Direct recombination and Auger deexcitation channels of La $4d \rightarrow 4f$ resonant excitations in LaB_6

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La $4d^9 4f^1$ excited states ($^1P_1$, $^3D_1$, and $^3P_1$) created by resonant photoexcitations $h\nu + 4d^{10} \rightarrow 4d^9 4f^1$ decay via direct recombination and Auger deexcitation channels as revealed from a photon energy dependence of photoemission spectra of LaB_6. The Auger deexcitation channel is dominant for $^3D_1$ and $^3P_1$ excited states below the $4d$ core-level threshold, while for the $^1P_1$ excited state above the threshold both channels are important to a comparable extent.

I. INTRODUCTION

The optical absorption spectra of solids containing rare-earth elements with an incompletely filled $4f$ shell show a group of weak narrow absorption peaks below the one-electron $4d$ core-level threshold and a broad strong absorption feature at ~10–20 eV above the threshold.[1–3] These spectral characteristics are interpreted as $4d \rightarrow 4f$ resonant excitations from the ground state $4d^{10}4f^n$ to various multiplet terms with a configuration $4d^9 4f^{n+1}$.[4–7] Because of a strong exchange interaction between the $4f^{n+1}$ electrons and the $4d$ hole, some of the multiplet terms have higher excitation energies than the one-electron $4d$ threshold and produce the broad strong absorption feature above the threshold. The broadening of the absorption feature above the threshold has been interpreted as due to autoionization decay of the $4d^9 4f^{n+1}$ configuration into other configurations.[4–7] Recently, photoemission spectra of γ-Ce,[8] CeP_5O_{14},[9] $(La,Ce)P_5O_{14}$,[9] and SmS[10] were measured as functions of photon energy, and it was found that emission from rare earth $5s$, $5p$, and $4f$ core levels as well as valence bands were strikingly enhanced at photon energies corresponding to the broad strong optical absorption feature above the threshold. This indicates that the excited configuration $4d^9 4f^{n+1}$ decays via direct recombination processes accompanied by emission from rare earth $5s$, $5p$, and $4f$ core levels as well as valence bands, i.e.,

$$\begin{aligned} 4d^9 4f^{n+1}(5s^2 5p^6 V^m) &\rightarrow 4d^{10}4f^n(5s^1 5p^6 V^m) + e \\ &\rightarrow 4d^{10}4f^n(5s^2 5p^5 V^m) + e \\ &\rightarrow 4d^{10}4f^{n-1}(5s^2 5p^6 V^m) + e \\ &\rightarrow 4d^{10}4f^n(5s^2 5p^6 V^{m-1}) + e \end{aligned}$$

where V denotes the valence levels, and e denotes the ejected electron. In the above and ensuing equations, unless needed for clarity we do not explicitly denote final-state screening charge(s). In the present study, we have made a similar experiment for the metallic lanthanum compound LaB_6 and have found that in addition to the direct recombination processes mentioned above, various Auger deexcitation processes including

$$\begin{aligned} 4d^9 4f^1(5s^2 5p^6 V^m) &\rightarrow 4d^{10}4f^{*1}(5s^1 5p^6 V^{m-1}) + e \\ &\rightarrow 4d^{10}4f^{*1}(5s^2 5p^5 V^{m-1}) + e \\ &\rightarrow 4d^{10}4f^{*1}(5s^2 5p^6 V^{m-2}) + e \end{aligned}$$

are also comparably important. Here $4f^{*1}$ denotes an electron which has been released from the exchange interaction with the $4d$ hole and enters an empty conduction band. In addition, the decay mechanisms for the $4d^9 4f^1$ excited states corresponding to the weak narrow optical absorption peaks below the $4d$ threshold have also been studied, and it has been found that although both the direct recombination and Auger deexcitation processes exist, the latter is dominant. LaB_6 is a convenient rare-earth compound for the present purpose in that constituent boron gives no core-level photoemission peak in the energy range of concern and that surface oxides can be easily removed by high-temperature heating under ultrahigh vacuum, unlike elemental rare earths.

II. EXPERIMENTAL

A single crystal of LaB_6 was grown by the floating zone method, and a thin slice ($\sim 6 \times 6 \times 0.5$ mm^3) parallel to (001) was cut and polished mechanically. Photoelectron energy distribution and photoemission partial yield spectra were measured using a double-stage cylindrical mirror analyzer (PHI model 250) and photons from the 240-MeV electron storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The total energy resolution of the system was ~0.6 eV at photon energies of ~100 eV. The sample was cleaned by heating to ~1800 K and measured with a working pressure of $\sim 8 \times 10^{-11}$ Torr (the pressure rose to $\sim 5 \times 10^{-9}$ Torr during heating and recovered to the 10^{-11} Torr range within 10 sec after heating).

III. RESULTS AND DISCUSSION

In a preliminary photoemission experiment, the La $4d_{3/2}$ and $4d_{5/2}$ core levels in LaB_6 have been observed at 107.0 and 104.0 eV below the Fermi level E_F, respectively (the spin-orbit splitting is 3.0 eV). That is, the one-electron La $4d$ core-level threshold in LaB_6 is 104.0 eV. As we will see later, the La $5p_{1/2}$, $5p_{3/2}$, and $5s$ core levels in LaB_6 are located at 20.2, 18.0, and 35.3 eV below E_F, respectively, and valence and filled conduction bands formed by the B $2s$ and $2p$ and La $5d$ and $6s$ valence orbitals extend from E_F to $\sim$12 eV below E_F. The B $1s$ core level is located at -188 eV relative to E_F.[11] It is theoretically predicted that the one-electron La $4f$ empty levels in LaB_6 form narrow bands located at $\sim$3 eV above E_F.[12]

In order to know La $4d \rightarrow 4f$ resonant excitation energies in LaB_6, a photoemission partial yield spectrum (Fig. 1) of LaB_6 was measured by setting the kinetic energy E_K of measured secondary electrons at 11 eV and by scanning the incident photon energy $h\nu$ in the range 90 eV $\lesssim h\nu \lesssim$ 140 eV, which includes the one-electron La $4d$ threshold 104.0 eV. Because of general similarity between photoemission partial yield spectra and corresponding optical absorption spectra[13] and the atomic nature of the La $4d \rightarrow 4f$ resonant excitations, the spectral features of Fig. 1 are essentially the same as those of optical absorption spectra of metallic La, $LaCl_3$, and LaF_3.[3] Because of a strong exchange interaction between the $4f$ electron excited and the $4d$ hole left behind, the spectrum in Fig. 1 extends above and below the one-electron $4d$ threshold 104.0 eV by over $\sim$20 eV. In Fig. 1, two weak narrow peaks at $h\nu = 97.5$ and 101.8 eV and a broad strong feature which has its maximum at $h\nu = 118.5$ eV are due to the $4d \rightarrow 4f$ resonant excitations from the $4d^{10}$ ground state $^1S_0$ to $4d^9 4f^1$ excitonic excited states $^3P_1$, $^3D_1$, and $^1P_1$, respectively,[4-7] as labeled in the figure. According to dipole transition selection rules, practically all the oscillator strength goes into the $^1S_0 \rightarrow {}^1P_1$ transition, but a slight admixture of $^1P_1$ into $^3P_1$ and $^3D_1$ produces the weak $^3P_1$ and $^3D_1$ peaks; dipole transitions of the type $4d^{10}(^1S_0) \rightarrow 4d^9 4f^1$ lead to $J = 1$ excited states which, in intermediate coupling, are linear combinations of $^1P_1$, $^3D_1$, and $^3P_1$. The intensity ratio of the $^3P_1$ peak to the $^3D_1$ peak, $\sim$1:7, agrees with an *ab initio* calculation (1:6.7)[7] for free La^{3+} but is lower than a scaled calculation (1:11.1).[6,7]

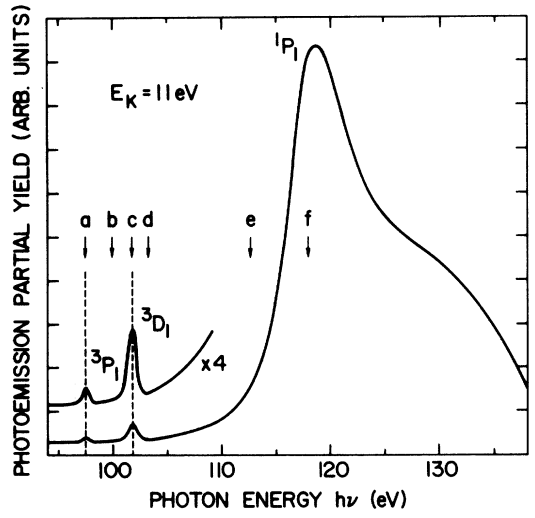

FIG. 1. Photoemission partial yield spectrum of LaB_6 (001) taken by setting the kinetic energy E_K of measured seondary electron at 11 eV and by scanning the photon energy $h\nu$ in the range 90 eV $\lesssim h\nu \lesssim$ 140 eV. Weak narrow peaks at $h\nu = 97.5$ and 101.8 eV and a broad strong feature having a maximum at $h\nu = 118.5$ eV are due to La $4d \rightarrow 4f$ resonant excitations from the $4d^{10}$ ground state $^1S_0$ to $4d^9 4f^1$ excited states $^3P_1$, $^3D_1$, and $^1P_1$, respectively. Arrows $a,b,\ldots,f$ show photon energies at which photoemission spectra in Fig. 2 were measured.

Shown in Fig. 2 are selected photoemission spectra of LaB_6 as a function of photon energy $h\nu$. The spectra $a,b,\ldots$, and f were measured at $h\nu$'s indicated by arrows $a,b,\ldots$, and f in Fig. 1, respectively, and are normalized with respect to incident photon flux. Three peaks at initial energies $E_i = -20.2$, -18.0, and -35.3 eV relative to E_F correspond to emission from the La $5p_{1/2}$, $5p_{3/2}$, and $5s$ core levels, respectively, and the features from E_F to $E_i \simeq -12$ eV correspond to emission from the valence and filled conduction bands. Striking spectral changes are observed in the spectra f, e, c, and a which were measured at resonant $h\nu$'s corresponding to the broad strong feature ($^1P_1$ feature) and the weak narrow peaks ($^3P_1$ and $^3D_1$ peaks) of Fig. 1. The other spectra (d,b) which were measured at off-resonant $h\nu$'s are very similar to each other and will be called "normal spectra" in the following.

In the spectra f and e, which were measured at resonant photon energies $h\nu = 118.0$ and 112.7 eV within the broad strong $^1P_1$ absorption feature of Fig. 1, the La $5s$ and $5p$ core level emission peaks are strongly enhanced. This can be interpreted by direct recombination decay processes of the excited configuration $4d^9 4f^1$ accompanied by emission from the La $5s$ and $5p$ core levels, i.e.,

$$4d^9 4f^1(5s^2 5p^6) \rightarrow 4d^{10} 4f^0(5s^1 5p^6) + e$$
$$\rightarrow 4d^{10} 4f^0(5s^2 5p^5) + e$$

A similar but much weaker enhancement is also observed for the spectra c and a which were measured at the $^3D_1$ and $^3P_1$ absorption peaks with $h\nu = 101.8$ and 97.5 eV, respectively.

By comparing spectra f and e measured at resonant photon energies $h\nu = 118.0$ and 112.7 eV correspond-

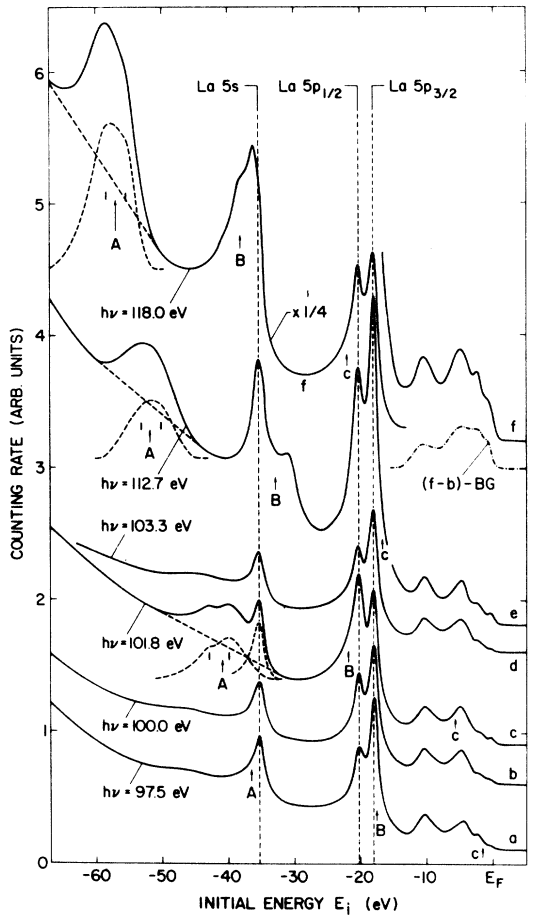

FIG. 2. Photoemission spectra for LaB_6 (001) as a function of photon energy. The spectra $a,b,\ldots,f$ were measured at photon energies indicated by arrows $a,b,\ldots,f$ in Fig. 1, respectively, and are normalized with respect to incident photon flux. Broken curves show the shape of some spectral peaks by subtracting a linear background. The dash-dotted curve labeled $(f-b)-\mathrm{BG}$ is the difference spectrum between spectra f and b with a linear background subtracted. As for arrows A, B, and C, see the text.

ing to the broad strong $^1P_1$ feature of Fig. 1 with the normal spectra d and b, one observes that the emission from the valence and filled conduction bands is also enhanced via the direct recombination decay process

$$4d^9 4f^1(V^m) \rightarrow 4d^{10}4f^0(V^{m-1}) + e \ .$$

The dash-dotted curve labeled $(f-b)-\mathrm{BG}$ (background) in Fig. 2 shows the difference spectrum between spectrum f and the normal spectrum b in the valence and filled conduction-band region with a linear background BG subtracted. This difference spectrum indicates that the region $E_i \gtrsim -3$ eV is much more strongly enhanced than the region $E_i \lesssim -3$ eV. In the direct recombination process mentioned above, the La-derived valence orbitals ($5d$ and $6s$) should play a more significant role than the B-derived valence orbitals ($2s$ and $2p$). The nonuniform enhancement in the valence and filled conduction-band region, therefore, indicates that the La-derived valence orbitals mainly mix into the region $E_i \gtrsim -3$ eV. This is consistent with a recent $X\alpha$-APW (augmented plane wave) energy-band calculation for LaB_6.[14] It is reasonable to expect a similar enhancement for the spectra c and a, which were measured at the $^3D_1$ and $^3P_1$ absorption peaks with $h\nu = 101.8$ and 97.5 eV, but the enhancement could not be detected because of its weakness.

In addition to the spectral enhancement discussed above, three extra peaks with fine structure appear in each spectrum (except for the normal spectra d and b) as indicated by arrows A, B, and C. Although these extra peaks often overlap the La $5s$ and $5p$ core-level peaks, apparent changes in relative intensity of the core-level peaks show that they exist for all the spectra other than d and b. Although peak C is practically invisible in the spectra c and a, its existence is expected from a discussion given below. The peaks A, B, and C are shifted from one spectrum to another such that their kinetic energies are nearly independent of $h\nu$ (the arrows A, B, and C show positions of constant kinetic energy: 61, 80, 96 eV, respectively). From this fact and a consideration of the binding energies of the La $4d$, $5s$, and $5p$ core levels and La-derived valence orbitals, we attribute the peaks A, B, and C to $N_{4,5}O_1V$, $N_{4,5}O_{2,3}V$, and $N_{4,5}VV$ Auger deexcitations of the excitonic excited states $4d^9 4f^1$, respectively. These are not ordinary Auger transitions in that the $4d^9 4f^1$ excited states ($^1P_1$, $^3D_1$, and $^3P_1$) have a strong exchange interaction between the $4f^1$ electron and the $4d$ hole and are different from the Auger transition with a single-hole excited state $4d^9$ as the initial state of the ordinary Auger transitions. Namely, the exchange interaction results in the creation of a $4d$ hole in the form of $4d^{10}4f^1$ at the $^3D_1$ and $^3P_1$ resonant photon energies $h\nu = 101.8$ and 97.5 eV *below* the one-electron $4d$ threshold 104.0 eV, and Auger deexcitations of the $4d^9 4f^1$ excited states produce the peaks A, B, and C in the spectra c and a. At other off-resonant $h\nu$'s below 104.0 eV, there is no mechanism for exciting $4d$ holes, and hence peaks A, B, and C are not observed in the normal spectra d and b measured at $h\nu = 103.3$ and 100.0 eV. The $N_{4,5}O_1V$, $N_{4,5}O_{2,3}V$, and $N_{4,5}VV$ Auger deexcitation processes responsible for the peaks A, B, and C are expressed as

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

respectively, where $4f^{*1}$ represents an electron which

has been released from the exchange interaction with the $4d$ hole and enters an empty conduction band. The exchange interaction between the $4f^*$ electron and the $5s$, $5p$, or valence band hole after the Auger deexcitation is much weaker since the electron and hole belong to different atomic shells.

In Fig. 2, peak A consists of two peaks separated by 3 eV as indicated by short vertical lines, which are due to the spin-orbit splitting of the $N_{4,5}(4d_{3/2,5/2})$ levels. The kinetic energies of the peaks are shifted by $\sim$0.5 eV to the higher kinetic energy side in spectrum c compared with spectra e and f. This shift can be basically interpreted by the fact that the nature of the excited $4f^1$ electron is different for the two cases. It is convenient for discussion to consider the difference between the kinetic energy of peak A, E_K^A, and that of the ordinary $N_{4,5}O_1V$ Auger electrons, E_K^{Auger} This difference $\delta E_K^A \equiv E_K^A - E_K^{\text{Auger}}$ is negative for spectrum c measured with $h\nu$ at the $^3D_1$ absorption peak, because the strong negative exchange energy between the localized excited $4f$ electron and the $4d$ hole is considerably released after Auger deexcitation to yield a $4f^{*1}$ electron and $5s$ hole pair (the change in Coulomb energy of the $4f$ electron plays a minor role). On the other hand, for spectra f and e measured with $h\nu$'s within the broad $^1P_1$ absorption feature above the $4d$ threshold, the excited $4f^1$ electron strongly interacts with the continuum excitation and is less localized. Therefore, the Auger deexcitation process resembles more closely the ordinary Auger decay and δE_K is expected to be smaller. Qualitatively, this explains the direction of shift of the Auger kinetic energy: lower kinetic energy for photoexcitation below threshold. A quantitative calculation is not yet available.

It is interesting to note that the direction of shift is opposite to that observed for other systems,[15–17] e.g., Xe (Ref. 17) which has the same electronic ground state configuration as that of a La^{3+} ion. In the case of Xe, the shift of $N_{4,5}O_{2,3}O_{2,3}$ Auger lines to higher kinetic energy with resonant excitation $4d \rightarrow np\,(n \geq 6)$ below threshold is due to the increase in binding energy (mainly Coulomb interaction) of the np electron after the Auger deexcitation process.[17] The exchange interaction between the $4d$ hole and the $np\,(n \geq 6)$ electron is relatively unimportant for Xe. A similar effect is probably also present for the $4f$ electron in the case of La^{3+}, but is apparently overriden by the stronger exchange interaction effect mentioned above. The changes in Auger line shape as evident in spectra c, e, and f are related to changes in relative intensity ratio of the two spin-orbit split members.

We can estimate the relative contribution, or ratio, of the Auger deexcitation channel to the direct recombination decay channel, R (Auger/direct), by comparing the integrated intensity of the peaks due to the Auger deexcitations with the integrated intensity enhanced by the direct recombination decay processes. In spectrum c of Fig. 2 which was measured at the $^3D_1$ resonant photon energy $h\nu = 101.8$ eV, R (Auger/direct) is estimated to be $\sim 10 \pm 2$. Because of overlapping of the spectral features, a reliable estimate for R cannot be made for spectrum a. In contrast, above the threshold the contribution of the direct recombination decay channel is comparable to that of the Auger deexcitation channel, that is, in spectra f and e measured at $h\nu = 118.0$ and 112.7 eV above the threshold, R (Auger/direct) does not exceed $\sim 1-2$.

IV. SUMMARY

Photoemission partial yield spectra of LaB_6 show two weak narrow peaks at $h\nu = 97.5$ and 101.8 eV and a broad strong feature having a maximum at $h\nu = 118.5$ eV which are due to La $4d \rightarrow 4f$ resonant excitations from the $4d^{10}$ ground state $^1S_0$ to the $4d^9 4f^1$ excitonic excited states $^3P_1$, $^3D_1$, and $^1P_1$, respectively. All the $4d^9 4f^1$ excited states $^3P_1$, $^3D_1$, and $^1P_1$ decay via the direct recombination and Auger deexcitation channels. The $^3D_1$ excited state below the one-electron $4d$ core-level threshold mainly decays via the Auger deexcitation channel. In contrast, for the $^1P_1$ excited state above threshold, the Auger deexcitation and direct recombination decay channels are comparable in strength.

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