PHYSICAL REVIEW B VOLUME 34, NUMBER 12 15 DECEMBER 1986

Sm $M_{4,5}$ emission spectra of Sm metal and SmB_6 with fluorescence-excitation and near-threshold electron-excitation methods

Osamu Aita, Kouichi Ichikawa, Makoto Okusawa, and Kenjiro Tsutsumi
College of Engineering, University of Osaka Prefecture, Mozu, Sakai, Osaka 591, Japan

(Received 2 April 1986; revised manuscript received 1 August 1986)

The Sm $M_{4,5}$ fluorescent emission and characteristic isochromat spectra of Sm metal and SmB_6 were measured to obtain information on the valence mixing of SmB_6. It was found that the fluorescent spectra do not exhibit resonant emission, which had been observed in the electron-excited spectra measured with relatively low electron-beam energy. The fluorescent spectrum of SmB_6 is quite similar to that of Sm metal and the fluorescent and characteristic isochromat spectra of SmB_6 show no distinct indication of the spectrum corresponding to the Sm^{2+} ion. The characteristic isochromat spectra at the photon energy of the resonant peak of these materials show that an electron-beam energy beyond 1085 eV is required for the generation of the resonant emission ($3d_{5/2}^{-1}4f^{n+1} \rightarrow 3d^{10}4f^{n}$), where n is equal to 5 for the Sm^{3+} ion. This is ascribed to the formation of the transient state $3d^{9}4f^{n+2}$, which is caused by both the electron excited from the $3d$ level and the incident electron losing the initial energy. The possibility of a valence change from divalent to trivalent is discussed as the reason no distinct indication of the spectrum corresponding to the Sm^{2+} ion in SmB_6 is observed.

I. INTRODUCTION

It has been known that x-ray emission spectroscopy is a useful method for obtaining information on the electronic structure of solids. For this purpose the electron-excitation method has been generally employed to create an initial ionized state with an inner-core electron ejected into the continuum. However, the analysis of the emission spectrum is very complicated in comparison with the absorption spectrum because a number of emission lines of various types, such as resonant emission[1–6] and satellite emission, appear in the spectrum in addition to the ordinary diagram line.

SmB_6 is known to be a mixed-valence compound between Sm^{2+} and Sm^{3+} ions from the measurements of the x-ray photoelectron spectra (XPS),[7,8] Sm L absorption spectra,[9,10] and so on.[11–13] Previously, we have measured the Sm $M_{4,5}$ emission and absorption spectra of SmB_6 and Sm metal to obtain the information on the valence mixing of SmB_6.[6] However, the spectrum of SmB_6 prominently exhibits the resonant peak of the Sm^{3+} ion and shows no distinct indication due to the Sm^{2+} ion.

Under electron bombardment, the inner-core electrons in the target material can absorb any part of the energy of the incident electrons, and thus will be easily excited to the normally unoccupied states. The resonant emission is caused by the recombination of an electron trapped to a localized unoccupied level with an initial core hole, and therefore, the process of the resonant emission is just the inverse process of photoabsorption.[1–6] Since the resonant emission peak is observed at the same energy position as the corresponding absorption peak, the emission spectrum is seriously affected by self-absorption.[6,14,15] Thus, the Sm $M_{4,5}$ emission spectrum which is not affected by self-absorption can be obtained only with lower electron-beam energies and thin specimens, but the ordinary diagram line can not be clearly separated from the resonant emission line because of the relatively high intensity of the resonant emission.[6]

On the contrary, in the case of the fluorescence-excitation method, the electron in the target material must absorb the whole quantum of energy of the incident photons. Since the contribution of photons with the energy of resonant line in the incident continuous radiation is very small relative to the rest of the continuous radiation spectrum and the primary photons penetrate deep into the specimen, resonant emission would not be easily detected with the fluorescence-excitation method.

In the present work, we aimed at studying the Sm $M_{4,5}$ emission spectra of Sm metal and SmB_6 with the fluorescence-excitation method, those spectra not being expected to be influenced by the intense resonant emission, and also at comparing these fluorescent spectra with the electron-excited spectra to obtain the information on the mixed-valence state of SmB_6. In addition to these measurements we measured the Sm $M_{4,5}$ emission spectrum with various electron-beam energies near the threshold, and also measured the characteristic isochromat spectrum on both Sm metal and SmB_6. It is another purpose of the present work to obtain the data on the excitation threshold of the emission lines by electron impact.

II. EXPERIMENT

Fluorescent $M_{4,5}$ emission spectra were obtained with a flat crystal vacuum spectrometer equipped with a fine Soller slit and a potassium acid phthalate (or thallium acid phthalate) crystal (Rigaku Geigerflex 3064M). A rhodium target x-ray tube was operated at 40 kV and 70 mA as a primary x-ray source. 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° 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 SmB_6 were prepared by evaporation onto aluminum substrates and covered by a thin aluminum film successively evaporated on them in order to avoid undesirable oxidation of the specimen.

For the measurements of the electron-excited spectra as well as the isochromat spectra, a different flat crystal vacuum spectrometer was used, which has almost the same resolution as that of the spectrometer used in the measurement of the fluorescent spectra to compare the profiles between the spectra measured with the different excitation methods. In this case, specimens of Sm metal and SmB_6 were prepared by evaporation onto a copper anode and also covered by a thin aluminum film. The Cu $L\alpha_{1,2}$ line was used as a reference line, whose wavelength was taken from the table as 13.336 Å.[16]

III. FLUORESCENT AND ELECTRON-EXCITED SPECTRA

The Sm $M_{4,5}$ emission spectra of Sm metal and SmB_6 are shown in Figs. 1 and 2, respectively. The spectra (a) and (b) were obtained with the fluorescence-excitation method. The spectra (b) were measured by the direct irradiation of the primary x rays onto the surface of the specimen, while the spectra (a) were measured by the use of a thin film of respective substances placed between the specimen and the primary x-ray source to reduce extremely the contribution of the photons with the energy of the resonant line in the incident continuous radiation. The spectra (c) and (d) were obtained with the electron-excitation method and the electron-beam energies are shown on the right-hand side in the figures. The absorption spectra of these substances measured previously[6] are shown by dashed lines for comparison.

Although SmB_6 is considered to be a mixed-valence compound between Sm^{2+} and Sm^{3+} ions, the spectrum of SmB_6 exhibits similar characteristic feature as that of Sm metal, which is almost a trivalent substance. According to the XPS data of SmB_6 by Aono *et al.*,[7] the binding energies of the Sm $3d_{5/2}$ levels of the Sm^{3+} and Sm^{2+} ions

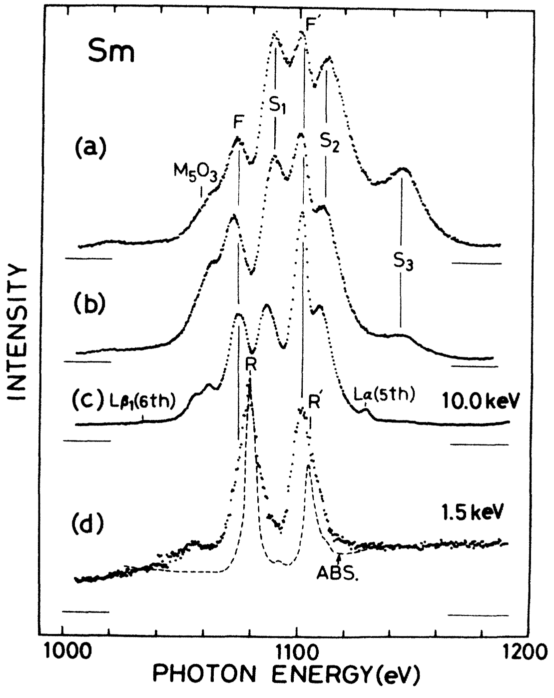


FIG. 1. Sm $M_{4,5}$ emission spectra of Sm metal. The spectra (a) and (b) are the fluorescent spectra obtained by the irradiation of the primary x rays through a thin film of Sm metal and by the direct irradiation of the primary x rays, respectively. The spectra (c) and (d) are the electron-excited spectra obtained with the electron-beam energies of 10.0 and 1.5 keV, respectively. The absorption spectrum measured previously (Ref. 6) is also shown by a dashed line.

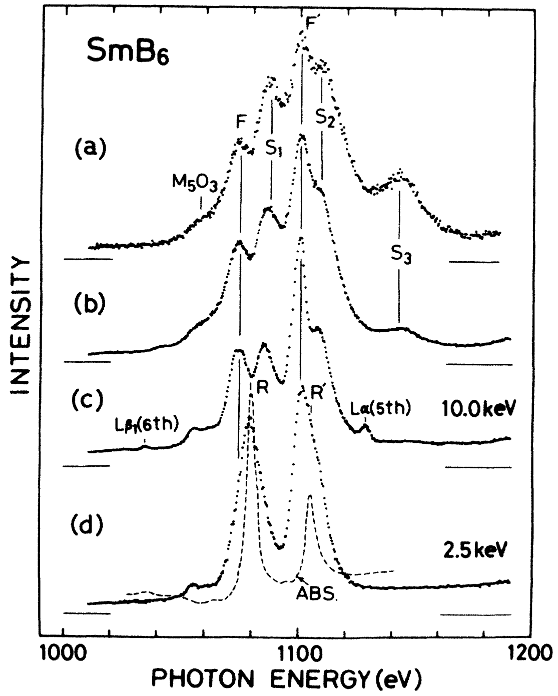


FIG. 2. Sm $M_{4,5}$ emission spectra of SmB_6. The spectra (a) and (b) are the fluorescent spectra obtained by the irradiation of the primary x rays through a thin film of SmB_6 and by the direct irradiation of the primary x rays, respectively. The spectra (c) and (d) are the electron-excited spectra obtained with the electron-beam energies of 10.0 and 2.5 keV, respectively. The absorption spectrum measured previously (Ref. 6) is also shown by a dashed line.

are 1082.2 and 1071.3 eV, respectively, while the Sm $4f$ binding energies of the Sm^{3+} and Sm^{2+} ions are 7.3 and 0.3 eV. Thus, the energy of the $M_5N_{6,7}$ emission line is expected to be located at 1075 eV for the Sm^{3+} ion and at 1071 eV for the Sm^{2+} ion. In the spectra (d) excited with the lowest electron-beam energy in both substances, the humps (F) observed at 1075 eV are attributed to the ordinary radiative transition ($M_5N_{6,7}$ line) from the occupied $4f$ level to the $3d_{5/2}$ level of the Sm^{3+} ion. The peaks (F') observed around 1101 eV in these spectra can be assigned as the M_4N_6 emission line of the Sm^{3+} ion by knowing the spin-orbit splitting of the $3d$ level to be 25.8 eV.[17]

The portions R(1079 eV) and R'(1105 eV) in the spectra (d) of these substances clearly coincide with the absorption peaks. While in the spectra (c) obtained with the electron-beam energy of 10.0 keV, the portions around the energies of the absorption peaks suffer appreciable effects of self-absorption. These facts suggest that the portions R and R' are interpreted as the resonant emissions caused by the transition $3d^94f^6 \rightarrow 3d^{10}4f^5$, as mentioned in the previous paper.[6] We did not clearly observe the ordinary emission line from the occupied $4f$ level to the $3d_{5/2}$ level of the Sm^{2+} ion, which is expected to be located at 1071 eV, though the contribution might be buried in the lower-energy tail of the intense resonant peak and the ordinary $M_5N_{6,7}$ emission line of the Sm^{3+} ion.

A remarkable difference is observed between the fluorescent spectra [(a) and (b) in Figs. 1 and 2] and the electron-excited spectra (d) measured with the lowest electron-beam energy. In the fluorescent spectra, no emission peak is observed at the energy position of the corresponding absorption peak. Moreover, no gross change was detected between the spectrum (b) measured by the direct irradiation of the primary x rays onto the specimen and the spectrum (a) measured by the irradiation through the thin film of respective substances. These facts suggest that even if the photons with the energy of resonant emission in the primary continuous radiation contribute to the excitation of the $3d$ electrons, the resultant resonant emission is too weak to be detected in the fluorescent spectrum. Thus, it is reasonable to consider that the present fluorescent spectra do not exhibit any resonant emission peak.

It is adequate to examine the fluorescent spectrum of SmB_6 to clarify whether the ordinary $M_5N_{6,7}$ emission due to the Sm^{2+} ion could be detected around 1071 eV or not, since the contribution of the resonant emission should be removed in the fluorescent spectrum. The spectra (a) and (b) in Fig. 2, however, do not exhibit clear structure around 1071 eV, but exhibit only the ordinary $M_5N_{6,7}$ emission (F) of the Sm^{3+} ion at 1075 eV. To make further investigation on this point the characteristic isochromat spectra of Sm metal and SmB_6 are presented in the next section.

In the fluorescent spectra the peaks S_1, S_2, and S_3 observed at 1087, 1109, and 1143 eV, respectively, are not interpreted as the ordinary diagram lines. Although the $M_4O_{2,3}$ emission line is located around 1087 eV, the observed peak is too intense in comparison with the M_5O_3 emission line around 1058 eV to be attributed solely to the $M_4O_{2,3}$ emission line because the intensity ratio of the M_5O_3 and $M_4O_{2,3}$ lines should be 3:2 by taking account of the statistical weights of the corresponding subshells.

It is well known that the Coster-Kronig transitions of the type M-MN are greatly enhanced over the competing Auger transitions M-NY, M-XY, where X and Y are the energy levels above the M level, and x-ray transitions M-N and M-Y in the high-atomic-number region.[18] Then, it is suspected that the doubly ionized state with the holes in the $3d$ and $4d$ shells is formed by the Coster-Kronig-type Auger transition $M_{2,3}$-$M_{4,5}N_{4,5}$ after the creation of the $3p$ core hole. Thus, we suggest that the intense satellites S_1 and S_2 may be caused by the $3d^94d^95p^6 \rightarrow 3d^{10}4d^95p^5$ transition. However, it remains to be seen in the future why the satellites S_1 and S_2 are so intense compared with the M_5O_3 ($3d^95p^6 \rightarrow 3d^{10}5p^5$) diagram line, even if the $3d^94d^9$ state is easily produced after the creation of the $3p$ core hole. Also, at present no definite assignment is given to the peak S_3 at 1143 eV, but it is possible that the doubly ionized state with holes in the $3d$ and $4p$ shells formed by the Coster-Kronig-type Auger transition $M_{2,3}$-$M_{4,5}N_{2,3}$ would take part in this peak.

IV. $M_{4,5}$ EMISSION SPECTRA EXCITED WITH ELECTRON-BEAM ENERGIES AROUND THE Sm $3d_{5/2}$ THRESHOLD

The Sm $M_{4,5}$ emission spectra of Sm metal obtained with the various incident electron-beam energies are shown in Fig. 3. The arrows indicate the energies of the incident electron beam. In the spectrum excited with the electron-beam energy of 1500 eV, the emission peak R

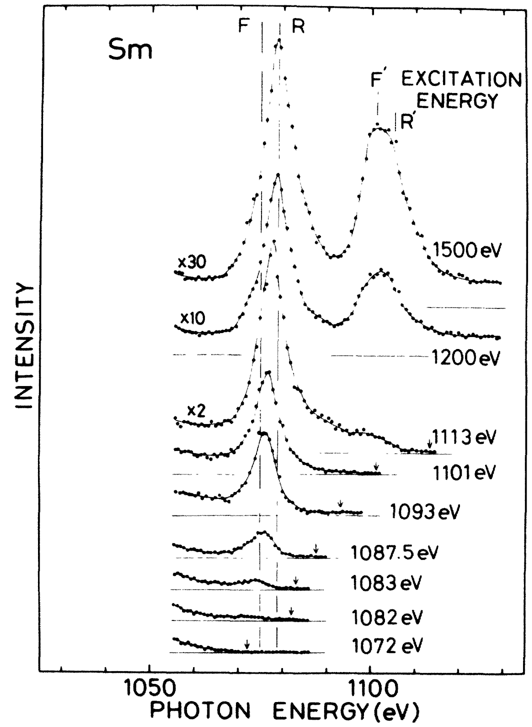


FIG. 3. Sm $M_{4,5}$ emission spectra of Sm metal obtained with various electron-beam energies.

(1079 eV), which coincides with the absorption peak, is assigned as the resonant emission caused by the transition $3d^94f^{n+1}\rightarrow 3d^{10}4f^n$, as mentioned previously. The energy position F (1075 eV) is the place where the ordinary $M_5N_{6,7}$ emission line of the Sm^{3+} ion should be observed. As seen in this figure, the peak at 1075 eV, which begins to rise at the excitation energy of about 1083 eV, gradually increases its intensity and then is buried in the tail of the resonant peak with the increase of the excitation energy. Thus, the peak observed at 1075 eV in Fig. 3 seems to originate from the ordinary $M_5N_{6,7}$ emission of the Sm^{3+} ion. The spectra of SmB_6 shown in Fig. 4 exhibit the similar features as those of Sm metal in spite of the mixed-valence character of SmB_6. It is noticed that no structure was observed around 1071 eV, where the ordinary $M_5N_{6,7}$ emission due to the Sm^{2+} ion is expected to be detected, even if the excitation energy exceeds the $3d_{5/2}$ threshold of the Sm^{2+} ion (1071.3 eV).

In the case of La metal, Liefeld *et al.*[19] have observed a peak on the low-energy side of the resonant peak in the $M_{4,5}$ emission spectrum when the incident-electron-beam energy has been successively increased across the La $3d_{5/2}$ threshold. Moreover, they have found that the intensity of this peak is resonantly enhanced when the continuous (bremsstrahlung) isochromat peak, which reflects the empty $4f$ level located at 5.5 eV above the Fermi level, is overlapped on this peak.[19] Thus, it has been suggested that this peak is interpreted as being due to the emission via an intermediate excited state by the following process:

$$3d^{10}4f^0+e\rightarrow 3d^94f^2\rightarrow 3d^{10}4f^1+h\nu\ , \qquad (1)$$

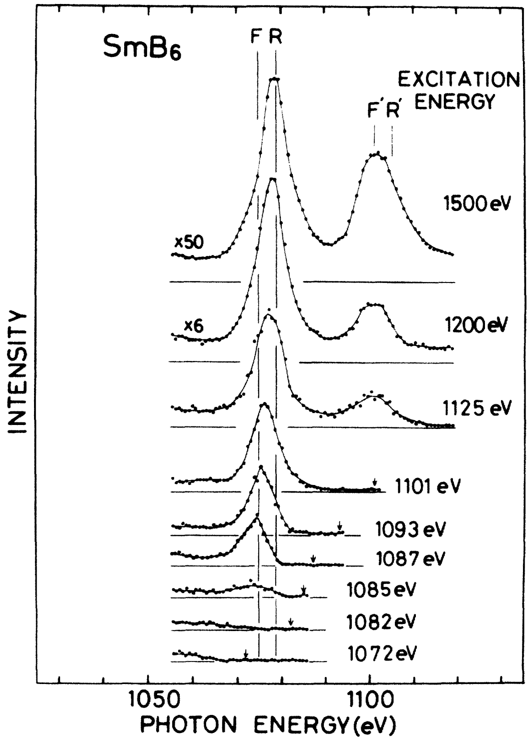


FIG. 4. Sm $M_{4,5}$ emission spectra of SmB_6 obtained with various electron-beam energies.

where e represents an electron impinged to excite the $3d$ electron of La atom. It has been also suggested that this intensity enhancement is due to the interference between the above emission process and the bremsstrahlung emission process

$$3d^{10}4f^0+e\rightarrow 3d^{10}4f^1+h\nu\ , \qquad (2)$$

because the initial and the final states of these two processes are the same.[5,19]

Now, as mentioned before, the peak observed at 1075 eV in Figs. 3 and 4 is interpreted as being due to the radiative transition ($M_5N_{6,7}$ line) from the occupied $4f$ level to the $3d_{5/2}$ level of the Sm^{3+} ion. However, as another possible interpretation of this peak, it is considered that the origin of this peak might be attributed to the successive transition

$$3d^{10}4f^n+e\rightarrow 3d^94f^{n+2}\rightarrow 3d^{10}4f^{n+1}+h\nu\ (1075\ \text{eV})\ , \qquad (3)$$

via the intermediate excited state $3d^94f^{n+2}$ as in the case of La metal reported by Liefeld *et al.*[19] In this case the intensity enhancement of this peak should be detected at the particular incident-electron-beam energy derived from Eq. (3). To confirm this possibility, we measured the characteristic isochromat spectra at the photon energy of 1075 eV for Sm metal and SmB_6. The results are shown in Figs. 5 and 6 with the spectra obtained at the photon energy of 1079 eV. Moreover, the continuum limit spectrum, which provides the information on the unoccupied state above the Fermi level, was measured with the electron-beam energy of 1500 eV as shown in Fig. 7. The abscissa represents the photon energy and also the energy referred to the Fermi level E_F which is placed at 1500 eV in the photon energy. The present continuum limit spectra of Sm metal and SmB_6, and also the bremsstrahlung isochromat spectra measured by other investigators[20,21] suggest that the unoccupied $4f$ level, which is measured as the $3d^{10}4f^6$ state, seems to be located within 8 eV above

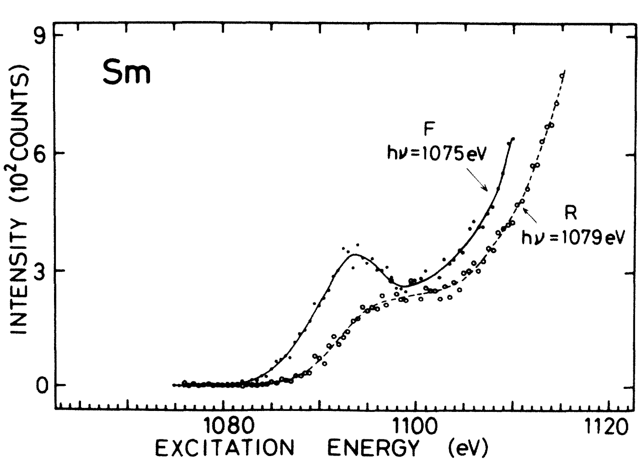


FIG. 5. Characteristic isochromat spectra measured at the photon energies of 1075 eV (F, solid line) and 1079 eV (R, dashed line) for Sm metal.

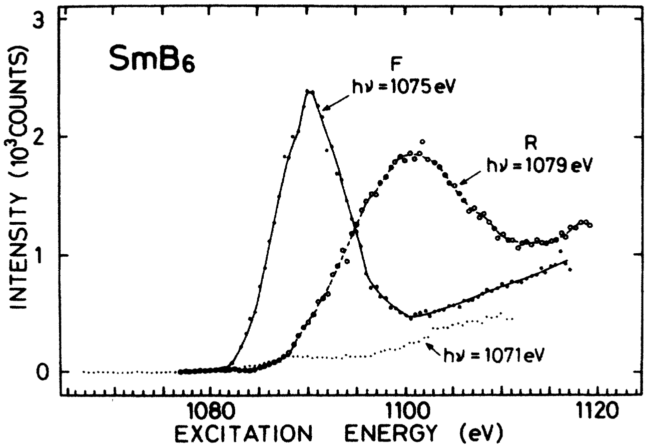


FIG. 6. Characteristic isochromat spectra measured at the photon energies of 1075 eV (*F*, solid line) and 1079 eV (*R*, dashed line) for SmB_6. The characteristic isochromat spectrum measured at the photon energy of 1071 eV is also shown by a dotted line.

the Fermi level in both substances.[22]. Thus, if the peak observed at 1075 eV is caused by the interference between the emission process

$$3d^94f^{n+2} \rightarrow 3d^{10}4f^{n+1} + h\nu \ (1075 \text{ eV})$$

and the bremsstrahlung emission process

$$3d^{10}4f^n \ (\text{ground state}) + e \rightarrow 3d^{10}4f^{n+1}(\sim 8 \text{ eV}) + h\nu ,$$

the resonantly enhanced peak should be expected to be observed around the incident electron-beam energy of 1083 eV in the characteristic isochromat spectrum measured at the photon energy of 1075 eV. However, we did not observe such a resonantly enhanced peak in the characteristic isochromat spectra of both substances, and also the peak *F* at 1075 eV does not reflect merely the unoccupied state above the Fermi level, because this peak seems not to show the energy shift corresponding to the difference of the excitation energy among the spectra in Figs. 3 and 4. Thus we rule out this possibility. The energy of the peak (1075 eV) agrees well with the binding-energy difference between the occupied 4*f* level and the $3d_{5/2}$ level of the Sm^{3+} ion. Then, we attribute this peak to the ordinary $M_5N_{6,7}$ emission line ($3d^94f^5 \rightarrow 3d^{10}4f^4$) in the Sm^{3+} ion.

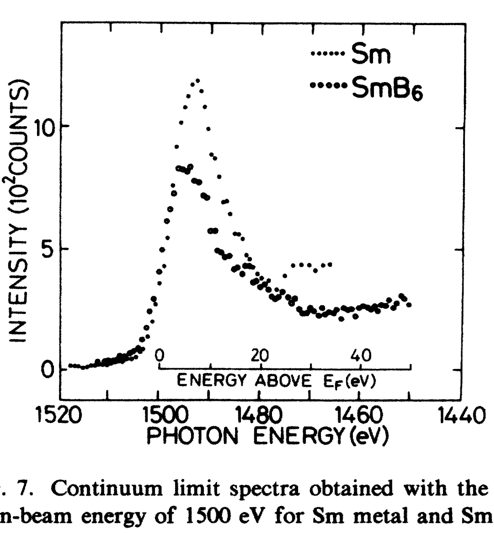
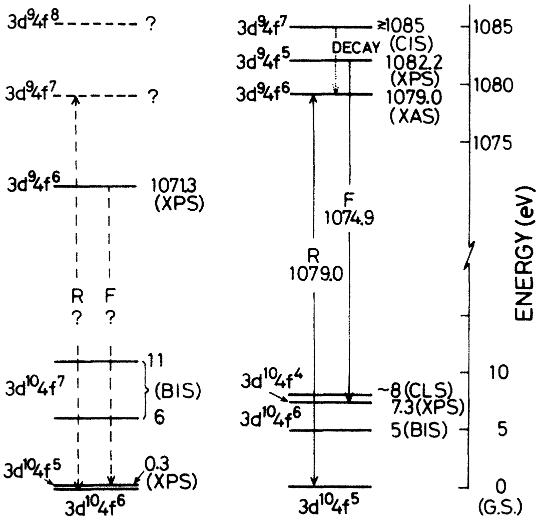


FIG. 7. Continuum limit spectra obtained with the incident electron-beam energy of 1500 eV for Sm metal and SmB_6. The abscissa represents the photon energy and also the energy referred to the Fermi level E_F.

In the case of the characteristic isochromat spectra measured at the photon energy of 1079 eV on Sm metal and SmB_6, the onset of the intensity rise occurs at an incident-electron-beam energy around 1085 eV. It should be noticed that the energy of this onset is larger than the energy of the resonant emission peak (1079 eV) and also exceeds the $3d_{5/2}$ threshold (1082.2 eV) of the Sm^{3+} ion. When an electron impinges on the Sm^{3+} ion to excite a 3*d* electron into an empty 4*f* level, the incident electron remains strongly influenced by the field produced by the sudden creation of a 3*d* core hole, after having spent almost its full energy under the inelastic collision, and is trapped to the empty 4*f* state of the Sm^{3+} ion forming the transient configuration $3d^94f^7$ together with the excited electron. This $3d^94f^7$ state may be above the 3*d* threshold in contrast with the case of La metal,[23] and thus can interact with the empty continuum states, immediately resulting in the creation of the initial configuration of the resonant emission $3d^94f^6$, whose energy (1079 eV) is lower than the $3d_{5/2}$ threshold (1082.2 eV). Then, the resonant emission $3d^94f^6 \rightarrow 3d^{10}4f^5$ occurs. Thus, we believe that the energy beyond the threshold to create the $3d^94f^7$ state, i.e., 1085 eV, is necessary at least for the excitation of the resonant emission by electron impact with the energy near the threshold. The schematic energy-level diagram is illustrated for the better understanding of the excited states of Sm ions in Fig. 8.

The characteristic isochromat spectrum of SmB_6 at a photon energy of 1071 eV was also measured in order to confirm whether the ordinary emission due to the transition $3d^94f^6 \rightarrow 3d^{10}4f^5$ in the Sm^{2+} ion is observed or not. As seen in Fig. 6, 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 Sm^{2+} ion (1071.3 eV). This fact may suggest that the contribution of the ordinary $M_5N_{6,7}$ emission of the Sm^{2+} ion is too small to be observed and is buried in the background. Also, in Figs. 2, 4, and 6 we could not observe the resonant emission of the Sm^{2+} ion in SmB_6. In the case of the electron-excitation method with the electron-beam energy near the threshold, two slow electrons, i.e., the incident electron that lost the initial energy and the electron excited from the 3*d* level, are strongly influenced by the atomic field of the excited atom as described above, and may form the transient state $3d^94f^8$ in the Sm^{2+} ion. This $3d^94f^8$ state may be well above the threshold and immediately decay to the $3d^94f^7$ state after interaction with the empty continuum state. Moreover, as inferred from the energy difference between the $3d^94f^6$ and $3d^94f^7$ states in the Sm^{3+} ion, this $3d^94f^7$ excited state in the Sm^{2+} ion, which is the initial state of the resonant emission of the Sm^{2+} ion, is located several eV



(b) Sm^{2+} (a) Sm^{3+}

FIG. 8. Energy-level diagrams for the Sm^{3+} ion (a), and for the Sm^{2+} ion (b) deduced from the observed peak positions in the various experiments. Each level has some width owing to the exchange interaction. The $3d^{10}4f^{n+1}$ states are obtained from the present continuum limit spectrum and the bremsstrahlung isochromat spectrum (Ref. 21). The $3d^{10}4f^{n+1}$ state of the Sm^{2+} ion has two prominent peaks. (CIS, characteristic isochromat spectrum; XPS, x-ray photoelectron spectrum; XAS, x-ray absorption spectrum; CLS, continuum limit spectrum; BIS, bremsstrahlung isochromat spectrum).

above the $3d_{5/2}$ threshold of the Sm^{2+} ion and thus can interact with the empty continuum state. This interaction might prevent the resonant emission of the Sm^{2+} ion from appearing as a distinct peak.

As another possible reason why the spectrum due to the Sm^{2+} ion is not observed, it is considered that the Sm^{2+} ion is possibly converted into the Sm^{3+} ion through the process in which the empty $5d$ state in the continuum might be filled by the extra electron, that is, the impinged electron or the released electron from the $3d$ level, under the influence of the field due to the $3d$ core hole.[6] Thus, the spectrum due to the Sm^{2+} ion is not clearly observed in the electron-excited spectra. In the fluorescent spectrum of SmB_6, it is still unknown whether the ordinary emission of the Sm^{2+} ion is observed or not. However, it is supposed that it may not be resolved from the intense ordinary emission of the Sm^{3+} ion at 1075 eV.

In the respective characteristic isochromat spectra shown in Figs. 5 and 6, a broad maximum or a plateau is observed about 10 eV above the onset of the intensity rise. This structure seems to be related to the density of empty states above the Fermi level, the excitation probability of the $3d$ electron, the probability of the radiative decay of the core hole, and so many factors. Detailed analysis of the characteristic isochromat spectra will be given elsewhere.

V. SUMMARY

The Sm $M_{4,5}$ fluorescent emission and characteristic isochromat spectra of Sm metal and SmB_6 were measured to obtain the information on the valence mixing of SmB_6. The fluorescent spectra were obtained by using the Rh target x-ray tube as a primary x-ray source, and compared with the electron-excited spectra. It was found that the present fluorescent spectra do not exhibit the resonant emission which has been observed in the electron-excited spectra measured with relatively low electron-beam energies. The fluorescent spectrum of SmB_6 is quite similar to that of Sm metal and shows no distinct indication of the spectrum corresponding to the Sm^{2+} ion, that is, the ordinary emission $M_{4,5}N_{6,7}$ for the Sm^{2+} ion was not observed though the contribution of the intense tail of the resonant emission was removed from this spectral region.

To clarify this problem, we measured the characteristic isochromat spectrum at the photon energy of 1071 eV where the ordinary emission due to the transition $4f \rightarrow 3d_{5/2}$ in the Sm^{2+} ion is expected to be observed. However, the measured isochromat spectrum showed still no clear indication of the ordinary emission corresponding to the Sm^{2+} ion. This fact may suggest that the contribution of the ordinary $M_5N_{6,7}$ emission of the Sm^{2+} ion is too small to be observed or a valence change occurs from divalent to trivalent through the process in which the empty $5d$ state in the continuum might be filled by the extra electron, that is, the impinged electron or the released electron from the $3d$ level, under the influence of the field due to the $3d$ core hole.

The peak was resolved on the low-energy side of the resonant peak in the Sm $M_{4,5}$ emission spectra excited with the electron-beam energies near the $3d_{5/2}$ threshold in both Sm metal and SmB_6. It was confirmed that this peak is not interpreted as the case of lanthanum, that is, the peak is not ascribed to the resonance-type transition

$$3d^{10}4f^5+e \rightarrow 3d^9 4f^7 \rightarrow 3d^{10}4f^6+h\nu ,$$

where e is an impinged electron. This peak was interpreted as the ordinary $M_5N_{6,7}$ emission line ($3d^9 4f^5 \rightarrow 3d^{10}4f^4$) in the Sm^{3+} ion from the XPS data.

The characteristic isochromat spectra measured at the photon energy of 1079 eV, i.e., at the position of the resonant peak for the Sm^{3+} ion, exhibit that the intensity of this peak rises at the electron-beam energy beyond 1085 eV in contrast with the photoabsorption process. This delayed onset of the intensity rise may be attributed to the creation of the transient state with the configuration $3d^9 4f^7$ under the electron excitation with energy near the threshold. Since this state may be well above the Fermi level, its interaction with the empty continuum states might immediately create the initial state of the resonant emission for the Sm^{3+} ion, $3d^9 4f^6$.

ACKNOWLEDGMENTS

The authors wish to thank Rigaku Denki Kogyo Co., Ltd. for providing the opportunity to use the apparatus for collecting the fluorescent emission spectra. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

[1] C. Bonnelle, *Advances in X-Ray Spectroscopy* (Pergamon, New York, 1982), Chap. 6.

[2] C. Bonnelle and R. C. Karnatak, J. Phys. (Paris), Colloq. **32**, C4-230 (1971).

[3] J. M. Mariot and R. C. Karnatak, J. Phys. F **4**, L223 (1974).

[4] R. C. Karnatak and P. M. De Narbonne, Jpn. J. Appl. Phys. Suppl. **17-2**, 127 (1978).

[5] P. Motais, E. Belin, and C. Bonnelle, in *Proceedings of the International Conference on Inner-Shell and X-ray Physics of Atoms and Solids, Stirling, 1980,* edited by D. J. Fabian, H. Kleinpoppen, and L. M. Watson (Plenum, New York, 1981), p. 451.

[6] O. Aita, T. Watanabe, Y. Fujimoto, and K. Tsutsumi, J. Phys. Soc. Jpn. **51**, 483 (1982).

[7] M. Aono, S. Kawai, S. Kono, M. Okusawa, T. Sagawa, and Y. Takehana, Solid State Commun. **16**, 13 (1975).

[8] J.-N. Chazalviel, M. Campagna, G. K. Wertheim, and P. M. Schmidt, Phys. Rev. B **14**, 4586 (1976).

[9] É. E. Vainstein, S. M. Blokhin, and Yu. B. Paderno, Fiz. Tverd. Tela (Leningrad) **6**, 2909 (1964) [Sov. Phys.—Solid State **6**, 2318 (1965)].

[10] M. Okusawa, Y. Iwasaki, K. Tsutsumi, M. Aono, and S. Kawai, Jpn. J. Appl. Phys. Suppl. **17-2**, 161 (1978).

[11] A. Menth, E. Buehler, and T. H. Geballe, Phys. Rev. Lett. **22**, 295 (1969).

[12] R. L. Cohen, M. Eibshutz, and K. W. West, Phys. Rev. Lett. **24**, 383 (1970).

[13] J. C. Nickerson, R. M. White, K. N. Lee, R. Bachmann, T. H. Geballe, and G. W. Hull, Jr., Phys. Rev. B **3**, 2030 (1971).

[14] E. A. Stewardson and J. E. Wilson, Proc. Phys. Soc. London, Sect. A **69**, 93 (1956).

[15] D. W. Fischer and W. L. Baun, J. Appl. Phys. **38**, 4830 (1967).

[16] J. A. Bearden, Rev. Mod. Phys. **39**, 78 (1976).

[17] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

[18] W. Banbynek, B. Crasemann, R. W. Fink, H.-U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. Venugopala Rao, Rev. Mod. Phys. **44**, 716 (1972).

[19] R. J. Liefeld, A. F. Burr, and M. B. Chamberlain, Phys. Rev. A **9**, 316 (1974).

[20] J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F **11**, 121 (1981).

[21] S.-J. Oh and J. W. Allen, Phys. Rev. B **29**, 589 (1984).

[22] The clear difference due to the Sm^{2+} and Sm^{3+} ions was not observed in the present continuum limit spectra of Sm metal and SmB_6. However, the intensity of the tail around 16 eV above the Fermi level is somewhat enhanced in the spectrum of SmB_6. This may represent the $3d^{10}4f^7$ state of the Sm^{2+} ion.

[23] J. Kanski, P. O. Nilson, and I. Curelaru, J. Phys. F **6**, 1073 (1976).