

$M_{4,5}$ emission spectra from Gd_2O_3 and Yb_2O_3

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The $M_{4,5}$ emission spectra from Gd_2O_3 and Yb_2O_3 have been obtained in fluorescence on a double-crystal spectrometer. The profiles differ from the $M_{4,5}$ emission spectra excited by electron impact. These differences are due to resonance radiation and substantiate the interpretation given by Bonnelle and Karnatak. The $M\alpha$ emission line was found to lie above (in energy) the M_5 -absorption resonance line in Yb_2O_3 , which is in contrast to Gd_2O_3 and general experience. It is suggested that this observation is a result of the discrete nature of the absorption lines. With the help of estimated binding energies for the final configurations $5p_{1/2,3/2}^5 4f^7$, the photoelectron spectrum of Gd_2O_3 is discussed.

I. INTRODUCTION

The x-ray emission and absorption of some lanthanide metals and their oxides in the $M_{4,5}$ region have recently been reported.¹⁻⁷ In the study by Bonnelle and Karnatak¹⁻⁴ the emission spectra were obtained by direct electron bombardment of the target at two or more accelerating voltages. From the coincidence of the absorption resonance lines with some features in the emission spectra and their relative increase of intensity at the lower accelerating voltage of the incident electrons, these emission features, labeled R by Bonnelle and Karnatak,¹⁻⁴ were identified as being due to resonance radiation, i.e., the reverse of absorption.

This phenomenon has also been found in the x-ray $S K\beta$ and L emission from gaseous SF_6 ,⁸ obtained with direct electron impact. The sulphur $L-K$ -absorption-spectra resonance lines were also shown to be in coincidence with features in the sulphur L and $K\beta$ emission spectra excited by electron bombardment. In addition, the sulphur $K\beta$ emission obtained in fluorescence *did not* exhibit a change of intensity in the region of the sulphur K -absorption line. The difference in sulphur $K\beta$ emission with mode of excitation is due to resonance radiation. Under electron bombardment the target molecular electrons can absorb any part of the energy of the incident electrons and thus will have easy access to the normally unoccupied states displayed by the respective inner-shell absorption spectrum. On the other hand, with photon excitation of the x-ray emission spectrum, the target electron must absorb the whole quantum of energy of the incident photons. Since the contribution of incident bremsstrahlung photons at the K -absorption resonance-line energy is very small relative to the rest of the bremsstrahlung spectrum of the source, reso-

nance radiation would not be easily detected with photon excitation of the spectrum. To investigate this phenomena further the fluorescence $M_{4,5}$ x-ray emission of Gd_2O_3 and Yb_2O_3 were obtained to compare with the previous experiments with these materials.

II. EXPERIMENTAL

A vacuum double-crystal spectrometer⁹ using RAP (rubidium acid phthalate) crystals was used to analyze the fluorescent radiation from specimens which were oriented 45° to both the direction of the primary x rays and the viewing direction of the spectrometer. The fluorescent radiation was detected by a gas-flow proportional counter followed by conventional charge-sensitive electronics and an automatic data logging system. Some pertinent experimental parameters are collected in Table I.

The 1×2 -cm specimens were prepared from slurries of powdered research grade Gd_2O_3 and Yb_2O_3 dispersed in mixtures of polystyrene dissolved in benzene. The mixed slurries were dispersed by eyedropper onto thin (1-mil) aluminum foil substrates and dried with a heat lamp. Specimen layers of about $\frac{1}{4}$ mm were built up and permitted to finally air dry overnight before mounting in vacuum chamber.

In Figs. 1 and 2 are shown the $M_{4,5}$ emission spectra of Gd (Gd_2O_3) and Yb (Yb_2O_3) obtained in fluorescence. The displayed spectra are the point-by-point average of three separate scans without any corrections, i.e., subtraction of background, unfolding, etc. The energy scale was set relative to Zn $L\beta_1$ at 1034.7 eV (11.983 Å)¹⁰ and Al $K\alpha_{1,2}$ at 1486.53 eV (8.3403 Å)¹¹ for the $M_{4,5}$ emission spectra of Gd (Gd_2O_3) and Yb (Yb_2O_3), respectively. See Appendix A for a further discussion of the calibration.

TABLE I. Experimental parameters for the measurements.

Specimen	Spectral region	X-ray tube		Counter gas and pressure
		Power	Anode	
Gd ₂ O ₃	Gd $M_{4,5}$	17 kV, 120 mA	Aluminum	CH ₄ , 200 Torr
Yb ₂ O ₃	Yb $M_{4,5}$	11 kV, 120 mA	Silver-plated copper	P10, 300 Torr

The fluorescent emission spectrum in Fig. 1, consisting of two well-defined peaks and some weak intensity structure flanking each peak, is quite different from the spectrum¹⁻⁴ obtained with direct electron excitation. The peaks at 1178 and 1209 eV are identified as the single active electron single-vacancy transitions (no spectator hole) $M\alpha$ ($M_5 \rightarrow N_6N_7$) and $M\beta$ ($M_4 \rightarrow N_6$), respectively. Note that the $M\alpha$ peak in Fig. 1 is not flattened as it is in the direct electron excited spectrum.¹⁻⁴ The low-intensity regions centered at 1184 and 1214 eV are due to self-absorption. The energy positions of these features correspond to the resonance-line peaks in the $M_{4,5}$ absorption^{1-4,7} and the R features in the $M_{4,5}$ emission spectra¹⁻⁴ by direct electron bombardment. The steep slope of the high-energy side of the $M\beta$ line in Fig. 1 is also due to self-absorption. It is clear from a comparison of the spectra that the absence of the resonance emission lines in Fig. 1 permits an easier measurement of the energy position of the lines $M\alpha$ ¹² and $M\beta$.

The Yb $M_{4,5}$ emission spectrum obtained in fluorescence from Yb₂O₃ is shown in Fig. 2. The spectrum consists of two lines with a small shoulder on the low-energy side of the more intense line. The smaller of the two peaks at 1567.2 eV is identified as the $M\beta$ ($M_4 \rightarrow N_6$) transition and is in accord with the literature.¹⁰ The larger peak at about 1523.7 eV is in good agreement with the

feature labeled S measured by Karnatak⁴ at 1523.4 eV. The break in the slope on the low-energy side of the large peak at about 1520 eV is attributed to self-absorption by the M_5 -absorption resonance line at 1520.4 eV.^{4,6,7} It is possible that the close proximity of the M_5 -absorption peak will shift the apparent emission peak position. However, since the M_5 -absorption cross section is relatively small,⁷ a self-absorption correction to the position of the 1523.7 eV-peak would probably amount to about 0.5 eV at most. Thus, the emission peak will be located at 1523 eV.

The 1523-eV emission peak is identified as the single-electron-single-vacancy transition $M\alpha$ ($M_5 \rightarrow N_{6,7}$). This is based on its dominant appearance, the absence of any other prominent feature in its immediate region, and the negligible probability of its origin from any resonance process.

III. DISCUSSION

A. Line positions

Acceptance of the above identification of the $M\alpha$ from Yb (Yb₂O₃) presents the interesting ob-

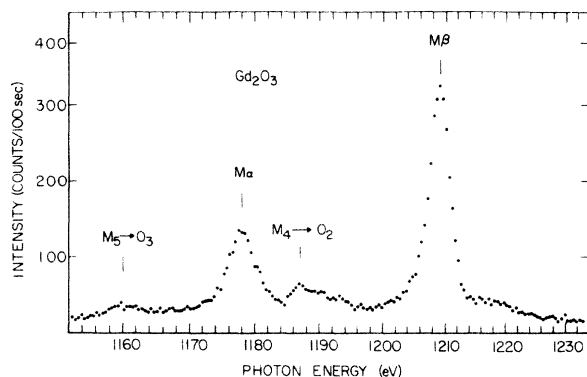


FIG. 1. $M_{4,5}$ emission spectrum from Gd₂O₃ obtained in fluorescence.

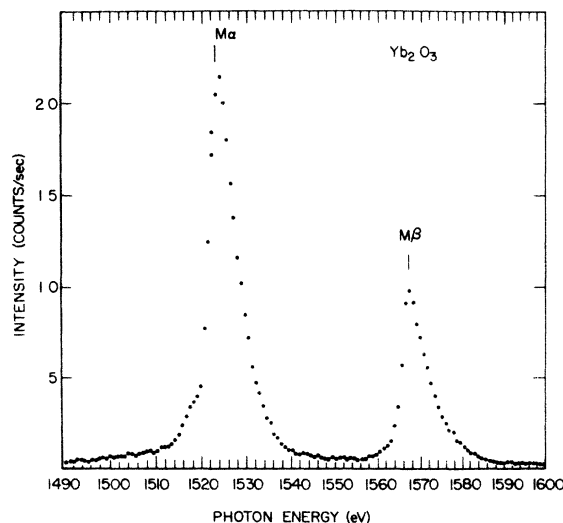


FIG. 2. $M_{4,5}$ emission spectrum from Yb₂O₃ obtained in fluorescence.

TABLE II. Binding energies of different excited states. The $4f$ and Z and $Z+1$ binding energies are from Ref. 5; $3d_{5/2}^9 4f^{n+1}$ are Refs. 4 and 7. All energies are in eV.

Z	$4f$	$3d_{5/2}^9 4f^n$	$3d_{5/2}^9 4f^{n+1}$	$3d_{5/2}^9 4f^n - 3d_{5/2}^9 4f^{n+1}$	$4f$ of $Z+1$
Gd	15.6	1193.6	1184	9.6	11.5 (Tb^{+3})
Yb	13.6	1536.6	1520	16.6	16 (Lu^{+3})

servation that the $M\alpha$ line appears to lie above (in energy) the M_5 -absorption resonance line, which is in contrast to the $M_{4,5}$ spectra of Gd and other rare earths. It is also in manifest contrast with one's general experience in this area.

Let us consider the energies of the $3d^9 4f^n$ and $3d^9 4f^{n+1}$ configurations for an insight into the reason for this apparent reversed appearance of the $M\alpha$ emission versus M_5 -absorption lines of Yb^{+3} in Yb_2O_3 . Recall that the final-state configuration of the $M\alpha$ emission line is the same as the configuration after the ejection of a $4f$ electron by photoelectron spectroscopy. Thus, by adding the binding energy of the $4f$ electron as determined by photoelectron spectroscopy to the energy of the $M\alpha$ emission line, one obtains the binding energy of the $3d_{5/2}$ electron to form the initial state configuration $3d_{5/2}^9 4f^n$. The M_5 -absorption line peak position¹³ gives the energy for excitation of $3d_{5/2}^{10} 4f^n - 3d_{5/2}^9 4f^{n+1}$. By taking the difference $3d_{5/2}^9 4f^n - 3d_{5/2}^9 4f^{n+1}$, an estimate of the binding energy of the most easily ionized $4f$ electron in the $(Z+1)^{+3}$ ion is obtained. A comparison of these estimated binding energies and experimental values from the literature are shown in Table II. The close agreement suggests that the energy position of $M\alpha$ with respect to the M_5 -absorption line is primarily dependent on the binding energies for the $4f$ electron of Z relative to $Z+1$ ions. This result also supports the interpretation of the $M_{4,5}$ absorption spectra of the lanthanides as discrete line transitions.¹⁴

The clear identification of the $M\alpha$ and $M\beta$ emission lines obtained in fluorescence also permits the measurement of the M_4 - M_5 spin-orbit splitting. The M_4 - M_5 splittings ascertained from the $L_3 \rightarrow M_{4,5}$ emission lines¹⁰ and this paper are collected in Table III. Note that the splittings derived from the $L_3 \rightarrow M_{4,5}$ lines are larger with differences of

TABLE III. M_4 - M_5 splitting.

Z	M_4 - M_5 splitting (in eV)		Differences
	$L_3 \rightarrow M_{4,5}$ (Ref. 10)	$M_{4,5} \rightarrow N_{6,7}$	
Gd	32.2	30.5	1.7
Yb	48.3	43.6	4.7

about 1.7 eV for Gd and 4.7 eV for Yb. These differences are attributed to electrostatic interaction between the open $3d$ and $4f$ shells. When the $4f$ shell ($N_{6,7}$) is completed and lies deeper in the atoms as at higher Z number, the M_4 - M_5 splittings from the $L_3 \rightarrow M_{4,5}$ and $M_{4,5} \rightarrow N_6$ emission lines are equal within experimental uncertainties.

B. $M\alpha$ and $M\beta$ intensities

An accurate measure of the $M\alpha$ and $M\beta$ emission line intensities in both electron and photon impact excited spectra are difficult to obtain. In the electron impact excited spectrum,¹⁻⁴ $M\alpha$ and $M\beta$ lines overlap with the high-energy satellites (multiple-vacancy transitions) and the resonance radiation lines; whereas, in the photon impact excited spectra, the $M\alpha$ and $M\beta$ profiles overlap the regions of self-absorption by the $M_{4,5}$ -absorption resonance lines and the high-energy satellites. With these limitations in mind, a rough measure of the line intensities will be made by using the peak height of the identified lines. For the Gd $M_{4,5}$ spectrum by electron impact, the $M\alpha/M\beta$ ratio is about $\frac{1}{2}$ and does not appear to vary much with incident electron accelerating voltage. The $M\alpha/M\beta$ ratio from the fluorescence spectrum (Fig. 1) is about the same, a little less than $\frac{1}{2}$. For the Yb $M_{4,5}$ emission spectrum by electron impact, the feature labeled S is taken as $M\alpha$, to give a $M\alpha/M\beta$ ratio of about 2 to 1. In the fluorescent spectrum (Fig. 2) the $M\alpha/M\beta$ is about the same, 2.2 to 1. It appears that the $M\alpha/M\beta$ ratio is independent of mode of excitation for the range of experimental conditions employed.

The intensity ratio $M\alpha/M\beta$ calculated on the basis of only the available $4f$ electrons is $\frac{7}{5}$ for Gd^{+3} and $\frac{13}{6}$ for Yb^{+3} . By considering both the statistically available initial states and $4f$ electrons, the $M\alpha/M\beta$ ratio is $\frac{7}{4}$ for Gd^{+3} and $\frac{13}{4}$ for Yb^{+3} . None of the above limiting cases correlates completely with experiment. It seems obvious then that a more detailed consideration of the emission process is needed, so as to take into account the angular correlations of these highly excited states, and the possible effect of shake up in the $4f$ shell for different lanthanide elements.

TABLE IV. Reference-line measurements using RAP crystals.

Emission line	λ (Å)	Bragg angle (deg)	Eff. $2d$ (deg)	Rocking curve full width at half-maximum (eV)
Zn $L\beta_1$	11.983 (Ref. 10)	27.372 ± 0.002	26.063 ± 0.002	0.84
Al $K\alpha_{1,2}$	8.3403 (Ref. 11)	18.673 ± 0.002	26.050 ± 0.003	0.92

C. Other features of the spectra

The low-intensity contributions at 1160 and 1187 eV in the $GdM_{4,5}$ spectrum of Gd_2O_3 (Fig. 1) are identified as $M_5 \rightarrow O_3$ and $M_4 \rightarrow O_2$, respectively. Multiple-vacancy transitions of the parent $M\alpha$ can also occur in the 1187-eV region, but their intensity would be expected to be comparable to the intensity distribution on the high-energy side of the $M\beta$ line in the 1220-eV region. Therefore, the identification of the 1187-eV feature as $M_4 \rightarrow O_2$ seems reasonable. Combining the $3d_{3/2,5/2}^9 4f^n$ binding energies with these transitions, we obtain the binding energies of 37.6 and 33.6 eV for the final-state configurations $5p_{1/2}^5 4f^7$ and $5p_{3/2}^5 4f^7$, respectively. The $O_2 \rightarrow O_3$ spin-orbit splitting of 4 eV is consistent with the 4-eV value given by Lotz¹⁵ in his electronic energy levels compilation.

The photoelectron spectrum⁵ of Gd_2O_3 has a small peak at 34 eV and a lesser peak at about 29 eV. The close correspondence of the estimated binding energy for $5p_{3/2}^5 4f^7$ of 33.6 eV to the photoelectron peak at 34 eV seems an obvious identification. There is not any peak in the 38-eV region of the photoelectron spectrum, but the intensity does not go down to zero. Thus, photoelectrons from the $5p_{1/2}$ level may be present in the 38-eV region of the spectrum, but it is not possible to specify their precise location. The relatively weak peak at 29 eV is probably due to the oxygen 2s photoelectrons.

From the estimated binding energies of $3d_{3/2}^9 4f^7$ and $5p_{3/2}^5 4f^7$, the $M_4 \rightarrow O_3$ transition for Gd is calculated to occur at about 1191 eV. The $M_3 \rightarrow N_1$ transition is estimated to appear at about 1168 eV from the electronic energy level compilation.¹⁵ In both these regions of the spectrum (Fig. 1) the emission intensities are above the background, but no clear peaks are evident.

IV. CONCLUSION

The fluorescent emission spectra in the $M_{4,5}$ region of Gd^{+3} (Gd_2O_3) and Yb^{+3} (Yb_2O_3) have been measured and found to be different than the emission spectra excited by electron impact. The differences are due to the absence of resonance radiation emission in the photon excited spectra as

anticipated from the previous work on the sulphur $K\beta$ from SF_6 . Resonance emission lines can be enhanced by using primary excitation sources with photons from emission lines with the same energy as the absorption resonance lines,^{8,16} or electrons whose energy distribution is peaked at the absorption resonance line energy.

A characteristic of the $M_{4,5}$ photoabsorption of the lanthanides is the strong discrete line structures. Sugar¹⁴ has shown that this phenomena is due to the penetration of the centrifugal potential barrier by the $4f$ orbitals, which results in a high degree of localization of the ejected electron into a $4f^{n+1}$ orbital. The prominence of the resonance radiation in the $M_{4,5}$ emission spectra by electron impact excitation, in spite of the possible competition with other modes of decay of the $3d^9 4f^{n+1}$ initial state, suggests an appreciable amount of overlap for the $4f^{n+1}$ orbital with the $3d$ shell. The $N_{4,5}$ emission spectra by electron impact excitations of the lanthanides should also exhibit resonance radiation at the positions of the strong photoabsorption peaks.

The emission line positions have been interpreted and shown to behave in accordance with the special character of the incomplete $4f$ shell of the lanthanides. Unfortunately, a complete explanation of the $M\alpha$ and $M\beta$ intensities are not at hand.

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APPENDIX

In the procedure¹⁷ to obtain an energy scale calibration for the individual spectra the absolute Bragg angle of the emission lines used for reference were measured. These measurements provide an energy scale calibration and together with the tabulated wavelengths^{10,11} permit the determination of the effective $2d$ grating space of the RAP crystals used. In Table IV are listed the measurements and values used to calibrate the energy scales of the spectra in this paper.

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