a layer of K^+ ions follows [6]. This means that when looking from a K^+ ion, most of the neighboring atoms are silicon. Therefore, the multi-atom resonance is considered to happen in silicon atoms that are located close to potassium. On the other hand, most of aluminum atoms are located far from potassium compared with silicon atoms, so the effect of the multi-atom resonance is considered to be weaker.

Although the detailed theory on the mechanism of the multi-atom resonance has not been established, the present phenomena is expected to be applied to the structural analysis for complex materials like environmental sample, as a new method to complement conventional XAFS. For example, we are now studying to specify the adsorption site of cesium or strontium that is trapped in clay minerals.

References

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