

High-resolution soft X-ray absorption spectroscopy of solids

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The present research deals with the high-resolution soft x-ray absorption spectra (XAS) of Si, Ce- and Sm- compounds measured at BL25SU of SPring-8. The spectra are compared with theoretical results. The Si 1s spectrum shows good agreement with the calculated empty density of states so far reported. The Ce 3d spectra are very sensitive to the local electronic structure. The Sm 3d XAS of SmS shows clear temperature dependence, which is partly explained by a calculation for Sm²⁺ ion.

Keywords: soft X-ray absorption spectroscopy, grating monochromator, empty density of states, multiplet structures.

1. Introduction

Soft x-ray absorption spectroscopy (XAS) of solids is very important to study not only the ground state electronic structures but also the final state interactions of core excited states. In XAS, the energy of the photons is varied through a core level and electrons are excited to states just above the Fermi level (E_F). Since the dipole transition dominates the process of photoabsorption, the electron of a core level with an orbital angular momentum l is excited to the unoccupied $l \pm 1$ final states influenced by solid state effects such as a crystal field and hybridization. Then core XAS has the site and symmetry selective properties.

The shape of XAS spectrum is affected by the interaction between the created core hole and the excited electron. When the final state interactions of system in XAS are not significant, the so-called one-electron approximation can be applied to the system. Then the shape of the XAS spectrum will directly reflect the density of empty states. For example, it will be shown later for the analysis of Si 1s XAS.

On the other hand, 3d XAS spectra of rare-earth elements often show complicated multiplet structures resulting from the large interactions between the core hole and the 4f electrons in the $3d^p 4f^{n+1}$ configuration (Thole et al., 1985). This leads to a series of final states with different symmetry and energies being known as final state multiplet structures. Among the rare-earth systems, various reports have been given for the studies of Ce and Sm compounds in that the hybridization of the strongly correlated 4f electrons with the conduction states is giving rise to unusual thermal, electric and magnetic properties partially scaled by the Kondo temperature, T_K .

On the experimental side, a varied-line-spacing plane grating monochromator (VLSPGM) at BL25SU of SPring-8 (Saitoh et al., 1995) provides very stable, highly resolved, high intensity (10^{11} photons/sec/100mA/0.02% b.w.) monochromatic light between 0.22 and 1.8 keV with negligible contribution of higher order lights by virtue of the twin-helical undulator (Saitoh et al., 2000a, Saitoh et al., 2000b). The resolving power in excess of 10^4 was measured between 245 and 867 eV from the photoabsorption spectra of several gases as well as photoemission spectra of Au. This bandwidth of the

monochromatic light is significantly smaller than the natural width of the core level excitations in this range, facilitating high accuracy spectroscopic research. Although the photon flux becomes few times lower, an energy region up to 2.1 keV can be satisfactorily covered. This photon energy range covered by the present VLSPGM is very interesting from the scientific point of view, since 1s thresholds of C, N, O as well as L and M thresholds of 3d and 4f elements are contained in this range. In addition, 1s thresholds of Al and Si lie within this range. These elements are very important not only for physical and chemical researches but also for semiconductor industrial applications.

In this paper we report on the Ce 3d XAS spectra of several Ce compounds and Sm 3d XAS of SmS measured at different temperatures as well as 1s XAS of Si.

2. Experimental

The XAS measurements were performed at twin-helical undulator beamline BL25SU of the SPring-8 with a grazing-incidence constant-deviation monochromator equipped with VLSPGs. The sample cooling was made by use of a closed cycle He refrigerator. The sample temperature was controlled between 20 and 300 K. Clean surfaces were obtained either by scraping or cleavage in situ just before the measurement. The spectra were recorded by the total photoelectron yield method in a vacuum of 5×10^{-8} Pa or better. The photocurrent from the mirror behind the exit slit was simultaneously monitored to normalize the sample current.

3. Results and Discussion

Figure 1 shows the 1s XAS spectrum of Si single crystal measured at room temperature. We have shown the fine structure at the threshold by the solid curve in the inset of Fig. 1, together with the density of states (DOS) above E_F consisting mostly of the 3p-character split by the spin-orbit coupling (Chelikowski & Cohen, 1974). The energy resolution was estimated to be about 0.2 eV from the measured photoemission spectrum near E_F of Pd metal at 1.5 keV. Similar experimental results were reported by using InSb monochromator (Nagashima et al., 1993, Hitchcock et al., 1993). Our VLSPGM is found to realize very high resolution even in this photon energy region usually covered by the crystal monochromator. The photon energy region up to 2.1 keV is also available at the VLSPGM beamline BL23SU of SPring-8 (Yoshigoe et al., 2000) for the XAS measurement. The spherical grating monochromator of SRI-CAT 2-ID-C at Advanced Photon Source has shown a high flux performance above 1.5 keV (Coulthard et al., 2000).

The fine structures in the first 70 eV from the threshold have been discussed in term of multiple scattering effects (Bianconi et al., 1987), which are interpreted with considering a geometrical structure of the finite cluster of atoms around the absorbing atom.

Figure 2 (a) shows the Ce 3d_{5/2} XAS spectra of CeRu₂Si₂, CeNi and CeRu₂ measured at 20K. The energy resolution was 0.1 eV or better. Smooth backgrounds have been subtracted from all the spectra. The intensity of the spectra is normalized at their maximum. The T_K of these compounds are ~20 K, ~150 K and of the order of 1000 K, respectively. The spectra show a strong variation not only for the spectral shape of the main 3d_{5/2} peaks around 882 eV but also for the intensity of the satellites at ~887 eV. The main and the satellite peaks are mainly ascribed to $3d^p 4f^2$ and $3d^p 4f^1$ final states, respectively. The multiplet structures of the main peak are rather smeared into a broader single peak for CeRu₂. The intensity of the $3d^p 4f^1$ satellite arising from the $4f^0$ initial state due to the hybridization increases on going from CeRu₂Si₂ to CeRu₂. This is closely related to the T_K of these compounds. Hence, observed spectra can be understood in detail including the multiplets and the satellite structures.

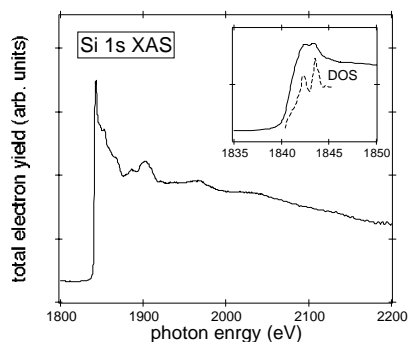


Figure 1
1s XAS spectrum of Si (solid lines). The inset shows the details around the threshold compared to the calculated DOS (dashed line).

In order to investigate local electronic structures of Ce compounds Ce 3d x-ray photoemission spectroscopy (XPS) as well as XAS have been widely performed. The Ce 3d XPS spectra show two- or three-peak structures besides the spin-orbit splitting, where each peak is rather broad and structureless. In XAS, however, the multiplet structures were only partially resolved by the unsatisfactory energy resolution of the monochromators so far employed. Then the multiplet structures are neglected and relative intensity of each peak has been often used for the analysis of both XPS and XAS spectra to estimate the 4f occupancy n_f and the hybridization strength (Fuggle et al, 1983a, Fuggle et al, 1983b, Vavassori et al., 1995). It is clearly demonstrated by our spectra that the multiplet structures give additional information for identification of electronic structure of Ce.

In order to explain the spectra in more detail we have carried out the calculation based on a cluster model including intra-atomic multiplets (Jo & Kotani, 1988). The initial (final) state is assumed to be a superposition of $3d^{10}4f^0$ and $3d^{10}4f^1\bar{\nu}$ ($3d^94f^1$ and $3d^94f^2\bar{\nu}$), where $\bar{\nu}$ represents a hole in the valence band. In this model the final-state features of XAS spectra are calculated with the parameters of the 4f level energy (ϵ_f) relative to the single level of the valence band, f - f Coulomb repulsion energy (U_{ff}), core hole-4f electron interaction ($-U_{fc}$) and the hybridization strength (V). The V is assumed to be unchanged between the initial and final states at this time.

Figure 2 (b) shows the tentative results of calculation, where the V is varied from 0.11 to 0.19 eV. The other parameters are reasonably fixed to $\epsilon_f = -1.3$, $U_{ff} = 6.7$, and $U_{fc} = 10$ eV. From the calculated spectra for $V = 0.11$ – 0.13 eV, it can be seen that the spectral change from CeRu₂Si₂ to CeNi is explained in terms of the increasing strength of V . Namely, the lower energy peak (A) intensity increases relative to the higher energy main peak (B) with increasing the relative intensity of the satellite (C). Our simple assumption, however, fails in explaining the CeRu₂ spectrum, where the calculation can not reproduce the observed spectrum with employing a stronger value of V . It is known that the calculated spectrum is drastically modified depending on the magnitude of used parameters. In other words, the high resolution XAS enables us to obtain much detailed information on the parameters characterizing the electronic structures of Ce compounds. Further analysis to reproduce the experimental spectra is under the way (Iwasaki et al.).

Figure 3 (a) summarizes Sm 3d XAS of semiconducting SmS measured at 300, 200, 100 and 20K. The energy resolution was set to 0.1 eV or better. It can be seen from the figure that the multiplet structures observed in the $3d_{5/2}$ and $3d_{3/2}$ regions clearly show temperature dependence. It can be summarized as follows. (i) At the top of the main absorption peak of $3d_{5/2}$ is seen a small dip which becomes noticeable at lower temperatures. (ii) The intensity of the small hump at 1096 eV becomes appreciable at higher temperatures.

(iii) The intensities of the $3d_{5/2}$ component decreases with increasing temperature compared to that of $3d_{3/2}$. It should be noted that there is no phase transition within this temperature range.

For SmS, photoemission (Campagna et al., 1974) and inverse photoemission (Oh & Allen, 1984) spectra have been measured and showed atomic like final state of $4f^5$ and $4f^7$ final states, respectively, suggesting that $4f^6$ (Sm²⁺) is dominant in the initial state. This 4f configuration of the initial state is supported by the recent calculation based on a multiband periodic Anderson model (Lehner et al., 1998). By comparing the overall spectral shape with atomic multiplet calculation for Sm³⁺ ($4f^5$) and Eu³⁺ ($4f^6$) (Imada & Jo, 1990), the latter agrees better to the experiment. Therefore, Sm is considered to be divalent ($4f^6$) in SmS.

The temperature dependence of the 3d XAS of Sm²⁺ can be ascribed to the contribution of the excited states in the initial state, because the energy separation between the lowest state ($J=0$) and the upper states ($J>1$) of the $4f^6$ configuration is given by the magnitude of spin-orbit interaction of several tens meV in the LS -coupling scheme. Therefore we performed the atomic full multiplet calculation by taking into account the first excited state ($J=1$) of the initial state in addition to the ground state ($J=0$).

The calculated temperature dependence is shown in Fig. 3 (b). Parameters for the multiplet calculation were taken from Thole et al. (1985). The characteristics (ii) and (iii) in the observed spectra are reproduced fairly well. Although the dip structure is predicted by the calculation with small broadening, its temperature dependence (i) is not reproduced in the calculation. This discrepancy is considered to be due to solid-state effects ignored in the present model calculation.

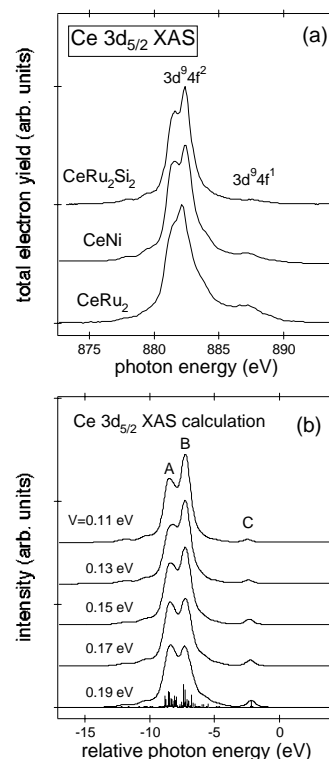
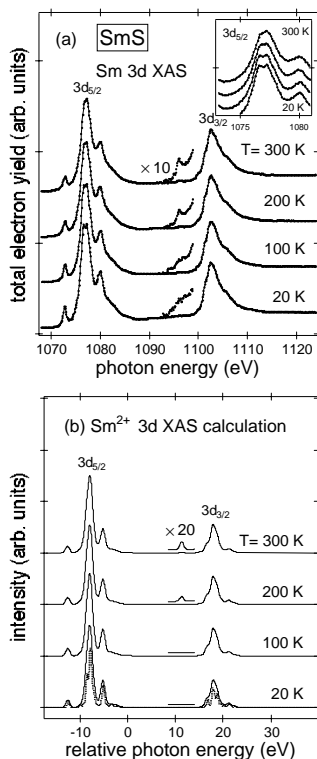


Figure 2

(a) Ce $3d_{5/2}$ XAS spectra of CeRu₂Si₂, CeNi and CeRu₂ measured at 20 K. (b) Spectral change of the calculated spectra of the Ce $3d_{5/2}$ XAS when V increases from 0.11 to 0.19 eV. Other parameters are fixed to $\epsilon_f = -1.3$, $U_{ff} = 6.7$, and $U_{fc} = 10$ eV. The Lorentzian FWHM broadening of 0.7 eV (solid curves) is used.


Figure 3

(a) Sm 3d XAS spectrum of SmS measured at different temperatures. The inset shows the details around the $3d_{5/2}$ peaks. (b) Calculated spectra for the $Sm\ 3d^{10}4f^6 \rightarrow 3d^9 4f^7$ transition for measured temperatures. The Lorentzian FWHM broadening of 0.8 eV (solid lines) and 0.4 eV (dashed line) is used.

The similar temperature dependence has been observed for Eu 3d XAS of Eu_2O_3 (Saitoh et al., 2000c), suggesting that it is a common phenomenon for $4f^6$ (Sm^{2+} and Eu^{3+}) configuration in the initial state. Further analysis is going on.

4. Conclusion

We have measured Si 1s, Ce 3d and Sm 3d XAS spectra and revealed that the high resolution XAS gives detailed information on the local electronic structures in solids. Proper analyses allowed us to do accurate estimation and identification of the electronic structures of solids.

References

- Bianconi, A., Del Sole, R., Selloni, A., Chiaradia, P., Fanfoni, M. & Davoli, I. (1987). *Solid State Commun.* **64**, 1313-1316.
- Bianconi, A., Di Cicco, A., Pavel, N.V., Benfatto, M., Marcelli, A., Natori, C.R., Pianetta P. & Woicik, J. (1987). *Phys. Rev. B*, **36**, 6426-6433.
- Campagna, M., Bucher, E., Wertheim, G.K., & Longinotti, L.D. (1974) *Phys. Rev. Lett.*, **33**, 165-168.
- Chelikowsky, J.R. & Cohen, M.L. (1974). *Phys. Rev. B*, **10**, 5096-5107.
- Coulthard, I., Antel, W.J., Frigo, S.P., Freeland, J.W., Moore, J., Calaway, W.S., Pellin, M.J., Mendelsohn, M., Sham, T.K., Naftel, S.J. & Stampfl, A.P.J. (2000). *J. Vac. Sci. Technol. A*, **18**, 1955-1958.
- Fuggle, J.C., Hillebrecht, F.U., Esteva, J.-M., Karnatak, R.C., Gunnarson, O. & Schönhammer, K. (1983a). *Phys. Rev. B*, **27**, 4637-4643.
- Fuggle, J.C., Hillebrecht, F.U., Zolnierenk, Z., Lässer, R., Feiburg, Ch., Gunnarson, O. & Schönhammer, K. (1983b). *Phys. Rev. B*, **27**, 7330-7341.
- Hitchcock, A.P., Tyliczszak, T., Abei, P., Xiong, J.Z., Sham, T.K., Baines, K.M., Mueller, K.A., Feng, X.H., Chen, J.M., Yang, B.X., Lu, Z.H., Baribeau, J.-M. & Jackman, T.E. (1993). *Surf. Sci.* **291**, 349-369.
- Imada, S. & Jo, T. (1990). *J. Phys. Soc. Jpn.*, **59**, 3358-3373.
- Iwasaki, T. et al., to be published.
- Jo, T. & Kotani, A. (1988). *Phys. Rev. B*, **38**, 830-833.
- Lehner, C., Richter M. & Eschrig, H. (1998). *Phys. Rev. B*, **58**, 6807-6817.
- Nagashima, N., Nakano, A., Ogata, K., Tamura, M., Sugawara K. & Hayakawa, K. (1993). *Phys. Rev. B*, **48**, 18257-18260.
- Oh, S.-J. & Allen, J.W. (1984). *Phys. Rev. B*, **29**, 589-592.
- Saitoh, Y., et al., (1998). *J. Synchrotron Rad.* **5**, 542-544.
- Saitoh, Y., et al., (2000a). *Rev. Sci. Instrum.*, **71**, 3254-3259.
- Saitoh, Y, et al., (2000b). *Nucl. Instrum. Methods.* to be published.
- Saitoh, Y., et al., (2000c). *Nucl. Instrum. Methods.* to be published.
- Thole, B.T., van der Laan, G., Fuggle, J.C., Sawatzky, G.A., Karnatak, R.C. & Esteva, J.-M. (1985). *Phys. Rev. B*, **32**, 5107-5118. The calculation for elements near the middle of the rare-earth series known to have some errors.
- Vavassori, P., Duo, L., Chiaia, G., Qvarford, M. & Lindau, I. (1995). *Phys. Rev. B*, **52**, 16503-16507.
- Yoshigoe, T. et al., (2000). in this proceedings.