Radiative decay of $4d^9 4f^{n+1}$ excited states in LaB_6 and CeB_6

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The $N_{4,5}$ emission spectra of LaB_6 and CeB_6 were measured to investigate the radiative decay of the $4d^9 4f^{n+1}$ excited states, where n is the number of $4f$ electrons in the ground state. These spectra show an intense and broad emission peak above the $N_{4,5}$ threshold in addition to sharp peaks below the threshold. The energy positions of these emission peaks are compared with those of the peaks in the absorption spectra and the existing results of resonant photoemission. The comparison shows that the fine structure below the threshold coincides in energy with the multiplet structures in the absorption spectrum, and that the intense emission peak is located in the energy region where the electron-emission peak due to the direct recombination of the $4f$ electron with the $4d$ hole has been observed in resonant photoemission. The peaks observed in the energy region below and above the $N_{4,5}$ threshold are attributed to the radiative decay of the $4d^9 4f^{n+1}$ excited states.

I. INTRODUCTION

The soft-x-ray-absorption spectra of rare-earth elements and their compounds show a group of weak and narrow absorption peaks below the $N_{4,5}$ threshold and an intense and broad absorption peak above the threshold.[1-5] These absorption features have been interpreted to be due to the transitions from the ground state $4d^{10}4f^n$ to the various multiplet states with the configuration $4d^9 4f^{n+1}$ (Refs. 6–9), where n is the number of $4f$ electrons in the ground state. Since the exchange interaction between the $4d$ hole and the $4f^{n+1}$ electrons is very strong, the multiplet states spread on both sides of the $N_{4,5}$ threshold. The transition to the multiplet states located above the threshold produces the intense and broad absorption peak characterized by the Fano-type resonance due to the autoionization.[6-9]

Recently, the investigation of the nonradiative decay process of the excited state $4d^9 4f^{n+1}$ has been extensively performed as a function of photon energies with the technique of the resonant photoemission in the energy region around the $N_{4,5}$ threshold.[10-15] The results of the above investigations show that such an excited state decays nonradiatively through the ordinary Auger process and the direct recombination process between the initial $4d$ hole and the $4f$ electron transferring the energy to an electron in the core levels or the valence band.[10-15]

On the other hand, the investigation of the radiative-decay process of the excited configuration $4d^9 4f^{n+1}$ has been made by only a few authors.[16,17] Fomichev *et al.*[16] have measured the $N_{4,5}$ emission spectra of metallic La and Ce with the electron-excitation method and observed the sharp peaks whose energy positions coincide with those of the absorption peaks below the $N_{4,5}$ threshold. The $N_{4,5}$ emission spectra of rare-earth metals from La to Lu obtained by Zimkina *et al.*[17] show a few broad peaks in the energy region around the $N_{4,5}$ threshold. They have interpreted these broad peaks as being due to two types of transitions, i.e., $4d^9 4f^n \rightarrow 4d^{10}4f^{n-1}+h\nu$ and $4d^9 4f^{n+1} \rightarrow 4d^{10}4f^n + h\nu$, because the emission peaks are wider and less definite than the maxima in the absorption spectra.

In the present study the rare-earth $N_{4,5}$ emission spectra of LaB_6 and CeB_6 were measured with the electron-excitation method. In the course of this study the La $N_{4,5}$ absorption spectrum was measured for reference. The purpose of the present study is to confirm whether or not the radiative decay from the multiplet states located above the $N_{4,5}$ threshold is observed as well as the emission from the localized states below the threshold.

II. EXPERIMENTAL PROCEDURES

Measurements were carried out by using a 2 m Vodar-type monochromator equipped with a platinum-coated 1200 lines/mm grating. The spectral window was estimated to be less than 0.4 eV in the energy region concerned. The detector was a windowless electron multiplier with a CsI photocathode and 19 dinodes. Step scanning and photon-counting methods in the control of the microcomputer were employed for the measurements.

In the case of emission measurements, samples were prepared *in situ* by electron-bombardment evaporation onto a Cu target of a Henke-type x-ray tube to avoid any contamination on the sample surface. Thickness of samples was measured with an oscillating-quartz thickness monitor calibrated by Tolansky interferometry. The x rays were taken off at the angle of 90°. The pressure in the x-ray tube was about 4×10^{-6} Pa during the measurements.

Continuous x rays from a tungsten target were used for the absorption measurements. The pressure in a sample chamber was about 1×10^{-6} Pa during the measurements. Absorption films were prepared *in situ* by electron-bombardment evaporation onto silver-coated nitrocellulose films on a nickel mesh.

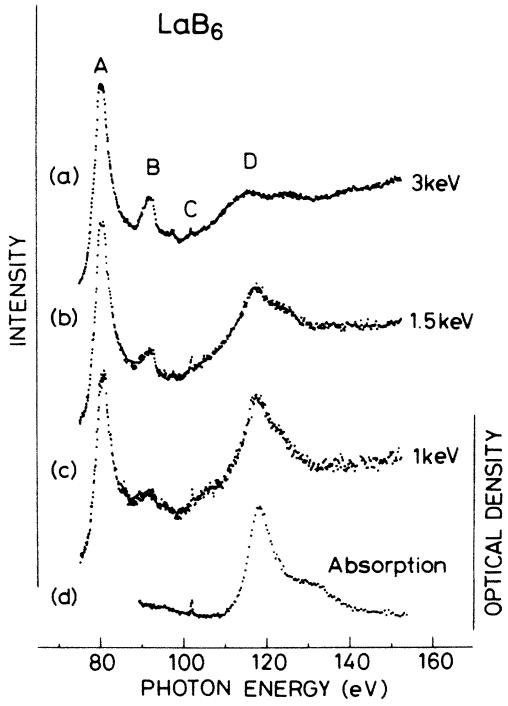

FIG. 1. (a)–(c), La $N_{4,5}$ emission spectra of LaB_6 obtained with various incident electron energies, and (d), the La $N_{4,5}$ absorption spectrum.

III. RESULTS AND DISCUSSION

A. La $N_{4,5}$ emission spectra of LaB_6

Figure 1 shows the La $N_{4,5}$ emission spectra of LaB_6 obtained with the sample of 3600 Å in thickness and also the La $N_{4,5}$ absorption spectrum. The energies of the incident electrons on the sample to excite the emission spectra are indicated on the right-hand side of the spectra. The intense peak A observed around 80 eV in the emission spectra may be caused by the electronic transition from the $5p_{1/2,3/2}$ level to the $4d_{3/2,5/2}$ level, whose binding energies are taken from the energy table by Bearden and Burr.[18] The second-order diffraction of the B K emission, peak B, is observed around 90 eV. The sharp peak C and the broad peak D are observed at about 102 and 117.5 eV, respectively. The intensity of the peak D relative to the peak A, which is caused by the transition between the inner-core levels, increases by decreasing the incident electron energy. This result suggests that the emission spectra are affected by the self-absorption. In fact, the strong absorption due to the electronic transition from the $4d$ level to the empty $4f$ level is observed in this energy region as shown at the bottom of this figure. One notices that the energy positions of the peaks C and D in the emission spectrum excited with 1 keV coincide with those of the absorption peaks. This result and the similarity in the spectral shape between the emission and the absorption spectra suggest that the peaks C and D observed in the emission spectrum are caused by the radiative decay from the excited configuration $4d^9 4f^1$ to the ground-state configuration $4d^{10} 4f^0$, namely, by the transition which is just the inverse process of the electronic transition in the $N_{4,5}$ absorption.

Before further discussions, we consider the possible emission lines arising from the transition between the inner-core levels of the La ion in the energy region concerned. Two emission processes from the $4d$ level to the $4p_{3/2}$ level and from the $4d$ level to the $4p_{1/2}$ level should be observed around 92.5 and 106.1 eV, respectively.[18] One of them overlaps with the peak caused by the second-order diffraction of the B K emission around 90 eV, and the other is observed as the weak shoulder around 106 eV in the spectrum excited with 1 keV.

The emission spectra show the weak peak at 97 eV. In this energy region the x-ray transition from the valence band to the La $4d$ level is expected. The energy-band calculation[19] predicts that the B $2p$ states produce the broad bonding band at about 5 eV below the Fermi level, and the state near the Fermi level is mainly composed of the La $5d$ orbital mixed with a small amount of the B $2sp$ orbitals. In fact, the B K emission spectrum of LaB_6 (Ref. 20) shows a main peak at about 4 eV below the Fermi level which is derived from the B $2p$ orbital and the shoulder at the Fermi level which is derived from the La $5d$ orbital, and has the total width of about 16 eV. On the other hand, the binding energies of the $4d_{3/2}$ and $4d_{5/2}$ levels are 107 and 104 eV, respectively.[12] Thus, the weak peak around 97 eV in the La $N_{4,5}$ emission spectra is assigned to be the valence-band emission. Its weak intensity is due to the localized nature of the La $4d$ level and the interatomic transition from the valence band which is mainly composed of the B $2p$ orbital.

The structures observed in the absorption spectrum of the La ion have been interpreted in terms of the multiplet states, ^3P, ^3D, and ^1P, caused by the exchange interaction between a $4d$ hole and a $4f$ electron at the $4d^9 4f^1$ final-state configuration.[6–9,16] The ^3P and ^3D states, which are located below the $N_{4,5}$ threshold due to the strong coupling between the $4d$ hole and the $4f$ electron, are observed at 97.4 and 101.8 eV, respectively, and give the fine structures in the absorption spectrum. On the other hand, the ^1P state, which is located above the $N_{4,5}$ threshold, is observed at about 118 eV and gives the intense and broad feature in the absorption spectrum because this state can rapidly autoionize to the continuum.[6]

In the present experiment, the electron bombardment is used to create a $4d$ hole in the rare-earth ion. The $4d^9 4f^1$ configuration is created by the direct excitation of the $4d$ electron or by trapping the incident electron to the empty $4f$ level after the excitation of the $4d$ electron, because the incident electron can continuously lose its kinetic energy exciting core electrons and/or valence electrons. Moreover, an empty $4f$ level can be filled by an electron from the valence band with a stabilization of energy because it is pulled down below the $N_{4,5}$ threshold in the presence of the $4d$ hole on the analogy to the $3d$ excitation in La metal.[21,22] Therefore, the radiative decay from the ^3D state to the ground state is observed in the $N_{4,5}$ emission spectra as the peak C. The emission intensity of the transition from the ^3P state may be very weak compared with that

from the ^3D state as expected from the absorption spectrum. Moreover, the emission from the valence band is observed in the energy region where the emission from the ^3P state is expected. Thus, the emission from the ^3P state is not clearly observed.

In the case of the excited state $4d^9 4f^1$ (^1P), the situation is more complicated. Since the ^1P state is located at about 10 eV above the $N_{4,5}$ threshold and there is a strong coupling between the discrete level and the continuum state,[6-9] the autoionization process can take place in contrast with the case of the ^3P and ^3D states.

Aono *et al.*[11,12] have measured the resonant photoemission of LaB_6 with the excitation-photon energies near the $N_{4,5}$ threshold and shown that the excited state $4d^9 4f^1$ (^1P) decays through the ordinary Auger processes and the direct recombination processes accompanied by electron emissions from the inner-core levels or the valence band, i.e.,

$$4d^9 4f^1(5s^2 5p^6 V^m) \rightarrow 4d^{10} 4f^0(5s^1 5p^6 V^m) + e \ ,$$
$$\rightarrow 4d^{10} 4f^0(5s^2 5p^5 V^m) + e, \text{ or}$$
$$\rightarrow 4d^{10} 4f^0(5s^2 5p^6 V^{m-1}) + e \ ,$$

where V denotes the valence band, m the number of valence electrons, and e the ejected electron. In addition to the above direct recombination processes, the $N_{4,5}$-$O_1 V$ and $N_{4,5}$-$O_{2,3} V$ Auger decay processes are also observed. The excitation-photon energy dependence of the electron emission shows the maximum at about 117 eV for the direct recombination processes and at about 119 eV for the Auger decay processes. This result of the direct recombination processes leads us to expect the radiative-decay process from the $4d^9 4f^1$ (^1P) state to the ground state, i.e.,

$$4d^9 4f^1 \rightarrow 4d^{10} 4f^0 + h\nu$$

(about 117.5 eV), because the $f \rightarrow d$ transition is optically allowed. Moreover, in contrast with the spectra measured by Zimkina *et al.*,[17] we do not need to consider the transition from the $4d^9 4f^n$ state to the $4d^{10} 4f^{n-1}$ state, because LaB_6 has no $4f$ electron in the ground state. Therefore, we conclude that the peak D in the emission spectra is caused by the radiative decay from the excited state $4d^9 4f^1$ (^1P) to the ground state.

B. Ce $N_{4,5}$ emission spectra of CeB_6

Figure 2 shows the Ce $N_{4,5}$ emission spectra of CeB_6 obtained with the sample of about 600 Å in thickness and with the incident electron energies of 1, 1.5, and 3 keV. The partial yield spectrum of CeB_6, which has been measured by Sugawara *et al.*[13] for photoelectrons with a kinetic energy of 8 eV, is also shown at the bottom of this figure. In general the partial yield spectrum is considered to show the similar structures as those in the absorption spectrum.[23]

The peak A observed at about 85 eV in the emission spectra is caused by the electronic transition from the $5p$ level to the $4d$ level, and the shoulder B around 95 eV by the transition between the $4d$ and $4p_{3/2}$ levels overlapping with the second-order diffraction of the B K emission.

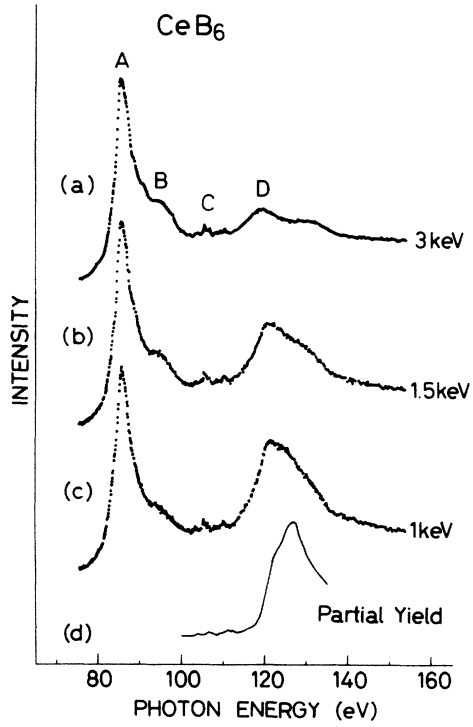

FIG. 2. (a)–(c), Ce $N_{4,5}$ emission spectra of CeB_6 obtained with various incident electron energies, and (d), the La $N_{4,5}$ partial yield spectrum obtained by Sugawara *et al.* (Ref. 13).

The shoulder around 115 eV may be assigned as the $4d \rightarrow 4p_{1/2}$ transition, because the energy difference between the $4d$ and $4p_{1/2}$ levels is 113.3 eV according to Bearden and Burr.[18] In the energy region labeled C, several sharp peaks are observed in the emission spectra. The broad peak D is observed at about 119 eV in the spectrum excited with 3 keV and shifts to 122 eV in the spectrum excited with 1 keV.

Since CeB_6 has nominally one $4f$ electron in the ground state, the electronic transition from the $4d^9 4f^1$ state to the $4d^{10} 4f^0$ state must be expected. According to Sugawara *et al.*[13] the $4f$ level is observed at 2.5 eV below the Fermi level. Though there is no experimental data on the $4d$ states in CeB_6, the x-ray photoelectron spectrum of the $4d$ states in γ-Ce, which has nominally one $4f$ electron, shows a few multiplet structures in the binding-energy range between 104.3 and 113.5 eV (Ref. 24). Thus, we expect that the ordinary x-ray emission due to the transition from the normally occupied $4f$ level to the $4d$ hole may occur in the energy range between 101.8 and 111.0 eV. Moreover, the structures in this emission, which must reflect the interaction between a $4f$ electron and a $4d$ hole at the initial state of the x-ray transition, may be similar to those in the La $N_{4,5}$ absorption spectrum of LaB_6, because the configuration of the initial state of the ordinary x-ray emission is the same as that of the final state of the La $N_{4,5}$ absorption. In this energy range several sharp peaks are observed in the emission spectrum excited with 1 keV in Fig. 3, where the detailed

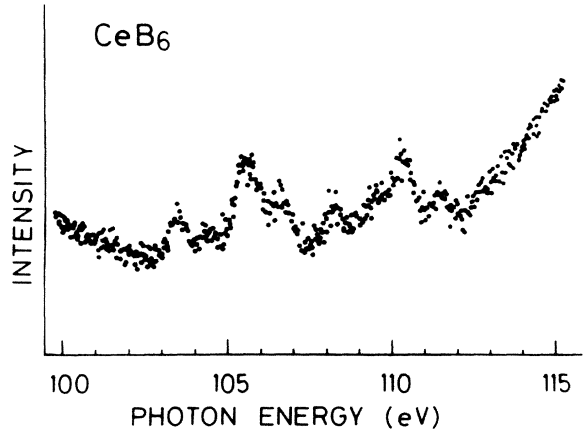

FIG. 3. Ce $N_{4,5}$ emission spectrum in the energy range between 100 and 115 eV.

structures in the energy range between 100 and 115 eV are shown in the expanded scale. However, the structures of the spectrum of CeB_6 in this energy range are quite different from the multiplet structures observed in the La $N_{4,5}$ absorption spectrum and show complicated structures.

In this energy region the other two emission processes are considered. One of them is the valence-band emission reflecting the B $2sp$ orbitals, and the other is the radiative decay from the $4d^9 4f^{n+1}$ states as in the case of LaB_6. However, the former does not contribute to the fine structures, because the valence-band emission does not show the fine structures, as inferred from the B K emission spectrum[20] and the photoelectron spectrum of this substance.[13]

In the partial yield spectrum several multiplet structures of the $4d^9 4f^2$ states are clearly seen in the energy range between 102 and 113 eV. Such fine structures are also seen in the emission spectrum in Fig. 3, although the energy positions of these structures slightly shift to the low-energy side from those observed in the partial yield spectrum. The small discrepancy in the energy positions of the structures is probably due to the different monochromator calibrations. Apart from the small discrepancy in the peak positions, there is fairly good correspondence between the present emission spectrum and the partial yield spectrum, although the intensity distribution among the peaks is different between these two spectra. Therefore, the fine structures between 102 and 113 eV in the emission spectra may be caused by the radiative decay from the $4d^9 4f^2$ state to the $4d^{10} 4f^1$ state and the ordinary emission from the $4d^9 4f^1$ state to the $4d^{10} 4f^0$ state may hardly contribute to the spectrum. The transition from the valence band may only contribute to the spectral distribution in this energy region with a smooth background as mentioned above.

Next we consider the origin of the intense and broad peak D. This peak is observed at about 119 eV in the emission spectrum excited with the incident electron energy of 3 keV and shifts to 122 eV in the spectrum excited with 1 keV as mentioned before. This suggests that the spectral profile of this peak is distorted by the self-absorption when the specimen is excited with high-energy electrons. However, the peak position obtained with 1.5 keV is almost the same as that obtained with 1 keV, and thus the spectrum excited with 1 keV may be hardly affected by the self-absorption.

The partial yield spectrum shows a broad peak at about 127 eV (Ref. 13), and this energy position does not coincide with that of the peak D in the emission spectrum excited with 1 keV in contrast with the case of LaB_6. Sugawara *et al.*[13] have measured the excitation-photon energy dependence of the Ce $5p_{3/2}$ and Ce $4f$ electrons and also the $N_{4,5}$-$O_1 V(N_{6,7})$ and $N_{4,5}$-$O_{2,3} V(N_{6,7})$ Auger electrons in CeB_6 around the excitation-photon energy of the $N_{4,5}$ threshold. They have shown that the $4d^9 4f^2$ state excited with the excitation-photon energy around 127 eV, where the main peak of the partial yield spectrum is observed, decays mainly through the Auger processes and hardly decays through the direct recombination process, while the $4d^9 4f^2$ state excited with the excitation-photon energy around 123 eV decays mainly through the direct recombination processes and the Auger process hardly contributes to the decay of this state. Then it should be considered that the electron excited to this $4d^9 4f^2$ state with energy around 123 eV may radiatively recombine with the $4d$ hole and causes the x-ray emission in addition to the electron emission due to the nonradiative direct recombination. In fact, the energy position of the peak D in Fig. 2 nearly coincides with that of the 123-eV peak in the spectrum of the resonant photoemission. Therefore, we conclude that the peak D at 122 eV in the x-ray emission spectra is caused by the radiative recombination between the $4f$ electron and the $4d$ hole, $4d^9 4f^{n+1} \rightarrow 4d^{10} 4f^n + h\nu$. The difference in the energy positions of the main peaks between the emission and the partial yield spectra is understood from the fact that, in the discussion mentioned above, the x-ray emission is related to the $4d^9 4f^2$ state which decays only through the direct recombination process but the partial yield spectrum reflects the $4d^9 4f^2$ states which decay through both of the direct recombination and the Auger decay processes.

In the case of LaB_6, both the Auger and the direct recombination decay processes have a maximum at nearly the same excitation-photon energy where the absorption peak is observed.[12] This may originate from the fact that the ^1P state is the only optically allowed state among the multiplet terms derived from the $4d^9 4f^1$ configuration located above the $N_{4,5}$ threshold, whereas in the case of CeB_6 many optically allowed states exist in the energy region concerned.[6] Thus, to interpret the present x-ray emission spectrum of CeB_6, the electron excited to some of multiplet states should radiatively recombine with the $4d$ hole and emit the x rays. In other words, the x-ray emission peak due to the radiative decay process from the $4d^9 4f^{n+1}$ states is observed only in the energy region where the nonradiative decay process due to the direct recombination of the $4f$ electron with the $4d$ hole occurs in the resonant photoemission.

IV. SUMMARY

The $N_{4,5}$ emission spectra of LaB_6 and CeB_6 were measured to investigate the radiative decay from the $4d^9 4f^{n+1}$ states. The measurements were performed with the low-energy electron incident on thin samples to minimize the influence of the self-absorption. The emission spectra of both substances show the intense and broad peak above the $N_{4,5}$ threshold in addition to the fine structures below the threshold where the multiplet structures are observed in the absorption spectrum. The fine structures in the emission spectra are attributed to the radiative decay of the $4d^9 4f^{n+1}$ to the $4d^{10} 4f^n$ states. The energy position of the intense and broad peak in the emission spectrum of LaB_6 nearly coincides with that of the giant absorption peak. On the other hand, in the case of CeB_6 the energy position of the intense peak is a few electron volts lower than that observed in the partial yield spectrum. These intense and broad emission peaks are also compared with the existing results of the excitation-photon energy dependence of the inner-core electrons and the $4f$ electron in the resonant photoemission of LaB_6 and CeB_6, and are interpreted to be due to the radiative decay from the $4d^9 4f^{n+1}$ state to the ground state. This conclusion implies that the radiative decay process from the excited state located above the $N_{4,5}$ threshold is expected in the energy region where the nonradiative decay process due to the direct recombination between the $4f$ electron and the $4d$ hole occurs, even though the interaction between the localized $4d^9 4f^{n+1}$ level and the continuum state is strong and the autoionization channels are present.

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