PHYSICAL REVIEW VOLUME 68, NUMBERS 11 AND 12 DECEMBER 1 AND 15, 1945

X-Ray Line Absorption in the *M*-Series for 62-Sm*

KENNETH C. RULE
*Institute of Physics, University of Upsala, Upsala, Sweden***

(Received October 11, 1945)

The M_{IV} and M_{V} absorption edges for 62-Sm were studied by use of evaporated films of Sm_2O_3 and $SmCl_3$. In view of data in the literature on M-absorption of the rare earths 70-Yb and 68-Er, it seemed possible that absorption lines would be found corresponding to transitions in which electrons from the M-shell are lifted to the inner N_{VII} and N_{VI} levels. When thin absorption films were employed, the entire absorption had the appearance of lines, but thick films revealed the definite edge-like character of the absorption. The M_{IV} and M_{V} edges are very similar and are both complex, four edges being distinguished in each case. In both cases the first pair of edges is separated from the latter pair by a minimum, which may correspond to transitions in which the electrons are lifted to the N_{VII} and N_{VI} levels.

INTRODUCTION

THE possibility of x-ray "line absorption" corresponding to the transitions $M_{\mathrm{IV}}N_{\mathrm{VI}}$ and $M_{\mathrm{V}}N_{\mathrm{VII}}$ enhances the interest of a study of the M_{IV}- and M_{V}-absorption edges for the elements of the rare earth group.[1,2] The present work reports measurements for the M_{IV}- and M_{V}-edges for 62-Sm.

EXPERIMENTAL

Apparatus

A curved mica crystal having a short radius of curvature, 498 mm, and a large area for reflection, 1.5×20 mm, was employed in the spectrograph in order to shorten the time required for exposure in the study of absorption edges at short wave-lengths. A cathode-ray oven, an integral part of the spectrograph, served for preparation of absorption films by evaporation of the substances to be studied and condensation on aluminum foil, 0.6μ thick. Details of construction of the apparatus have been previously described.[3]

Operation

When exposing for the absorption edges the effective voltage was maintained at 1.6 kv, which is less than two times the excitation potential for the M_{V}-edge. Because the high-potential circuit was not provided with condensers, some second-order radiation was excited at the potential peaks, but third-order radiation was not excited. A tungsten anticathode provided the continuous radiation. The reference substances were KCl ($19-K\ K\alpha_1\lambda = 3733.68$ x.u.) and ZnO ($30-\mathrm{Zn}\ K\alpha_1\lambda = 1432.17$ x.u.).[4]

Sm_2O_3 was prepared from samarium nitrate. $SmCl_3$ was prepared from the oxide by heating at 600°C in a current of S_2Cl_2. Films of Sm_2O_3 were made by evaporating the oxide from a crucible of Mo or graphite. Films of $SmCl_3$ were formed by evaporation from a crucible of Mo. The $SmCl_3$ was not entirely free from oxide. Inasmuch as evaporation of the chloride required only a power output of about 10 watts, while evaporation of the oxide required at least 200 watts, contamination of the film of $SmCl_3$ with evaporated oxide was not probable. The thickness of each film was determined after the absorption measurements had been carried out by weighing the film and its aluminum base.

Since it would have been of interest to observe the absorption edges for metallic Sm, attempts were made to prepare a film of the metal by reduction of the oxide in the crucible and subsequent evaporation of the metal. Because of its high volatility, reduction of $SmCl_3$ in the high vacuum required for the operation of the cathode-ray oven was not attempted. During the short

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* This work was aided by the G. Hilmer Lundbeck fellowship of the American Scandinavian Foundation.

** Present address: South Charleston Division, Westvaco Chlorine Products Corporation, South Charleston, West Virginia.

[1] Ernst Lindberg, Dissertation, Nova Acta Reg. Soc. Sci. Uppsalenius **7**, Ser. IV, No. 7 (1931).

[2] Sandström, Dissertation, Nova Acta Reg. Soc. Sci. Uppsalenius **9**, Ser. IV, No. 2 (1935).

[3] Kenneth C. Rule, Phys. Rev. **66**, 199 (1944).

[4] Manne Siegbahn, *Spektroskopie der Röntgenstrahlen* (Verlagsbuchhandlung Julius Springer, Berlin, 1931), second edition.

time available for pursuing these experiments satisfactory results were not attained with the oxide.

All measurements were made on photometer curves with an abscissa enlargement of 3×. A millimeter netting was copied onto the paper and the enlargement was determined by making a photometer curve of scratches on a plate, whose distances apart had been measured in a comparator. The photometer curves could be read to 0.1 mm = 0.03 mm on the plate = 1.1 x.u. (34 x.u./mm). Inasmuch as the full opening (18–20 mm) of the crystal was employed at the glancing angle of 36°, a focusing defect of 4.7 x.u. was to be expected,[2] but observation of the shifts of the reference lines when 20-mm and 8-mm openings and an abscissa enlargement of 10× were employed showed that the wave-length error introduced by the focusing defect did not exceed 0.4 x.u.

Data and Discussion

The first plates exposed, employing films of SmO_2, bore the appearances of "line absorption." One strong absorption line, preceded by a weaker line at longer wave-lengths, was found for each of the edges, M_V and M_{IV}. Because plates exposed from subsequent films had a different appearance, however, the "lines" having become broader, it was suspected that the results depended upon the thickness of the absorption film. Since the thickness could not be measured accurately, a series of four plates was exposed from an absorption film whose thickness was increased between each exposure by further evaporation of Sm_2O_3. The evaporation times were chosen so as to increase the thickness approximately in the ratios 1:3:10:30. The final thickness of the film was found to be 0.8 mg/cm². The photometer curves made from these four plates are reproduced in Fig. 1.

A complete gradation from an appearance of "line absorption" to true edges is apparent in this series. Further, the absorption for the weak "lines" on the long wave side of the main ones increases relatively as the thickness increases, whereby one or two long wave components of the edge arise. It is obvious that the absorption cannot depend in principle upon the film thickness, but the absorption for each different wave-length is simply more or less dominant depending on the relations between the absorption coefficients and the film thickness.

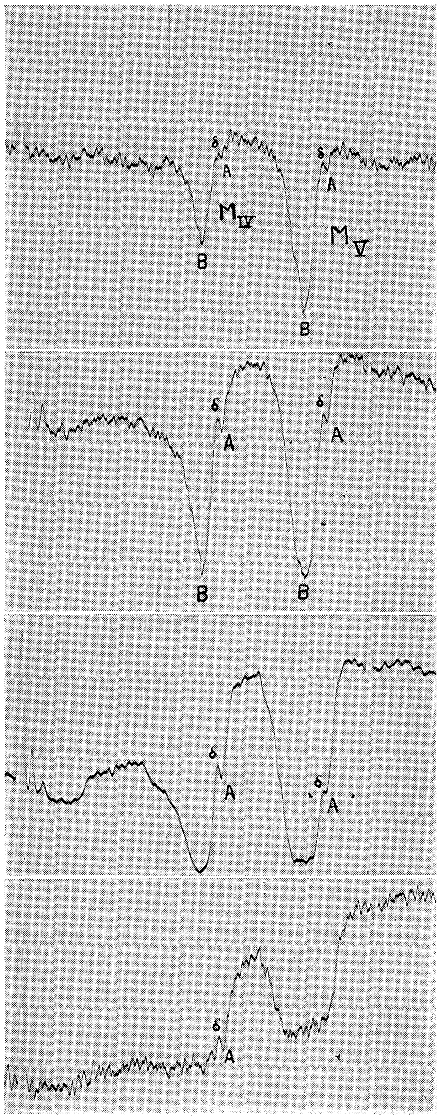

FIG. 1. Photometer curves of M_{IV} and M_V absorption edges of Sm in Sm_2O_3. Thickness of absorption film increases successively from uppermost to lowermost curve.

An entirely analogous group of plates, with absorption varying from line-like to edge-like, was obtained also for $SmCl_3$ absorption films of varying thicknesses. In the case of this substance a new absorption film was produced for each new plate, in order to avoid the danger that a single film, whose thickness was periodically aug-

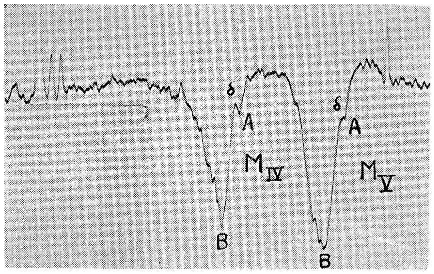

FIG. 2. Photometer curve of M_{IV} and M_V absorption edges of Sm in $SmCl_3$, thin absorption film.

mented, might slowly pick up moisture under a series of long runs. A photometer curve corresponding to the absorption by a relatively thin film of $SmCl_3$ is shown in Fig. 2. The wave-length values for the edges are recorded in Table I. There are no differences of significance between the values obtained with Sm_2O_3 and $SmCl_3$ as absorption films. The agreement is best, in particular, for those details, such as the minima *A* and *B*, which could be measured most accurately. In the following discussion only the data for the oxide will be quoted, but the discussion applies just as well to the results for the chloride.

For each of the edges, M_{IV} and M_V, there appear to be four components. Two of these precede the minima on the long wave side and two follow them. With a spectrograph of greater dispersion or a photographic emulsion of grain size smaller than Agfa 18°/10 Din, other components might possibly be found. A minimum on the photometer curves corresponds, of course, to a maximum in absorption.

The similarity between the M_{IV}- and M_V-edges is striking. For the M_V-edge the minima *A* and *B* differ by 51 x.u., for the M_{IV}-edge by 47 x.u. The first edge, K_1, precedes the minimum *B* by 71 x.u. for the M_V-edge, and by 64 x.u. for the M_{IV}-edge. This similarity indicates that the end levels for M_{IV}- and M_V-absorption are identical.

These results can be compared with Lindberg's data[1] for the $M_{IV}N_{VI}$- and M_VN_{VII}-emission lines for Sm (Table I). The components of the β-line correspond to the $M_{IV}N_{VI}$-transition, those of the α-line to the M_VN_{VII}- and perhaps M_VN_{VI}-transitions. For both the M_{IV}- and M_V-edges absorption begins at a wave-length corresponding to the longest wave components of the β- and α-lines. It is remarkable that the minimum, *A*, in the M_{IV}-edge has almost exactly the same wave-length as the β_I (or $M_{IV}N_{VI}$) line, which may indicate that this minimum is an "absorption line." However, none of the emission lines that have been observed in the α-group corresponds to the minimum, *A*, in the M_V-edge. Table II gives the average wave-length values and the v/R-values for the edges as well as the energy values for the M_{IV}- and M_V-levels as calculated by Raoult[5] from her measurements of the L_{III}-edge for Sm and Siegbahn's values for the *L*-emission lines.[4] The comparison shows, as usual, that the measured values of the energy levels are lower (about 1 percent) than the calculated values.

Similar measurements would have to be made for other rare-earth elements, especially for 63-Eu, for which the β_{II} and β_{III} lines are missing, to determine definitely whether or not the correspondence between the minima *A* and the long wave satellite β_I represents an absorption transition in which the electrons are lifted to the N_{VI} level. This investigation has shown that with homogeneous absorption films of the proper thicknesses the M_V- and M_{IV}-edges for an element of as low an atomic weight as 62-Sm can

TABLE I. Wave-length values in *x* units for the M_{IV}- and M_V-edges and *M*-emission lines for 68-Sm. Figures in parentheses represent the number of measurements (plates) included in the average; the preceding figures show the average deviations from the averages.

	Sm_2O_3			$SmCl_3$			Sulfate	
				M_V-edge			M_V-emission lines[1]	
K_1	11531.1	1.0	(4)	11534.8	5.4	(2)	α_{III}	11532
K_2	11519.4	1.8	(7)	11516.8	1.2	(3)		
A	11511.1	2.7	(8)	11510.2	1.4	(3)		
δ	11500.5	1.6	(7)	11504.7	0.7	(3)		
K_3	11493.7	1.8	(7)	11494.7	4.1	(4)		
K_4	11482.1	3.6	(7)	11482.0	6.3	(4)	α_{II}	11475
B	11460.1	1.4	(4)	11459.8	0.5	(2)	α_I	11406
				M_{IV}-edge			M_{IV}-emission lines[1]	
K_1	11267.6	2.3	(6)	11270.1	2.9	(3)	β_{III}	11271
K_2	11255.9	1.9	(6)	11258.8	2.1	(3)	β_{II}	11254
A	11250.4	0.8	(7)	11250.4	0.7	(4)		
δ	11240.1	2.1	(7)	11241.3	0.7	(3)	β_I	11238
K_3	11232.3	3.1	(7)	11228.0	3.1	(3)		
K_4	11224.4	1.5	(4)	11217.8		(1)		
B	11203.2	1.4	(6)	11204.9	0.0	(2)		
							β'	11147

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[5] Mme. Raoult, Comptes rendus **207**, 434 (1939).

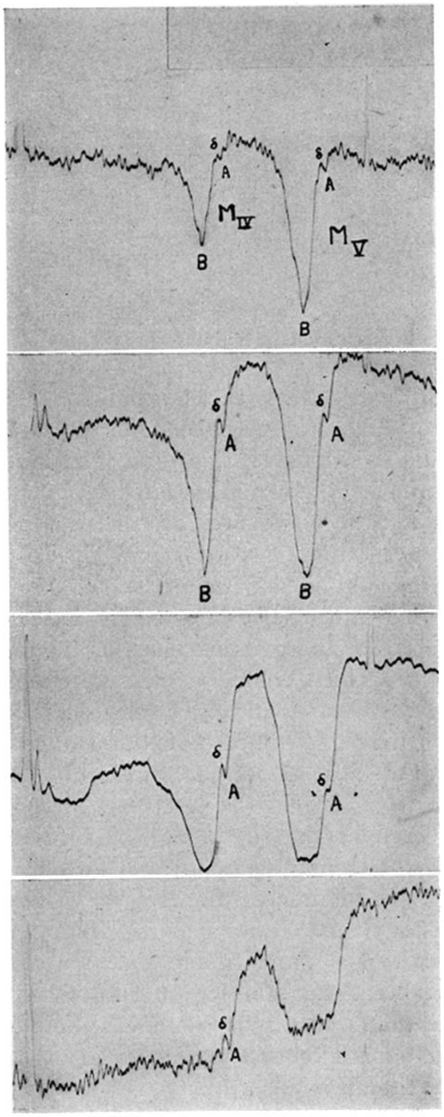
be brought out with great contrast. Furthermore, the observed dependence of the appearance of the absorption edges upon the thickness of the absorption film may bring into question whether the "absorption lines" found by Lindberg for the M_V-edges for 70-Yb and 68-Er were actually due to line-absorption or to the use of excessively thin absorption films.

TABLE II. Average wave-lengths and v/R-values for the edges and calculated energy levels for 68-Sm.

	M_V			M_{IV}	
	x.u.	v/R		x.u.	v/R
K_1	11532.3	79.02	K_1	11268.4	80.87
K_2	11518.6	79.11	K_2	11256.9	80.95
A	11510.8	79.17	A	11250.4	81.00
δ	11501.8	79.23	δ	11240.5	81.07
K_3	11491.1	79.28	K_3	11231.1	81.14
K_4	11482.1	79.36	K	11223.1	81.20
B	11660.0	79.52	B	11203.6	81.34
M_V-level (Raoult[5])		79.94	M_{IV}-level[5]		82.12

ACKNOWLEDGMENTS

The author, a fellow of the American Scandinavian Foundation from 1938 to 1940, wishes to acknowledge his deep indebtedness to Professor Axel E. Lindh, Director of the Physical Institute of the University of Upsala, whose generosity and hospitality made possible the work reported here, as well as previously reported work on the K-absorption edge of 11-Na. Professor Lindh placed a gifted mechanic, Hr. John Amberntson, at the author's disposal for the construction of the spectrograph desired, generously provided all the materials required, and granted complete freedom of choice of the problem and method of investigation. Fil. lic. Philip Haglund provided the mica crystal, and he, assistant Åke Nilsson, and many other scientists at the Institute were unfailingly willing to advise the author in the techniques of curved-crystal, x-ray spectroscopy. Such hospitality is all the more remarkable, extended as it was to a foreigner during the year 1940 and the spring of 1941.



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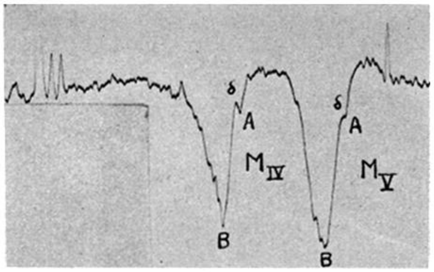

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