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**4f STATE WITH THE 3d CORE HOLE OF La, Sm AND SmB<sub>6</sub>**

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Abstract - The Sm M<sub>4,5</sub> emission and characteristic isochromat spectra of Sm metal and a mixed-valence compound SmB<sub>6</sub> and the La M<sub>4,5</sub> fluorescent emission spectrum of La metal were measured to obtain the information on the 4f state with the 3d core hole. In the case of Sm metal and SmB<sub>6</sub> it was found that an electron-beam energy larger than the energy of the resonant emission (1079 eV) and also the threshold of the 3d<sub>5/2</sub> level (1082.2 eV) is required for the generation of the resonant emission ( $3d_{5/2}4f^{n+1} \rightarrow 3d^{10}4f^n$ ), where n is equal to 5 for the Sm<sup>3+</sup> ion. The hole-induced shakedown process was observed in the M<sub>4,5</sub> fluorescent emission spectrum of La metal.

INTRODUCTION

The electronic energy states of rare earths and their compounds have become a subject of much interest in recent years because of the rather diverse electrical and magnetic properties of these substances /1/. It has been known that such properties are attributed to the unfilled 4f level which is localized around the rare-earth ion. The properties of samarium hexaboride SmB<sub>6</sub>, which is known to be a homogeneous mixed-valence compound, have been studied extensively by many experimental techniques, and the mixed-valence character of this substance has been discussed /2-7/. Crecelius et al. /8/ have found a shakedown satellite in the 3d<sub>5/2</sub> x-ray photoelectron spectrum (XPS) of La metal and interpreted it as the 3d<sub>5/2</sub> line when the 4f level, which is empty in the ground state, is filled by an electron from the conduction-band states in the presence of a 3d core hole.

In the present work, we measured the Sm M<sub>4,5</sub> emission spectrum with various electron-beam energies near the Sm 3d<sub>5/2</sub> threshold and also the characteristic isochromat spectrum on Sm metal and SmB<sub>6</sub> to obtain the information on the excitation threshold of the emission lines by electron impact /9/. Moreover, the M<sub>4,5</sub> emission spectrum of La metal was measured with the fluorescence excitation method to observe the x-ray emission from the excited configuration and to confirm the possibility of a hole-induced shakedown transition /10/.

EXPERIMENTAL PROCEDURE

The electron-excited M<sub>4,5</sub> emission and isochromat spectra were obtained with a

flat crystal vacuum spectrometer equipped with a fine Soller slit and a potassium acid phthalate crystal. The spectral window is about 2.5 eV in the Sm  $M_{4,5}$  spectral region. Intensity measurements were carried out automatically for a preset counting time at a regular interval of  $0.01^\circ$  of the Bragg angle by means of a step-scanning method. The detector was a gas-flow proportional counter equipped with a thin polypropylene window and an argon gas with 10% of methane by volume. Specimens of Sm metal and  $\text{SmB}_6$  were prepared by evaporation onto a copper anode.

For the measurement of the fluorescent  $M_{4,5}$  emission spectrum of La metal, a rhodium target x-ray tube operated at 40 kV and 70 mA was used as a primary source. In this case, specimen of La metal was prepared by evaporation onto an aluminum substrate and covered by a thin aluminum film.

## RESULTS AND DISCUSSION

The Sm  $M_{4,5}$  emission spectra of Sm metal and  $\text{SmB}_6$  obtained with various incident electron-beam energies are shown in Figs. 1 and 2, respectively. The arrows indicate the energies of the incident electron beam. The spectra of  $\text{SmB}_6$  exhibit the similar features as those of Sm metal in spite of the mixed-valence character of  $\text{SmB}_6$ . In the spectrum excited with the electron-beam energy of 1500 eV, the emission peaks R (1079 eV) and R' (1105 eV), which coincide with the absorption peaks  $3d^9 4f^{n+1} \rightarrow 3d^{10} 4f^n$ , where n is equal to 5 for the  $\text{Sm}^{3+}$  ion. The peak F (1075 eV), which begins to rise at the excitation energy of about 1083 eV, gradually increases its intensity and then buried in the tail of the resonant peak with the increase of the excitation energy. To see the onset of the intensity rise of this peak we measured the characteristic isochromat spectra at the photon energy of the peak F at 1075 eV on Sm metal and  $\text{SmB}_6$ . The results are shown in Figs. 3 and 4 together

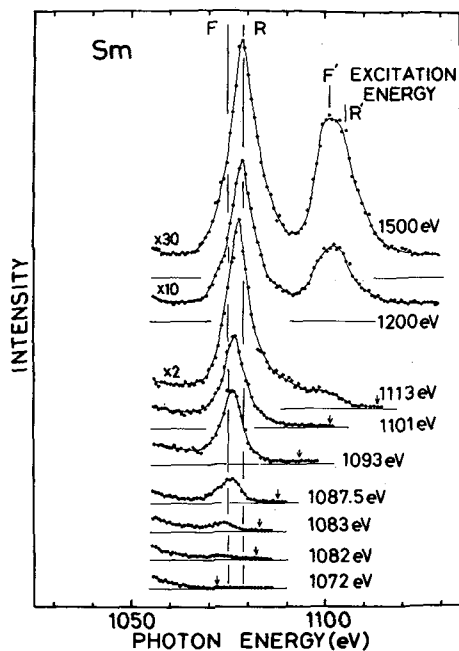


Fig. 1 - Sm  $M_{4,5}$  emission spectra of Sm metal obtained with various electron-beam energies.

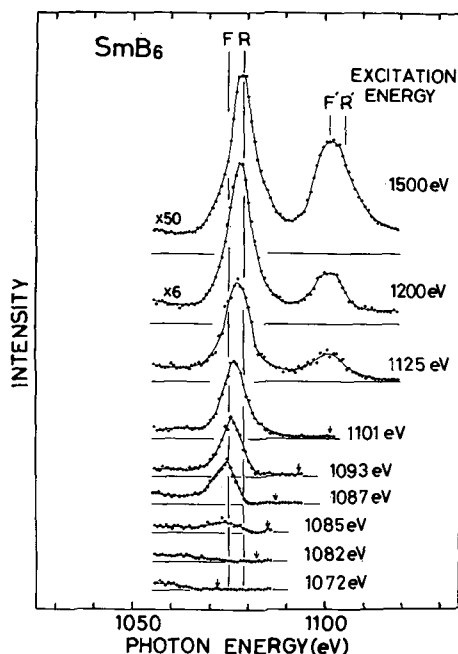


Fig. 2 - Sm  $M_{4,5}$  emission spectra of  $\text{SmB}_6$  obtained with various electron-beam energies.

with the spectra obtained at the photon energy of the peak R at 1079 eV. The intensity of the peak F at 1075 eV clearly begins to rise at the electron-beam energy beyond the  $3d_{5/2}$  threshold (1082.2 eV) of the  $\text{Sm}^{3+}$  ion. Moreover, the energy of this peak (1075 eV) agrees well with the binding-energy difference between the occupied  $4f$  and the  $3d_{5/2}$  levels of the  $\text{Sm}^{3+}$  ion obtained from the XPS data /3/. Thus, we attribute this peak F to the ordinary  $M_{5N6,7}$  emission line ( $3d^9 4f^5 \rightarrow 3d^{10} 4f^4$ ) of the  $\text{Sm}^{3+}$  ion. The position F' can be assigned as the ordinary  $M_{4N6}$  emission by knowing the spin-orbit splitting of the  $3d$  level to be 25.8 eV.

The characteristic isochromat spectra measured at the photon energy of 1079 eV, i.e., at the position of the resonant peak R of the  $\text{Sm}^{3+}$  ion, exhibit that the intensity of this peak rises at the electron-beam energy beyond 1085 eV in contrast to the photoabsorption process. This delayed onset of the intensity rise may be attributed to the creation of the transient state with the configuration  $3d^9 4f^7$ , which is caused by both the electron excited from the  $3d$  level and the incident electron losing the initial energy due to the inelastic collision. Since this state may be located well above the Fermi level, the interaction of this state with the empty continuum states might immediately create the initial state ( $3d^9 4f^6$ ) of the resonant emission of the  $\text{Sm}^{3+}$  ion, whose energy (1079 eV) is lower than the  $3d_{5/2}$  threshold (1082.2 eV). Then, the resonant emission  $3d^9 4f^6 \rightarrow 3d^{10} 4f^5$  occurs. Thus, we believe that the energy of 1085 eV is necessary at least for the excitation of the resonant emission by electron impact.

The characteristic isochromat spectrum of  $\text{SmB}_6$  at the photon energy of 1071 eV, which is the binding-energy difference between the filled  $4f$  and the  $3d_{5/2}$  levels of the  $\text{Sm}^{2+}$  ion obtained from the XPS data /3/, was measured in order to confirm whether the ordinary emission due to the transition  $3d^9 4f^6 \rightarrow 3d^{10} 4f^5$  in the  $\text{Sm}^{2+}$  ion is observed or not. However, the intensity of this spectrum does not increase appreciably even if the incident-electron-beam energy is beyond the  $3d_{5/2}$  binding energy of the  $\text{Sm}^{2+}$  ion (1071.3 eV). This fact may suggest that the contribution of the ordinary  $M_{5N6,7}$  emission of the  $\text{Sm}^{2+}$  ion is too small to be observed or a valence change occurs from divalent to trivalent under the electron impact.

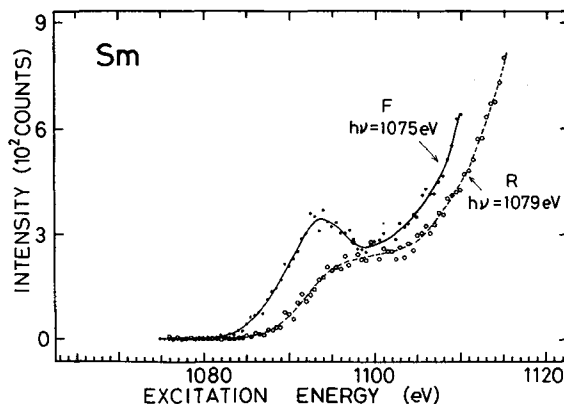


Fig. 3 - Characteristic isochromat spectra measured at the photon energies of 1075 eV (F, solid line) and 1079 eV (R, dashed line) on Sm metal.

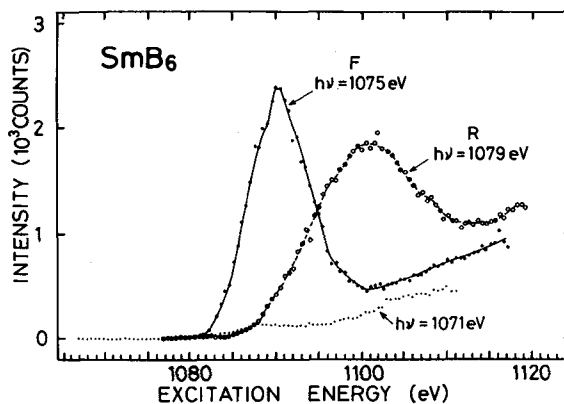


Fig. 4 - Characteristic isochromat spectra measured at the photon energies of 1075 eV (F, solid line), 1079 eV (R, dashed line) and 1071 eV (dotted line) on  $\text{SmB}_6$ .

The fluorescent  $M_{4,5}$  emission spectrum of La metal is shown in Fig. 5 together with the electron-excited spectra with various electron-beam energies. The  $M_{4,5}$  absorption spectrum measured by Mariot and Karnatak /11/ is also shown by a dashed line. In the spectra (c) and (d), the peaks R and R' may be ascribed to the resonant emission  $3d^{9/4}f^1 \rightarrow 3d^{10/4}f^0$  because the energy positions of these peaks coincide with those of the absorption peaks. The general feature of the fluorescent emission spectrum (a) resembles that of the spectrum (b) which was obtained with the electron excitation method with the electron-beam energy of 10.0 keV and suffered the self-absorption effect. In the present fluorescent spectrum rather-high-energy photons (Rh L) were irradiated on the specimen so that a 3d core electron is merely excited far into the continuum, and thus there is no possibility of the resonant emission caused by the same origin as with the electron excitation method. However, this result indicates that the shakedown transition from the conduction-band states to the empty 4f level occurs in the presence of a 3d core hole as pointed out by Crecelius et al. /8/. Also, the satellite S was observed on the low energy side of the  $M_{5/2}$  ( $3d_{5/2}^0 \rightarrow 5p_{3/2}^0$ ) diagram, line D and, attributed to the transition  $3d_{5/2}^1 \rightarrow 5p_{3/2}^1$ . This gives further evidence of the hole-induced shakedown transition. It is noticed that the intensity of the low binding energy satellite in the  $3d_{5/2}$  XPS of rare earths decreases from La to Nd as the overlap between the increasingly core-like 4f and conduction electrons decreases /8, 12/. Thus, in Sm metal and SmB<sub>6</sub> the shakedown effects should be negligibly small.

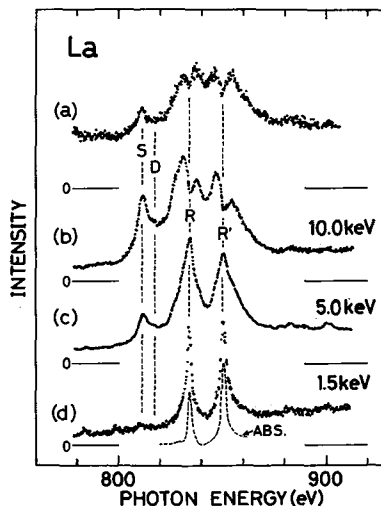


Fig. 5 -  $M_{4,5}$  spectra of La metal. Spectrum (a) is the fluorescent spectrum. Spectra (b), (c) and (d) are the electron-excited spectra obtained with the electron-beam energies of 10.0, 5.0 and 1.5 keV, respectively. The  $M_{4,5}$  absorption spectrum measured by Mariot and Karnatak /11/ is also shown by a dashed line.

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