

Hole-induced shakedown process in the $M_{4,5}$ fluorescent emission spectrum of lanthanum

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The hole-induced shakedown process is observed in the x-ray $M_{4,5}$ fluorescent emission spectrum of lanthanum. Comparison of the $M_{4,5}$ fluorescent emission spectrum of lanthanum (the $4f$ level is empty in the ground state) with the electron-excited spectra shows that x-ray emission, which is caused by transitions from occupied $4f$ states to empty $3d$ states, appears even in the fluorescent spectrum of lanthanum. This result indicates that the shakedown transition from the conduction-band states to the empty $4f$ level occurs in the presence of a $3d$ core hole. Also, a satellite was observed on the low-energy side of the M_{5O_3} diagram line and attributed to the transition $3d_{5/2}^{-1}4f^1 \rightarrow 5p_{3/2}^{-1}4f^1$. This gives further evidence of the hole-induced shakedown transition.

I. INTRODUCTION

Multielectron excitations called shakeup, shakeoff, and shakedown transitions have been observed in the x-ray photoemission spectra^{1,2} (XPS) and the x-ray-absorption spectrum.³ The multielectron excitation is produced by the sudden creation of the core-hole potential induced by the absorption of an x-ray photon, and causes satellites in addition to a main line in the case of the XPS. Crecelius *et al.*⁴ have found a shakedown satellite in the $3d_{5/2}$ XPS of lanthanum, which appears on the lower-binding-energy side of the main line. On the basis of the fact that the energy of the $3d^9 4f^1$ configuration is clearly lower than that of the $3d^9 4f^0$ configuration,⁴⁻⁶ they have interpreted it as the $3d_{5/2}$ line when the $4f$ level, which is empty in the ground state, is filled by an electron from the conduction-band states in the presence of a $3d$ core hole.

In the x-ray $M_{4,5}$ emission study with the fluorescence x-ray excitation method the electron in the target material must absorb the whole quantum energy of the incident photon for fluorescence excitation and is photoexcited into the continuum. Thus, there is no possibility to excite the $3d$ core electron to the normally empty $4f$ level of lanthanum with the fluorescence excitation method. However, if the hole-induced shakedown transition occurs and the normally empty $4f$ level is populated when the $3d$ core hole is created in lanthanum, the x-ray emission $3d^9 4f^1 \rightarrow 3d^{10} 4f^0$ should be observed even with the fluorescence excitation method.

In the present study, we aimed at confirming the hole-induced shakedown process independently of the XPS. We measured the $M_{4,5}$ emission spectrum of lanthanum with the fluorescence excitation method using a rhodium target x-ray tube as a primary source, and compared it with the electron-excited spectra in order to observe the x-ray emission from the excited configuration $3d^9 4f^1$ and to confirm the possibility of a hole-induced shakedown transition.

II. EXPERIMENTAL

Fluorescent $M_{4,5}$ emission spectrum of lanthanum was obtained with a flat crystal vacuum spectrometer

equipped with a fine Soller slit and a 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. In this procedure the La $M_{4,5}$ spectrum seems to be excited mainly by the Rh L emission ($L\alpha_1$, 2697 eV) and the contribution of the incident bremsstrahlung is very small because no spectra such as La L spectra (the binding energy of the La L_3 level is 5483 eV) excited by the high energy photons in the bremsstrahlung were observed in the present experiment. The spectral window is about 1.8 eV in the La $M_{4,5}$ spectral region. Intensity measurements were carried out automatically for a preset counting time at regular intervals of 0.01° in 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 a P-10 gas (an argon gas with 10% of methane by volume). Specimens were prepared by vacuum evaporation of metal pellets onto aluminum substrates and covered by a thin aluminum film successively evaporated onto them to avoid undesirable oxidation of the specimens.

For the measurements of the electron-excited spectra a different flat crystal vacuum spectrometer was used, which has almost the same resolution as that of the spectrometer used for the measurement of the fluorescent spectrum. In this case, specimens were prepared by vacuum evaporation onto a copper target and also covered by a thin aluminum film. The Cu $L\alpha$ line was used as a reference line, whose wavelength was taken from the table as 13.336 Å.⁷

III. RESULTS AND DISCUSSION

The $M_{4,5}$ emission spectra of lanthanum are shown in Fig. 1. Spectrum (a) was obtained with the fluorescence excitation method, and the other three spectra (b), (c), and (d) were obtained with the electron-excitation method with electron-beam energies of 10.0, 5.0, and 1.5 keV, respectively. The $M_{4,5}$ absorption spectrum measured by Mariot and Karnatak⁵ is also shown by a dashed line for comparison. In spectra (c) and (d), peaks R and R' observed at 834.2 and 850.5 eV, respectively, may be as-

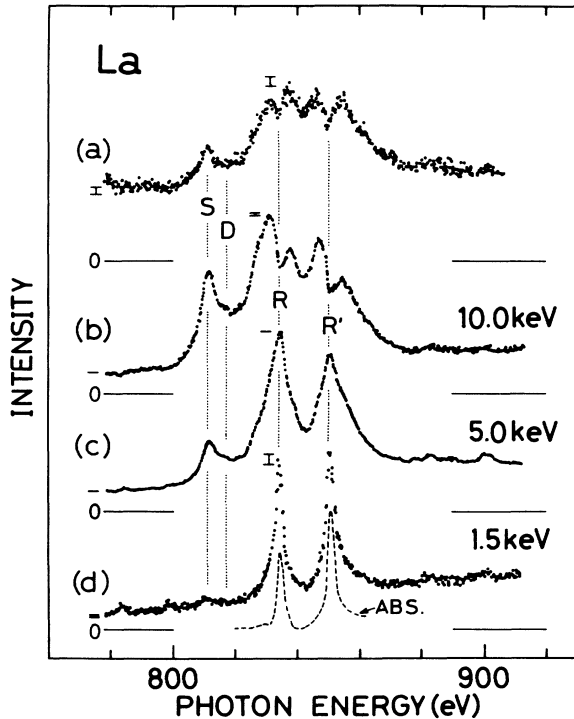


FIG. 1. $M_{4,5}$ spectra of lanthanum. Spectrum (a) is the fluorescent spectrum. Spectra (b), (c), and (d) are the electron-excited spectra obtained with the electron-beam energies of 10.0, 5.0, and 1.5 keV, respectively. The $M_{4,5}$ absorption spectrum measured by Mariot and Karnatak (Ref. 5) is shown by a dashed line for comparison. Error bars are shown in the figure. R and R' indicate the resonant emission lines ($3d^9 4f^1 \rightarrow 3d^{10} 4f^0$). D and S indicate the diagram line M_5O_3 and its satellite ($3d_{5/2}^{-1} 4f^1 \rightarrow 5p_{3/2}^{-1} 4f^1$), respectively. The locations of the diagram lines M_4O_2 and M_4O_3 and their satellites ($3d_{3/2}^{-1} 4f^1 \rightarrow 5p_{1/2,3/2}^{-1} 4f^1$), which were not clearly observed, are in the energy region of the resonant emission line R .

cribed to the resonant emission $3d^9 4f^1 \rightarrow 3d^{10} 4f^0$ because the energy positions of these peaks coincide with those of the absorption peaks. The resonant emission is caused by the recombination of an electron trapped to the unoccupied $4f$ level with an initial core hole.^{5,8-12} In other words, the process of the resonant emission is just the inverse process of photoabsorption. Thus, the resonant emission peak is observed at the same energy position as the corresponding absorption peak. Under the electron bombardment the inner-core electrons in the target material can absorb any part of the energy of the incident electron and thus will be easily excited to the normally empty $4f$ level. In spectrum (c) excited with the electron-beam energy of 5.0 keV, the width of the resonant emission line becomes broader in comparison with spectrum (d), because the intensity of the peaks in spectrum (c) is slightly reduced by the influence of self-absorption. Spectrum (b) is considerably affected by the self-absorption, and dips appear at the peak positions of the resonant emission since the electron beam with an energy of 10.0

keV, which has relatively large penetration depth, was used and x rays were generated deep in the target. It is a common feature of the resonant emission spectra obtained with the electron beam of the high energy that dips, instead of peaks, appear due to the self-absorption at the energy positions of the absorption peaks.^{12,13}

The general feature of the fluorescent emission spectrum (a) resembles that of spectrum (b) which was obtained with the electron-excitation method and suffered the self-absorption effect. Remarkable peaks appear on both sides of the dip positions which coincide with the resonant peak positions. In the fluorescence excitation there is no incident electron and the possible mechanism of the initial excitation is restricted to one-electron transitions in contrast with the electron-excitation method. The rather-high-energy photons (Rh L) were irradiated on the specimen so that a $3d$ core electron is merely excited far into the continuum in the present case, and thus there is no possibility of the resonant emission caused by the same origin as with the electron-excitation method. However, if the hole-induced shakedown transition occurs from the conduction-band states to the empty $4f$ level of lanthanum, we can expect the resonant emission $3d^9 4f^1 \rightarrow 3d^{10} 4f^0$ as mentioned before.

When a $3d$ core hole is created in lanthanum, a modification of the electronic distribution is expected even with the fluorescence-excitation method. The XPS shows that a lower-binding-energy satellite appears at 832.4 eV with a width of about 5 eV in the $3d_{5/2}$ spectrum.⁴ This peak has been interpreted as the $3d_{5/2}$ line when the $4f$ level is filled by an electron from the conduction-band states, resulting in a stabilization of energy. Therefore, the $3d^9 4f^1$ configuration, which is the initial state of the resonant emission, can be formed during the fluorescence excitation and the relaxation processes. Thus we believe that the remarkable peaks observed on both sides of each dip in the fluorescent spectrum are the contribution of the resonant emission and the dips around 834 and 850 eV, which coincide in energy with the absorption peaks and also with the resonant emission peaks R and R' in the electron-excited spectrum, may be caused by the erosion due to the self-absorption,^{12,13} as for the case of spectrum (b) excited with the high-energy electron. The difference in the relative intensities of the multi-peaked structures between the fluorescent spectrum (a) and spectrum (b) may be caused by the different penetration depths between photons and electrons used for each excitation method and by the different contributions of the diagram lines M_4O_2 and M_4O_3 to the resonant emission line because they overlap with the resonant emission line (the energies of these lines are given below).

Next, we present further evidence of the hole-induced shakedown transition. According to the XPS data,^{1,4} the M_5O_3 , M_4O_2 , and M_4O_3 diagram lines are expected to be located at 818.8, 833.1, and 835.6 eV, respectively. In comparison with those numerical values a faint peak D observed around 818 eV in spectra (b) and (c) could be assigned as the ordinary M_5O_3 emission line, and the ordinary M_4O_2 and M_4O_3 emission lines may overlap with the resonant emission (R) around 834 eV. Therefore, the emission line S clearly observed at 812 eV is not interpreted-

TABLE I. Energy values (eV) of important structures in the $M_{4,5}$ spectra of lanthanum.

	Present		Others		XPS ^{a,b}
	Fluorescent spectrum	Electron-excited spectra	Electron-excited spectrum ^c	Absorption spectrum ^d	Difference between binding energy
S	812	812	812.4		
M_5O_3	818	818	819.0		818.8
M_4O_2					833.1
R	834 ^e	834.2	834.9	834.8	832.4 ^f with width of 5 eV
M_4O_3					835.6
R'	850 ^e	850.5	851.5	850.7	

^aReference 1.

^bReference 4.

^cReference 14.

^dReference 5.

^eObserved as the dip.

^fEnergy position of the $3d_{5/2}$ XPS satellite given in Ref. 4.

ed as a diagram line. A similar peak is observed at the same energy, 812.4 eV, in the electron-excited spectrum of lanthanum by Motais *et al.*¹⁴ They have interpreted this rather intense satellite (more intense than the main line), which appears on the low-energy side of the M_5O_3 diagram line, as the transition $3d_{5/2}^{-1}4f^1 \rightarrow 5p_{3/2}^{-1}4f^1$ (Ref. 14). We believe that the emission line S observed at 812 eV even in the fluorescent spectrum corresponds to this satellite, and this gives further evidence of the hole-induced shakedown transition from the conduction-band states to the empty $4f$ level. The corresponding satellites of M_4O_2 and M_4O_3 , that is, the transitions $3d_{3/2}^{-1}4f^1 \rightarrow 5p_{1/2,3/2}^{-1}4f^1$, should be observed around 827 and 830 eV, but they might be hidden in the resonant emission (R) around 834 eV. Table I gives the energy values of the important structures pertaining to this paper together with the energy values obtained with the other spectroscopies.

It is noticed that the ordinary M_5O_3 emission line observed around 818 eV is less intense than the peak S around 812 eV. This phenomenon has also been observed in the electron-excited spectrum by Motais *et al.*¹⁴ as mentioned above. On the other hand, according to Crecelius *et al.*⁴ screening of the core hole by the conduction electrons provides an effective process competing with the shakedown process from the conduction-band states to the empty $4f$ level, and the main line observed in the $3d$ XPS, which corresponds to the screened core hole, is ascribed to the dominant final state. It should remain to be seen. Finally, it should be noted that the $4f$ level in lanthanum seems to be easily filled by an electron from the conduction-band states compared with other rare earths because the intensity ratio of the $3d$ XPS satellite to the main line becomes small with increasing atomic number,

that is, with increasing the number of $4f$ electrons in the ground state.⁴

IV. SUMMARY

The hole-induced shakedown process was observed in the x-ray $M_{4,5}$ fluorescent emission spectrum of lanthanum. Comparison of the $M_{4,5}$ fluorescent emission spectrum of lanthanum ($4f$ level is empty in the ground state) with the electron-excited spectra shows that the x-ray emission, which is caused by the transition from occupied $4f$ states to empty $3d$ states, appears even in the fluorescent spectrum of lanthanum which was generated by the photoexcitation of the La $3d$ core electron into the continuum. This result indicates that the shakedown transition from the conduction-band states to the empty $4f$ level occurs in the presence of a $3d$ core hole, because the energy of the $3d^9 4f^1$ configuration of lanthanum is lower than that of the $3d^9 4f^0$ configuration as pointed out by Crecelius *et al.*⁴ Also, the satellite was observed on the low-energy side of the M_5O_3 diagram line and was attributed to the transition $3d_{5/2}^{-1}4f^1 \rightarrow 5p_{3/2}^{-1}4f^1$. This gives further evidence of the hole-induced shakedown transition.

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