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Soft-x-ray-excited soft-x-ray appearance-potential spectra of Sm and SmB_6 in the Sm 3*d* electron excitation region

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The resonant process previously proposed in electron-excited Sm $M_{4,5}$ emission spectra of Sm and SmB_6 was confirmed by a study of soft-x-ray-excited soft-x-ray appearance-potential spectra (XXAPS). Two peaks were observed in the XXAPS at photon energies equal to energies of the prominent peaks in the Sm $M_{4,5}$ absorption spectra. These peaks are attributed to the resonant process $3d^{10}4f^{n}\leftrightarrow 3d^{9}4f^{n+1}$, where n is the number of $4f$ electrons in the ground state. In addition to the resonant peak in the M_5 spectral region, the resonant peak in the M_4 spectral region, which was not separately observed from the diagram line M_4N_6 in electron-excited emission spectra, was clearly observed in XXAPS.

I. INTRODUCTION

The $M_{4,5}$ emission spectra of rare-earth elements have been investigated by several groups with the electron-excitation method.[1-8] It was pointed out by Stewardson *et al.*[1,2] that peaks in the $M_{4,5}$ emission spectrum of erbium coincide in energy with peaks in the $M_{4,5}$ absorption spectrum. Bonnelle *et al.*[4-6] observed emission peaks at the same energy positions as corresponding absorption peaks in the $M_{4,5}$ spectra of some rare-earth elements and interpreted them as electron-stimulated resonant emission.

Previously we investigated the Sm $M_{4,5}$ emission spectra of Sm and SmB_6 with the electron-excitation method using electron-beam energies near the threshold of the Sm 3*d* electron excitation.[8] In that study peaks were observed in emission spectra at the same energy positions as absorption peaks and were ascribed to resonant emission caused by the inverse process of photoabsorption. Furthermore, characteristic isochromat spectra were measured at the photon energies of the resonant emission peak ($3d_{5/2}^{-1}4f^{n+1}\leftrightarrow 3d^{10}4f^{n}$: 1079 eV for $n=5$) and the ordinary emission peak $M_5N_{6,7}$ ($3d_{5/2}^{-1}4f^{n}\rightarrow 3d^{10}4f^{n-1}$: 1075 eV for $n=5$), where n is the number of $4f$ electrons in the ground state, namely, 5 for the Sm^{3+} ion and 6 for the Sm^{2+} ion. It was found that an electron-beam energy above 1085 eV is required to produce the resonant peak, which is greater than the energy of the resonant peak (1079 eV) as well as the $3d_{5/2}$ threshold (1082.2 eV) of the Sm^{3+} ion ($n=5$). On the other hand, the intensity of the ordinary emission peak $M_5N_{6,7}$ rises at about a photon-excitation energy of 1082 eV, which is the threshold of the $3d_{5/2}$ level. To interpret these phenomena, it was proposed that the transient state $3d^{9}4f^{5+2}$, in which one electron is promoted from the 3*d* level to an *f* level and the incident electron is also accommodated in an *f* level, is created by electron impact with electron-beam energies greater than 1085 eV as well as the threshold of the $3d_{5/2}$ level and this transient state decays subsequently to the state $3d^{9}4f^{5+1}$. Thus, the experiment was unable to obtain direct evidence that the peaks observed in the electron-excited emission spectrum at the same energies as in the absorption spectrum are resonant emission peaks caused by the inverse process of photoabsorption. Moreover, in the electron-excited emission spectrum, the resonant emission peak in the M_4 spectral region was not clearly separated from ordinary emission M_4N_6. In addition, the Sm $M_{4,5}$ electron-excited emission spectrum and absorption spectrum of SmB_6, which is known to be a mixed-valence compound between Sm^{2+} and Sm^{3+} ions, exhibited prominently the resonant peak of the Sm^{3+} ion and did not show distinct indication due to the Sm^{2+} ion.

To confirm resonant behavior in the Sm $M_{4,5}$ emission spectrum proposed in previous papers,[7,8] it is necessary to measure the emission spectrum with the photon-excitation method because the extra electron, i.e., the incident electron in the case of electron excitation, is not present in this method. Thus, in the present study we investigate soft-x-ray-excited soft-x-ray appearance-potential spectra[9] (XXAPS) of Sm and SmB_6 in the Sm 3*d* electron excitation region. Since XXAPS is excited by photon irradiation with scanning the photon energy, it is expected that a distinct peak will be obtained if the resonant process occurs. Another prospect is that we might observe indications of Sm^{2+} in SmB_6, which was not observed in the electron-excited emission spectrum.

II. EXPERIMENTAL PROCEDURES

XXAPS were obtained by collecting fluorescence x rays from the sample under irradiation by monochromatic x rays. The primary photon energy was scanned by using a flat crystal vacuum spectrometer equipped with a fine Soller slit and a potassium acid phthalate crystal ($2d = 26.64$ Å). The angle between the direction of the primary monochromatic x-ray beam and the sample surface was 15° and the takeoff angle of the emitted fluorescence x rays from the sample was 80°. The detector subtended a solid angle of about $(0.02)4\pi$. A tungsten target x-ray tube was operated at 13 keV and 40 mA to obtain continuous x rays. The spectral window due to the Soller slit is about 0.7 eV at a photon energy of 1100 eV. Intensity measurements were carried out automatically for a preset counting time by means of a step-scanning method at a regular interval of 0.01° of the Bragg angle, which corresponds to about 0.4 eV at a photon energy of 1100 eV. The intensity of incident x rays is almost constant (1900 counts/s) in the energy region measured here and that of the XXAPS peak at 1079 eV is about 0.2 counts/s after subtracting the background. The detector was a gas-flow proportional counter equipped with a polypropylene window (about 1 μm thick) covered with aluminum (about 0.01 μm thick) and argon gas with 10% of methane by volume.

Specimens of Sm and SmB_6 were prepared by evaporation onto copper plates at a pressure of 2×10^{-7} Torr and subsequently covered by a thin evaporated aluminum film to avoid undesirable oxidation of the specimens. The Cu $L\alpha$ line was used as a reference line. Its wavelength was taken from tabulated values as 13.366 Å.[10] To see effects due to scattering and/or reflection of the incident monochromatic x rays from the sample, the XXAPS of Gd, whose absorption spectrum has no structure in the Sm $M_{4,5}$ spectral region, was measured. This spectrum has no structure, showing only a slight increase of background intensity as the photon energy of primary monochromatic x rays is increased.

III. RESULTS AND DISCUSSION

The XXAPS of Sm and SmB_6 in the Sm $3d$ electron-excitation region are shown in Figs. 1 and 2, respectively, together with respective Sm $M_{4,5}$ absorption spectra (dashed lines) and emission spectra obtained previously with the electron-excitation method (solid lines).[8] Since emission peaks coincide in energy with absorption peaks, the emission spectrum obtained with the electron-excitation method is affected significantly by self-absorption at relatively high electron energies. Therefore, in Figs. 1 and 2, we show emission spectra obtained at low electron energies to reduce the effect of self-absorption.

Peaks observed in electron-excited emission spectra were assigned by comparing peak energies with x-ray photoelectron spectra and absorption spectra. As mentioned in a previous paper,[8] the shoulder (F) observed at 1075 eV is attributed to the ordinary radiative transition from the occupied $4f$ level to the $3d_{5/2}$ level of the Sm^{3+} ion ($M_5N_{6,7}$ line). The shoulder (F') observed at 1101 eV can be assigned to the M_4N_6 emission line of the Sm^{3+} ion in view of the spin-orbit splitting of the $3d$ level (25.8 eV).[10] The regions R (1079 eV) and R' (1105 eV) in electron-excited emission spectra coincide with absorption peaks and are therefore reduced, at high electron energies, by self-absorption. Thus, these regions are interpreted as resonant emission caused by the transition $3d^9 4f^{n+1} \leftrightarrow 3d^{10} 4f^n$.

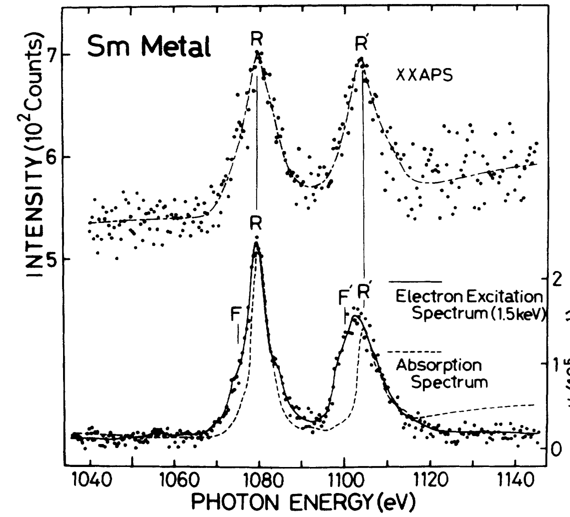

FIG. 1. The XXAPS (dash-dotted line) of Sm in the Sm $3d$ electron-excitation region together with the electron-excited Sm $M_{4,5}$ emission spectrum (solid line) and the absorption spectrum (dashed line).

In the XXAPS, the lower-energy peak appears at a photon-excitation energy of 1079 eV, which is equal to the energy of the Sm M_5 absorption peak R, and the higher-energy peak appears at 1105 eV, which coincides with the M_4 absorption peak R'. These facts imply that the peaks in the XXAPS would be caused by the transition $3d^9 4f^{n+1} \rightarrow 3d^{10} 4f^n$. In the XXAPS measurement, however, all the fluorescence radiation from the sample is collected. Thus, energy of x rays contributing to the peak

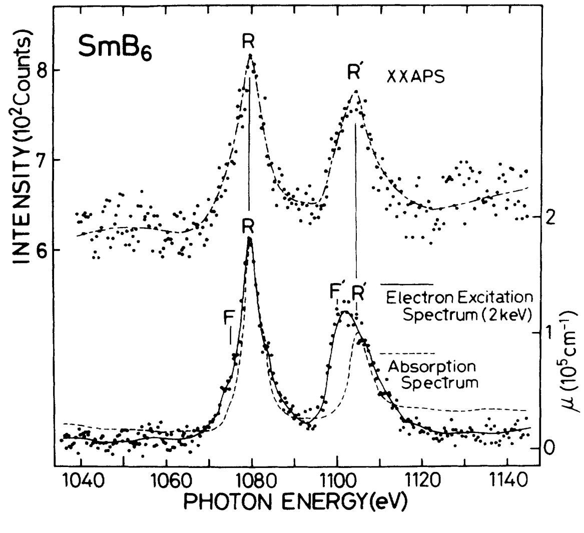

FIG. 2. The XXAPS (dash-dotted line) of SmB_6 in the Sm $3d$ electron-excitation region together with the electron-excited Sm $M_{4,5}$ emission spectrum (solid line) and the absorption spectrum (dashed line).

in the XXAPS cannot be determined only from the XXAPS.

The incident x-ray photons are absorbed by two main types of absorption processes, i.e., photoelectric and scattering processes. The mass absorption coefficient is written $\mu=\tau+\sigma$, where τ is the photoelectric absorption coefficient and σ is the scattering absorption coefficient. σ is much smaller than τ for the absorption of x rays with energy lower than about 25 keV in elements heavier than Fe and is almost independent of the photon energy.[11] Under irradiation by monochromatic x rays with enough energy to excite Sm $3d$ electrons, electrons in shallower levels are also excited. Therefore, in addition to the Sm M emission lines, other emission lines such as Sm N and Sm O emission lines are also produced. For excitation of the core electron in level i to the continuum, τ_i shows a step- or a sawtooth-shaped distribution as a function of x-ray photon energy and is zero in the energy region below the threshold of this level. On the other hand, for excitation of the core electron to a discrete level, τ_i resembles a spike shape at the energy corresponding to the transition between the core level and the discrete level and is zero elsewhere. Thus, for excitation of a core electron to the continuum, the intensity distribution of the emitted x rays would be step- or sawtooth-shaped as a function of photon energy and be spike- or line-shaped at the energy for excitation to a discrete level. Therefore, peaks R and R' observed in the XXAPS should be due to excitation of the $3d$ electron to a localized upper discrete level, such as an empty $4f$ level, and might consist mainly of the emission line due to the transition $3d^94f^{n+1}\rightarrow 3d^{10}4f^n$.

When the sample is irradiated by monochromatic x rays at an energy equal to the absorption peak R, there is an order of magnitude more holes created in the Sm $3d$ levels than in shallow levels, judging from the peak-to-background ratio around peak R in the absorption spectra. Moreover, the gas-flow proportional counter, with its polypropylene window covered with a thin aluminum film, is not sensitive to photons with an energy lower than 500 eV, where the Sm N and Sm O emission appears, due to the increase of the absorption coefficient of the window materials.[12] The signals due to low-energy x-ray photons are also eliminated by a pulse-height analyzer in the counting system. Therefore, the XXAPS intensity is mainly due to the Sm M series emission.

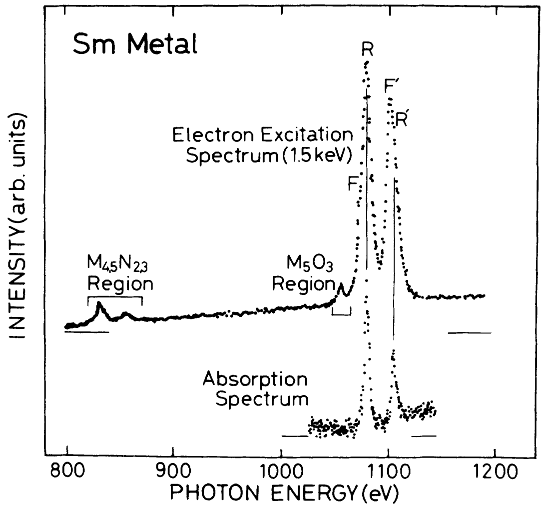

FIG. 3. The Sm M emission spectrum measured with the electron-excitation method and the Sm $M_{4,5}$ absorption spectrum for Sm.

To investigate which emission line in the M series contributes most to the XXAPS peak, we obtained the electron-excited Sm M emission spectrum of Sm measured at 1.5 keV to reduce the effect of self-absorption. The results are shown in Fig. 3 together with the Sm $M_{4,5}$ absorption spectrum. Though the electron-excited emission spectrum is not the same as that excited with monochromatic x rays with energy of the R or R' peak, the intensity ratio of the respective emission lines excited with monochromatic x rays may be estimated from the electron-excited emission spectrum. In addition to ordinary emission lines due to the transitions $3d^94f^n\rightarrow 3d^{10}4f^{n-1}$ ($M_{4,5}N_{6,7}$), $3d^95p^64f^n\rightarrow 3d^{10}5p^54f^n$ ($M_{4,5}O_{2,3}$), and $3d^94p^64f^n\rightarrow 3d^{10}4p^54f^n$ ($M_{4,5}N_{2,3}$), emission lines due to transitions possible at resonance $3d^94f^{n+1}\rightarrow 3d^{10}4f^n$ (resonant emission R, R'), $3d^95p^64f^{n+1}\rightarrow 3d^{10}5p^54f^{n+1}$, and $3d^94p^64f^{n+1}\rightarrow 3d^{10}4p^54f^{n+1}$ should be observed. The energies of the latter two emission lines for the Sm^{3+} ion may be estimated from the binding-energy difference between the Sm $3d$ and Sm $4p$ (or $5p$) levels of the Sm^{2+} ion. From x-ray photoelectron spectra of SmB_6,[13,14] the energies of the transitions $3d_{5/2}^{-1}4p^64f^n\rightarrow 3d^{10}4p_{3/2}^{-1}4f^n$ (M_5N_3) and $3d_{5/2}^{-1}5p^64f^n\rightarrow 3d^{10}5p_{3/2}^{-1}4f^n$ (M_5O_3) are 831.2 and 1060.7 eV, respectively, and those of the transitions $3d_{5/2}^{-1}4p^64f^{n+1}\rightarrow 3d^{10}4p_{3/2}^{-1}4f^{n+1}$ and $3d_{5/2}^{-1}5p^64f^{n+1}\rightarrow 3d^{10}5p_{3/2}^{-1}4f^{n+1}$ are 830.3 and 1054.2 eV, respectively. Therefore, emission lines due to the latter two transitions may be expected to appear several eV away from the diagram lines M_5N_3 and M_5O_3, respectively. Since the binding energy of the Sm $3d_{3/2}$ level is not given, the energies of the transitions $3d_{3/2}^{-1}4p^64f^{n+1}\rightarrow 3d^{10}4p^54f^{n+1}$ and $3d_{3/2}^{-1}5p^64f^{n+1}\rightarrow 3d^{10}5p^54f^{n+1}$ cannot be estimated, but they may also be expected to appear several eV away from the corresponding lines $M_4N_{2,3}$ and $M_4O_{2,3}$, respectively. As seen in Fig. 3, the resonant emission R and R' ($3d^94f^{n+1}\rightarrow 3d^{10}4f^n$) is more intense than the emission in the $M_{4,5}N_{2,3}$ and the $M_{4,5}O_{2,3}$ spectral regions. Thus, the resonant emission contributes most to the XXAPS peak intensity. It should be noted that resonant behavior in the M_4 spectral region, which was not clearly observed in the electron-excited emission spectrum, is confirmed in the present study because the XXAPS spectrum shows a clear peak at the resonant energy.

Let us consider the intensity of the XXAPS. By using an equation representing the intensity of the emitted radiation from the sample of a single element under irradiation by monochromatic x rays,[15] the intensity of peak R (or R') in the XXAPS is given by

$$I=\frac{d\Omega}{4\pi}I_0(h\nu_R)\tau_{3d}(h\nu_R)\omega_{3d}g_{3d,4f}$$
$$\times\frac{1}{[\tau_{3d}(h\nu_R)+\sigma][1+(\sin\alpha/\sin\beta)]}\,, \quad (1)$$

where $d\Omega/4\pi$ is the geometrical factor for the detector solid angle, $I_0(h\nu_R)$ is the intensity of the incident monochromatic radiation, $\tau_{3d}(h\nu_R)$ is the photoelectric mass absorption coefficient due to excitation of an electron in the $3d$ level at photon energy $h\nu_R$, ω_{3d} is the fluorescence yield for the $3d$ level, $g_{3d,4f}$ is the probability of an electronic transition from the $3d$ level to the $4f$ level, ν_R is the frequency of the resonant emission line which, in XXAPS, is the same as the primary x-ray frequency, α is the angle between the direction of the incident x-ray beam and the sample surface, and β is the takeoff angle of the emitted x rays. Assuming that the values of ω and g for peak R' are the same as those for peak R, the intensity ratio R/R' is given by

$$\frac{\tau_{3d}(h\nu_R)\mu(h\nu_{R'})}{\tau_{3d}(h\nu_{R'})\mu(h\nu_R)}\,. \quad (2)$$

This ratio can be estimated to be 1/0.85 from the absorption spectrum, in good agreement with the intensity ratio R/R' in the XXAPS. This fact confirms that the peaks in the XXAPS are caused mainly by resonant emission. The self-absorption, observed as a dip at the resonant energy position in the electron-excited emission spectrum,[7] is not observed in the XXAPS as expected from Eq. (1).

The XXAPS of SmB_6 shows a structure similar to the XXAPS of Sm. Two peaks are observed whose energy positions, widths, and relative intensities are almost the same as those of Sm. As the main features of the $M_{4,5}$ absorption spectra of SmB_6 and Sm are quite similar, the SmB_6 spectrum is dominated by $3d$ excitation of the Sm^{3+} ion and the spectrum due to the Sm^{2+} ion was not observed.

The theoretical analysis of the core-excitation spectra of the mixed-valence system has been performed by Gunnarsson and Schönnhammer[16] for Ce compounds on the basis of the Anderson impurity model by taking into account the attractive core-hole potential and the hybridization between an f state and conduction states. Further theoretical investigation has been progressed by Kotani, Jo, and Parlebas[17] for the core-excitation spectra of the rare-earth system, and the core-excitation spectra of mixed-valence Ce compounds have been successfully interpreted. Also, Fujimori has studied the $3d$ core-level photoelectron spectra of Ce compounds by considering strong correlations among $4f$ electrons.[18] In the case of Sm compounds, however, only the theoretical calculation by Thole *et al.*[19] is available, which has been carried out inclusive of the $3d^9 4f^{n+1}$ multiplet structures. According to them, the M_5 and M_4 absorption peaks of the Sm^{2+} ion appear at about 2.5-eV lower energy positions than those of the Sm^{3+} ion and both spectra have widths of several eV. In fact, the Sm $M_{4,5}$ absorption spectrum of mixed-valent $Sm_{0.3}Y_{0.7}S$ measured by Kaindl *et al.*[20] with a total-electron yield mode shows clearly the peak due to the Sm^{2+} ion. However, in the present XXAPS, the Sm^{2+} component was not observed. Several reasons for this problem are considered. (1) The data points are so scattered that the peak due to the Sm^{2+} ion cannot be observed. (2) If the divalent component is attributed to the surface layer even in SmB_6, XXAPS and soft-x-ray absorption spectra do not clearly show the divalent component because they are not surface sensitive, in contrast to the electron-yield spectrum. In fact, the surface layer of trivalent metallic Sm has a large divalent component.[21] (3) The samples of SmB_6 might be oxidized. However, the intensity ratio between the M_5 and M_4 absorption peaks of Sm_2O_3 measured previously is different from those of Sm and SmB_6.[7] The intensity ratio of the M_5 and M_4 peaks in XXAPS is different from that derived from the absorption spectrum of Sm_2O_3. Furthermore, the M_5 and M_4 absorption peaks of Sm_2O_3 show some structures which are not observed in the spectrum of Sm. Such small structures are not observed in the present XXAPS. Thus, we consider that the present specimens are not oxidized significantly.

Unfortunately, we did not observe any step- or sawtooth-shaped distribution of the XXAPS due to the excitation of the $3d$ electron to the continuum because the intensity of the primary monochromatic x rays was too weak and the emitted diagram lines would be too weak to be observed in the XXAPS. However, this would be improved if we could use more intense primary x rays such as synchrotron radiation for excitation of the XXAPS.

IV. SUMMARY

The resonant process, which was previously proposed in the electron-excited Sm $M_{4,5}$ emission spectra of Sm and SmB_6, was confirmed by a study of the XXAPS in the Sm $3d$ electron-excitation region. Two peaks were observed in the XXAPS at photon-excitation energies equal to energies of the prominent peaks in the resonant process $3d^{10}4f^n \leftrightarrow 3d^9 4f^{n+1}$, where n is the number of $4f$ electrons in the ground state. In addition to the resonant peak in the M_5 spectral region, the resonant peak in the M_4 spectral region, which was not separately observed from the diagram line M_4N_6 in the electron-excited emission spectra, was clearly observed.

Absorption spectra indicate that the intensity ratio between the two peaks in the XXAPS is 1/0.85. This ratio corresponds well to the intensity ratio of the XXAPS peaks observed in the M_5 and M_4 spectral regions. This fact confirms that the peaks in the XXAPS are caused by the resonant emission process.

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