THE PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 162, NO. 1 5 OCTOBER 1967

M_{IV} and M_V Absorption Lines and Edges of $_{64}$Gd, $_{66}$Dy, and $_{70}$Yb†

HASSAN F. ZANDY

Department of Physics, University of Bridgeport, Bridgeport, Connecticut

(Received 23 November 1966; revised manuscript received 12 June 1967)

The M_{IV} and M_V edges of $_{64}$Gd, $_{66}$Dy, and $_{70}$Yb were measured using a high-intensity-focusing x-ray spectrograph operating in vacuum. An absorption line is detected on the long-wavelength side of the M_{IV} edge of $_{64}$Gd and a weaker one at the M_V edge of $_{66}$Dy. For $_{70}$Yb, however, the M_V absorption has the appearance of a strong "white line." No absorption line has been observed at the M_V edge of $_{64}$Gd nor at the M_{IV} edges of $_{66}$Dy and $_{70}$Yb. The significance of the occurrence and absence of absorption lines in the filling of the $4f$ shell of the "heavy" rare earths and the effect of the absorber thickness on the shape of the absorption profile are discussed.

I. INTRODUCTION

IN the periodic table, the group of transition elements known as the rare earths exhibits the most exclusive example of the successive occupation of an inner level deep in the atom by the additional electron, as the atomic number increases. The M_{IV} and M_V absorption spectra of these elements are of special interest, because they arise from electron transitions between the $M_{IV,V}$ levels and the $4f$ shell.

The first systematic study of the M emission and absorption spectra of $_{68}$Er and $_{70}$Yb was carried out by Lindberg[1] in 1931, using a vacuum spectrometer of the Siegbahn type.[2] Lindberg's results showed the disappearance of simple character of the $M\alpha$ and $M\beta$ lines for these elements. This was explained to be because of the vacancy in the $4f$ shell which causes the splitting of the N_{VI} and N_{VII} sublevels, giving rise to higher multiplicities. Thus, the identification of each component line became extremely difficult. Moreover, Lindberg's results for the wavelengths of many such lines did not agree with values calculated from the energy-level tables.

To clear up this discrepancy, "fine structures" accompanying the M_{IV} and M_V edges of these elements need to be examined more closely. Because of the application of the selection rules to both emission and absorption lines arising from transitions between the same levels, one would expect an absorption line to accompany the M_{IV} and/or M_V edge of the element for which the $4f$ shell is still incomplete.

For this purpose, a curved crystal vacuum spectrograph was specially designed and built leading to the experimental results on the fine structures of $_{59}$Pr, $_{60}$Nd, $_{62}$Sm, and $_{63}$Eu, which were reported earlier.[3] This paper deals with the results obtained for $_{64}$Gd, $_{66}$Dy, and $_{70}$Yb and the thickness effect of the absorber on the sharpness and detailed nature of absorption lines and edges.

II. EXPERIMENTAL RESULTS

Unlike the four elements reported earlier for which absorption lines appeared at both the M_{IV} and M_V edges, here an absorption line was detected only at the long-wavelength sides of the M_{IV} edge of $_{64}$Gd and M_V edge of $_{66}$Dy, while the entire feature of the M_V absorption for $_{70}$Yb revealed the appearance of a strong absorption line just as in optical spectra.

Absorbers were prepared by evaporating a known weight of the oxide of the element from a heated tantalum strip onto an aluminum foil 0.6 μ thick, under a vacuum of 10^{-5} Torr.

Wavelengths of the reference lines are all taken from Ref. 4. Energy-level values for M_{IV} and M_V edges of $_{64}$Gd and $_{70}$Yb are those calculated by Nishina,[5] but for

† This work is the extension of research initiated at the University of Leicester in England, while the author was on leave from the University of Tehran, Iran.

[1] E. Lindberg, Nova Acta Reg. Soc. Sci., Upsalla, Ser. IV, 7, 68 (1931).

[2] M. Siegbahn, *Spectroskopie der Röntgenstrahlen* (Springer-Verlag, Berlin, 1931), 2nd ed., Vol. 88.

[3] H. F. Zandy, Proc. Phys. Soc. (London), 65, 1015 (1952).

[4] Y. Cauchois and H. Hulubei, *Long. d'onde des Emissions et Discontinuités d'Absorption X*, (Hermann & Cie., Paris, 1947).

[5] Y. Nishina, Phil. Mag. 49, 530 (1925).

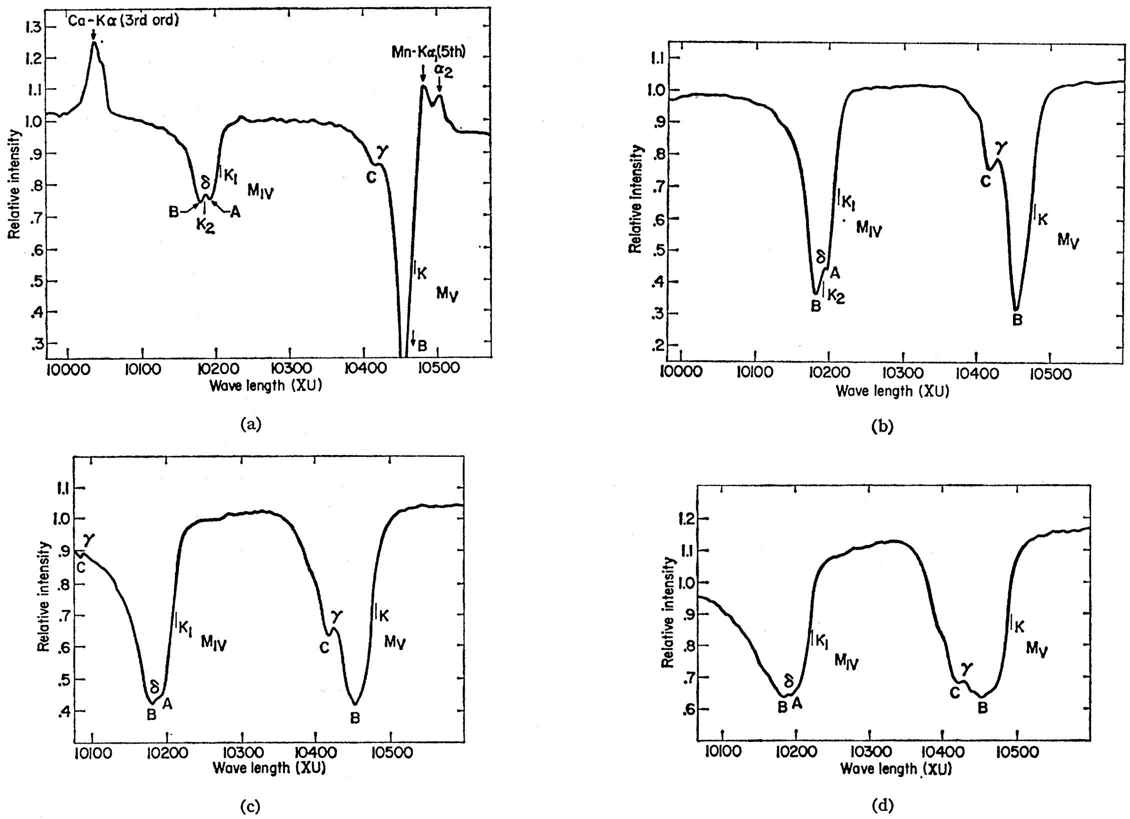


FIG. 1. Microphotometer curves of M_{IV} and M_V absorption of $_{64}$Gd. Thickness of absorbers: (a) 0.023 mg/cm², (b) 0.031 mg/cm², (c) 0.102 mg/cm², (d) 0.115 mg/cm².

$_{66}$Dy, Barrère's values[6] are consulted. Exposure times ranged from 560 mA-h for Gd down to 260 mA-h for Dy and 120 mA-h for Yb. Notations used on the microphotometer curves and in the tables are as follows:

The main absorption line arising from transition to $N_{VI,VII}$ levels is denoted by A, other absorption lines accompanying the edge carry letters D and C, and the dark bands separating them from the main absorption are denoted by δ and α, respectively. The lowest part of the curve corresponding to maximum absorption is denoted by the B throughout.

TABLE I. M_{IV} and M_V edges of $_{64}$Gd.

Edge		Expt. λ (mean) (xu)	Expt. ν/R (mean)	Calc. ν/R (mean)	Corresponding emission λ (xu)	
M_{IV}	K_1	10204	89.30	90.0	10233	$M\beta_I$
	A	10193	89.40			
	∂	10188	89.45			
	K_2	10185	89.47			
	B	10180	89.52			
M_V	K_1	10460	87.12	87.7	10508	$M\alpha_{III}$
	B	10441	87.28			
	α	10416	87.49		10428	$M\alpha_{II}$
	C	10406	87.57			

[6] G. Barrère, J. Phys. (Paris) **8**, 72 (1947).

If there is no absorption line present, then the main edge is simply marked K; but where there is an absorption line, then the absorption edge on its long wavelength side is marked K_1 and that on the short-wavelength side K_2.

In Tables I–III, average values of the wavelengths of the absorption lines and edges deduced from each film, ν/R, and the M-emission lines corresponding to absorption values are given for each element investigated.

III. DISCUSSION AND CONCLUSION

Microphotometer curves of the M_{IV} and M_V edges of the rare earths studied here are arranged in the order of increasing thickness of absorbers in Figs. 1–3. These curves reveal the striking influence of the absorber thickness upon the width of the absorption, as pointed out by Sandström,[7] Rule,[8] and Parratt *et al.*[9]: For thin absorbers [Figs. 1(a), 1(b), and 2(a)] absorption has the appearance of a line, but with increasing thickness of the absorber, there is a gradual broadening of the absorption profile in the direction of shorter wavelength,

[7] A. Sandström, Z. Physik **65**, 635 (1930).
[8] K. C. Rule, Phys. Rev. **66**, 199 (1944).
[9] L. G. Parratt, C. F. Hempstead, and E. L. Jossem, Phys. Rev. **105**, 1228 (1957).

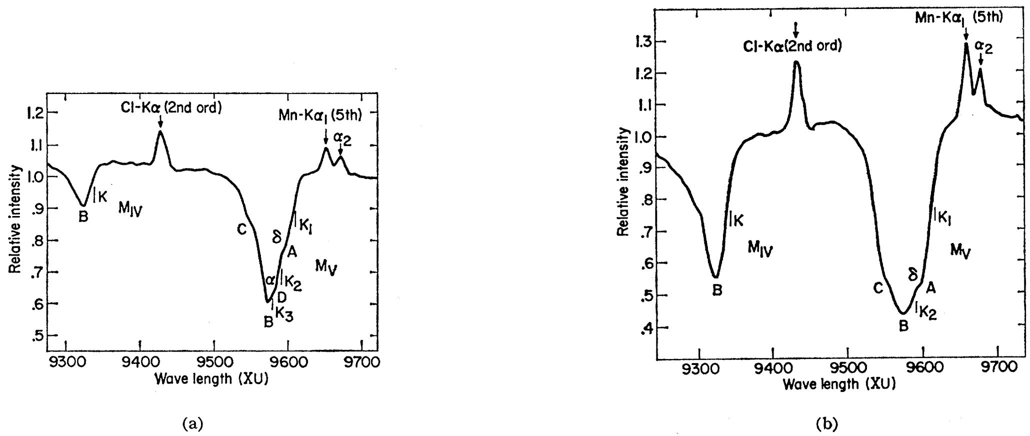


FIG. 2. Microphotometer curves of M_{IV} and M_V absorption of $_{66}$Dy. Thickness of absorbers: (a) 0.115 mg/cm², (b) 0.140 mg/cm².

resulting in the edgelike appearance of the absorption, Figs. 1(d) and 2(b). For $_{70}$Yb, however, the linelike character of absorption has persisted for thicknesses ranging from 0.031 mg/cm² to 0.127 mg/cm², Fig. 3. Vainshtein *et al.*[10] have used much thicker absorbers, 5–6 mg/cm², to record the fine structure of the L_{III} edge of $_{70}$Yb.

There is a remarkably close agreement between wavelengths of the M_V absorption line and the $M\alpha$ of $_{70}$Yb. This indicates the existence of relative transition probabilities which involve the wave function characters of the initial and final states, viz., $M_{IV,V}$ and N_{VII} levels, in accord with the selection rules. Moreover, the linelike character of the absorption may suggest that, for $_{70}$Yb, absorption takes place selectively to the N_{VII} sublevel, so that the probability of any transition to the range of conduction electrons or to the levels in the crystal lattice must be extremely low.

No definite conclusion could be drawn on the M_{IV} edge of $_{70}$Yb, because the Al-K absorption formed by the aluminum foil carrying Yb_2O_3 almost coincided with the edge, making its measurement somewhat uncertain. Because the supply of the oxide had been exhausted, no attempt was made to evaporate fresh oxide onto a more suitable metal foil. Further measurements need to be made for the element $_{68}$Er, and also for still thicker absorbers of $_{70}$Yb, to determine whether or not the linelike shape of the absorption remains persistent.

Figure 1(b) for $_{64}$Gd reveals the presence of a distinct absorption line at the M_{IV} edge separated from the main edge by a narrow and rather faint dark band. The absence of an absorption line at the M_V edge of this element may suggest that the seven electrons in the $4f$ shell must have very nearly filled the N_{VII} sublevel, so that the probability of any transition to this sublevel is extremely low. In a rather similar manner, Veldkamp[11] observed that absorption lines appearing at the L_{II} and L_{III} edges of the elements of W group, due to transition to the incomplete $O_{IV,V}$ level, disappear entirely at $_{79}$Pt, for which one electron is missing in the $5d$ shell.

Beyond $_{64}$Gd, the absorption line disappears at the M_{IV} edge of $_{66}$Dy, but becomes visible at the M_V edge. For this element, therefore, the N_{VI} sublevel must be full while the N_{VII} is in the process of filling up. Moreover, the M_{IV} absorption, unlike the M_V edge, has the character of a line absorption, indicating that it could

TABLE II. M_{IV} and M_V edges of $_{66}$Dy.

Edge		Expt. λ (mean) (xu)	Expt. ν/R (mean)	Calc. ν/R (mean)	Corresponding emission λ (xu)	
M_{IV}	K	9334	97.63	98.18	9345	$M\beta_1$
	B	9321	97.77		9310	$M\beta'$
M_V	K_1	9603	94.89	95.36	9608	$M\alpha_V$
	A	9589	95.03			
	α	9588	95.04		9587	$M\alpha_{IV}$
	K_2	9583	95.09			
	D	9577	95.15		9574	$M\alpha_{III}$
	K_3	9572	95.20			
	B	9567	95.25			
	C	9547	95.45		9555	$M\alpha_{II}$

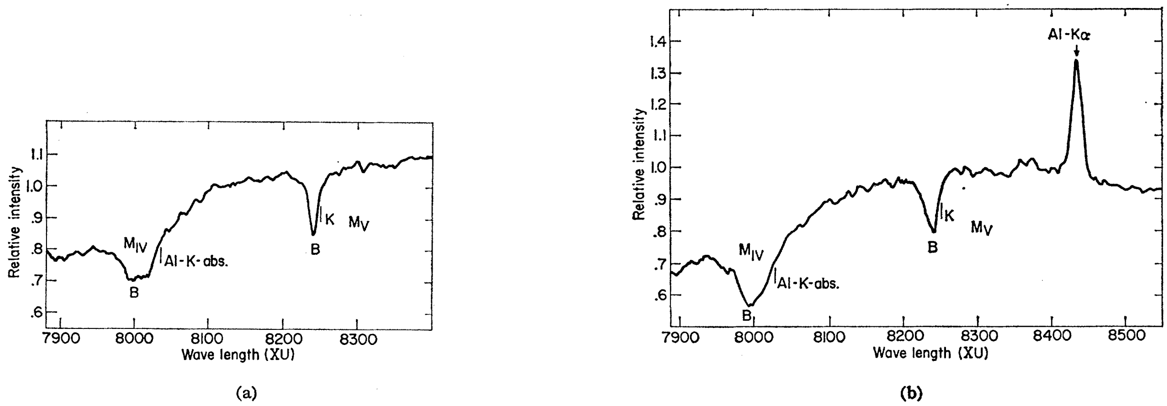
TABLE III. M_{IV} and M_V edges of $_{70}$Yb.

Edge		Expt. λ (mean) xu	Expt. ν/R (mean)	Lindberg[a] λ xu	Lindberg[a] ν/R	Calc. ν/R (mean)	Corresponding emission λ xu	
M_{IV}	K	7898	115.38					
	B	7896	115.41			116.4	7893	$M\beta$
M_V	K	8145	111.88					
	B	8136	112.00	8138	111.98	112.8	8138	$M\alpha_{II}$

[a] Reference 1.

[10] E. E. Vainshtein, S. M. Blokhin, and Yu. B. Paderno, Fiz. Tver. Tela 6, 2909 (1964) [English transl.: Soviet Phys.—Solid State, 6, 2318 (1965)].

[11] J. Veldkamp, Physica 2, 25 (1935).



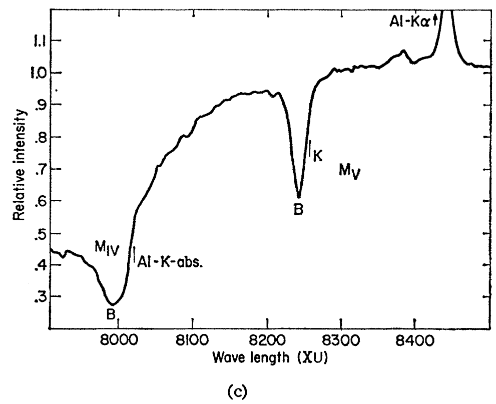


FIG. 3. Microphotometer curves of $M_{\rm IV}$ and $M_{\rm V}$ absorption of $_{70}$Yb. Thickness of absorbers: (a) 0.031 mg/cm^2, (b) 0.076 mg/cm^2, (c) 0.127 mg/cm^2.

very well arise from transitions mainly to the first vacant level allowed by the selection rules, such as $O_{\rm VI,VII}$ level, for example.

For $_{70}$Yb, the 13 electrons of the $4f$ shell have filled the $N_{\rm VI}$ and nearly so the $N_{\rm VII}$ sublevels; thus no absorption line has been detected at either edge. The appearance of the $M_{\rm V}$ edge as a strong absorption line seems to indicate that here, the whole of the absorption must take place selectively to the incomplete $N_{\rm VII}$ sublevel.

Absorption lines have been observed by Cauchois[12] at the $M_{\rm IV}$ and $M_{\rm V}$ edges of $_{94}$Pu and $_{95}$Am separated from the main edges by 1.2 and 1.5 eV, respectively. In our measurements, the separation ranges from 0.96 eV for the $M_{\rm IV}$ edge of $_{64}$Gd to 0.81 eV for the $M_{\rm V}$ edge of $_{66}$Dy.

Lastly, the observed change in the appearance of the profile of the absorption edge, produced by increasing thickness of absorbers, bring into question the true position of the main edge.[9,10] Since the thickest absorber used here is still within the range of optimum thickness, it seems appropriate to regard points marked K_1 or K on the microphotometer curves as true positions of edges. Thus, the values given in Tables I–III, against K_1 or K, should be considered as the nearest wavelength values for these edges. It can finally be concluded that in an absorption process, electrons are lifted to the first incomplete level in the atom, provided that such transitions are allowed by the selection rules.

[12] Y. Cauchois, C. Bonnelle, and L. de Bersuder, Compt. Rend. **257**, 2980 (1963).

ACKNOWLEDGMENTS

The author would like to thank Professor E. A. Stewardson, for his invaluable advice and discussion throughout this work. My thanks are also due to Professor Y. Cauchois for having graciously given the author every opportunity to visit her research laboratories and discuss the design and operation of the spectrograph. Finally, I wish to thank the University of Tehran and the University of Bridgeport for having each granted me a leave of absence, which made this work possible.