Splitting of the $4d_{3/2}$ and $4d_{5/2}$ levels in the rare-earth elements and their oxides

S. I. Salem and Bruce L. Scott

Department of Physics-Astronomy, California State University Long Beach, Long Beach, California 90840

(Received 4 May 1973)

Systematic measurements have been made on the $L\beta_{2,15}[L_3-N_{4,5}]$ and the $L\gamma_1[L_2-N_4]$ x-ray emission lines of the rare earths: ${}_{59}$ Pr, ${}_{60}$ Nd, ${}_{62}$ Sm, ${}_{63}$ Eu, ${}_{64}$ Gd, ${}_{65}$ Tb, ${}_{66}$ Dy, ${}_{67}$ Ho, ${}_{68}$ Er, ${}_{69}$ Tm, and ${}_{70}$ Yb. Each element was studied both in the metallic and oxidized states. The exchange interaction between the 4f and the 4d electrons splits both levels and results in sets of x-ray emission lines that are characteristic of the rare-earth elements alone, and that appear at the low-energy sides of the $L\beta_{2,15}$ and $L\gamma_1$ lines. A computer program was devised to unfold the complex structures, in order to obtain the energy separation and relative transition probabilities of the constituent lines. The effect of oxidation on the splitting of the 4d levels, although insignificant for low- and high-Z elements, was found to be more than expected for elements with atomic number in the neighborhood of 65. It is quite possible that the structures studied consist of more than two discrete emission lines; that is, each of the 4d levels splits into more than two levels, expecially in the low-atomic-number elements. A theoretical interpretation of these results as a simple exchange interaction does not fit the results satisfactorily, so that more theoretical work is needed.

INTRODUCTION

The rare-earth elements have partially filled 4f shells resulting in an electronic configuration parallel to that existing in the transition elements $21 \leq Z \leq 29$, where the 3*d* shells are partially filled. Asymmetry in the $K\alpha_1$ and $K\alpha_2$ x-ray emission lines of the transition elements has been observed,¹⁻³ and has been interpreted as being the result of the interaction between the 3d and the 2pelectrons. Such an interaction results in the splitting of each of the $2p_{3/2}$ and $2p_{1/2}$ electronic levels.⁴ The effect of the partially filled 4f levels in the rare-earth elements on the shape of the $L\beta_{2,15}[L_3 - N_{4,5}]$ and the $L\gamma_1[L_2 - N_4]$ x-ray emission lines has been detected,⁵ it is an order of magnitude greater than what has been observed as asymmetry in the $K\alpha_1$ and $K\alpha_2$ lines of the transition elements.

The 4f electrons in the rare earth elements are not all in the same discrete energy level.⁶ The photoabsorption spectra of rare-earth elements exhibits several broad peaks above the 4d absorption edge.^{7,8} Their position and magnitude have been explained on the basis of an exchange interaction which splits the $4d^94f^{N+1}$ configuration.^{9,10} Such a multiplet splitting has recently been observed in gaseous monatomic ₆₃Eu and several transition elements, and their compounds,¹¹ where the effect of covalent chemical bonding seems to be well understood.¹²

Although some work has been done on the effect of unpaired valence electrons on the photoabsorption spectra of both rare-earth and transition elements, very little has been said about the effect of such states on radiative transitions to innershell vacanices especially in the rare-earth elements.¹³ The photometric work in Ref. 13 covers only a few oxide samples and is far from being a thorough study. Similarly no known work has been done on the elements of the second cycle, $38 \le Z \le 46$. These elements possess a filled Kr core with electrons in the 5s state and a partially filled 4d shell. One expects the exchange interaction to split the 4p levels of these elements, and radiative transitions from these levels should exhibit structures similar to those reported in this paper for the rare earth elements.

In this work systematic measurements have been made on the $L\beta_{2,15}$ and $L\gamma_1$ x-ray emission lines of the elements ${}_{59}$ Pr, ${}_{60}$ Nd, ${}_{62}$ Sm, ${}_{63}$ Eu, ${}_{64}$ Gd, ${}_{65}$ Tb, ${}_{66}$ Dy, ${}_{67}$ Ho, ${}_{68}$ Er, ${}_{69}$ Tm, and ${}_{70}$ Yb both in the metallic and oxidized states. The new emission lines



FIG. 1. Computer unfolding of the $L\beta_{2,15}$ complex of $_{65}$ Tb metal into two Lorentz-shaped lines.

690

9

observed at the low-energy sides of the diagram lines of these elements have been studied, and their positions and areas, relative to those of the $L\beta_{2,15}$ and $L\gamma_1$, emission lines have been computed.

EXPERIMENTAL

For each element studied, two samples were prepared. One was a metallic foil 0.13 mm thick and 99.9% pure. The second was the oxide of the element transformed into a glassy pellet in a KBr pellet press. The oxide samples were also 99.9% pure. Whether metallic or oxide the sample was placed at the surface of a $_{29}$ Cu dish filled with melted $_{31}$ Ga. The sample was then gently pressed into the gallium to insure good thermal contact.

The gallium solidifies holding the sample in the appropriate position. The copper dish is then tightly fitted to a water-cooled anode assembly. Such arrangement proved very satisfactory in keeping the samples from evaporating under electron bombardment.^{14,15} Because of the low evaporation point of Sm₂O₃ it was hard to maintain the desired stability in the sample under bombardment; and several samples evaporated before recording three successful runs. The constantenergy electron beam used in ionizing the target elements was provided by a $_{74}$ W filament fitted in a stainless-steel focusing cup. An insulated transformer supplied the filament with the heating current. A power supply connected in series with a voltage regulator and a ripple suppressor, and



FIG. 2. Energy distribution of the $L\beta_{2,15}$ complex for the indicated rare-earth elements in metallic form. The solid lines are from Eq. (1), and the bars indicate statistical errors.

9

delivering a steady voltage with less than 0.3%ripple at a full load of 120 keV and 30 mA was used to accelerate the electron beam. The samples under study were exposed to the electron beam in a locally designed and built x-ray tube which is continuously pumped to a pressure of about 10⁻⁶ mm of Hg. Generally, the samples were bombarded with an electron beam of 0.5 mA and 20 keV.

The emission spectra of the studied samples was analyzed using a modified single-crystal highangle goniometer, and a NaI scintillation detector. The intensity of the emission lines and the accompanying profiles was measured by stepping the spectrometer through the Bragg angle 2θ in steps of 0.01 deg. At each position the number of counts was taken for three one-minute intervals and averaged. Several runs were made for each of the studied samples, and only the average values are reported.

DATA ANALYSIS

The experimental data were fitted by the sum of two Lorentz-shaped lines having a constant background,

$$I(E) = B + \frac{I_1}{1 + (E - E_1)^2 / \Gamma_1^2} + \frac{I_2}{1 + (E - E_2)^2 / \Gamma_2^2}, \quad (1)$$

where I(E) is the intensity as a function of the energy, E, and is proportional to the observed number of counts. E_1 and E_2 are the energies of the constituent lines, Γ_1 and Γ_2 their half-widths,



FIG. 3. Energy distribution of the $L\gamma_1$ complex for the indicated rare-earth elements in metallic form. The solid lines are from Eq. (1) and the bars indicate statistical errors.

TABLE I. Relative transition probabilities A'/A and the energy separation ΔE for the $L\beta_{2,15}$ complex for the rare-earth elements and their oxides. The indicated errors are the average absolute deviation from the average of the computer fitted values obtained using Eq. (1).

Atomic		Metal		Oxide	
number	Symbol	A' /A	ΔE (eV)	A' /A	ΔE (eV)
59	Pr	0	•••	0	•••
60	Nd	0.02 ± 0.01	23.4 ± 2.0	0.05 ± 0.02	25.2 ± 2.0
62	Sm	0.21 ± 0.01	25.9 ± 1.6	0.11 ± 0.03	28.0 ± 1.4
63	Eu	0.19 ± 0.03	24.6 ± 0.6	0.21 ± 0.04	25.8 ± 2.5
64	Gd	0.56 ± 0.11	23.3 ± 2.0	0.41 ± 0.11	25.1 ± 1.3
65	Tb	0.24 ± 0.02	26.0 ± 0.1	0.38 ± 0.06	22.4 ± 0.2
66	Dy	0.40 ± 0.03	20.3 ± 0.5	0.57 ± 0.10	16.7 ± 2.2
67	Но	0.46 ± 0.25	18.2 ± 2.2	0.55 ± 0.11	14.6 ± 1.3
68	Er	0.43 ± 0.16	17.8 ± 2.0	0.30 ± 0.13	14.4 ± 0.8
69	Tm	0.23 ^a	13.4 ^a	0.12 ± 0.02	10.9 ± 0.2
70	Yb	0	•••	0	•••

^a Only a single point was available.

and I_1 and I_2 their intensities; and B is the assumed constant background.

An independent fit was made to each of the different experimental measurements, and the parameters B, I_1 , I_2 , Γ_1 , Γ_2 , E_1 , and E_2 were determined by minimizing the function χ^2 , given in Eq. (2), using the square root of the experimental value as a weighting factor as is appropriate for statistical errors:

$$\chi^{2} = \sum_{i=1}^{N} \left\{ \left[I_{i} - I(E_{i}) \right] / \sqrt{I_{i}} \right\}^{2} .$$
 (2)



FIG. 4. Relative transition probabilities A'/A, of the wing lines to the main lines as a function of atomic number. The top graph is the $L\beta_{2,15}$ complex and the bottom is the $L\gamma_1$ complex for both metallic and oxidized samples. The error bars represent average absolute deviations from the average value for several independent fits of Eq. (1) to the sets.

energy separations ΔE for the $L\gamma_1$ complex for the rare-earth elements and their oxides. The indicated errors are the average absolute deviation from the average of the computer-fitted values obtained using Eq.(1). Atomic Metal Oxide

TABLE II. Relative transition probabilities A'/A and

Atomic	M		etal	Ох	Oxide	
number	Symbol	A' /A	$\Delta E (eV)$	A' /A	$\Delta E (eV)$	
59	Pr	0.15±0.10	25.5 ± 2.4	0.09 ± 0.03	24.3±2.7	
60	Nd	0.33 ± 0.07	23.2 ± 0.7	0.19 ± 0.05	20.1 ± 0.3	
62	Sm	0.35 ± 0.05	19.2 ± 3.0	0.48 ^a	21.5 ^a	
63	Eu	0.36 ± 0.01	21.5 ± 0.3	0.59 ^a	21.8 ^a	
64	Gd	0.30 ± 0.04	23.7 ± 0.6	0.55 ± 0.03	21.5 ± 0.4	
65	Tb	0.36 ± 0.07	21.0 ± 0.8	0.62 ± 0.23	19.6 ± 0.4	
66	Dy	0.36 ± 0.01	18.4 ± 0.1	0.56 ± 0.03	17.4 ± 0.6	
67	Но	0.26 ± 0.03	16.1 ± 0.3	0.27 ± 0.14	17.8 ± 1.7	
68	Er	0.10 ± 0.02	12.8 ± 4.8	0.16 ± 0.02	18.9 ± 2.0	
69	Tm	0.05 ± 0.01	13.3 ± 0.9	0	•••	
70	Yb	0	•••	0		

^a Only a single point was available.

The energy E_i of each data point was calculated in each run by matching the interpolated peak of the experimental data with the energy value recorded for that line in Bearden's tables.¹⁶ It was assumed that the energy of the diagram lines was independent of the sample form. The chemical line shift between metal and oxide samples was neglected as it has an insignificant effect on the final results. In Eq. (2), N is the number of data points in a particular run, and I_i is the observed number of counts at the energy E_i . These calculations were carried out using a CDC3150. Figure 1



FIG. 5. Energy separation ΔE of the wing line from the main line as a function of atomic number. The top graph is the $L\beta_{2,15}$ complex and the bottom is the $L\gamma_1$ complex for both metallic and oxidized samples. The error bars represent average absolute deviations from the average value for several independent fits of Eq. (1) to the data sets.

shows the $L\beta_{2,15}$ complex from metallic ₆₅Tb separated into its "assumed" two constituent lines. Similar computer fits for several line complexes are shown in Figs. 2 and 3, where the points are experimental, the solid lines are from Eq. (1), and the error bars represent statistical counting errors only.

RESULTS AND DISCUSSION

Fitting the experimental data by the sum of two Lorentz-shaped lines gave the results summarized in Tables I and II and in Figs. 4 and 5. The indicated errors are the average absolute deviation of an individual run from the average of all runs taken for that particular line. This number is, then a measure of the accuracy to which the parameters in Eq. (1) can be determined from the experimental data. The ratio of the radiative transition probability of the weaker line to that of the main (diagram) line is denoted by A'/A and is given by $I_2 \Gamma_2/I_1 \Gamma_1$, while $\Delta E = E_1 - E_2$ is their energy separation. A zero in these tables indicates that the data could not distinguish between a single line or two lines one of which is quite weak.

Figure 4 presents the ratio A'/A as a function of atomic number for both the $L\beta_{2,15}$ and the $L\gamma_1$ complexes, and exhibits two main characteristics: (a) The ratio A'/A for $L\beta_{2,15}$ is shifted towards high Z relative to that of $L\gamma_1$, and (b) for medium atomic number elements, A'/A has a significantly higher value for the oxides than for the metallic samples. To emphasize this point composite results for $_{65}$ Tb $L\beta_{2,15}$ from metallic and oxide samples are normalized to the same intensity and superposed (Fig. 6).

The outer electronic configurations of rare-



FIG. 6. Composite of four runs of $L\beta_{2,15}$ complex from a metal sample (dashed curve) and four runs of the $L\beta_{2,15}$ complex from an oxide sample (solid curve) are compared. All eight runs were computer normalized to the same height.

earth atoms is altered when they enter into chemical composition (oxidation), which in general removes the 6s electrons and reduces by one the number of electrons in the 4f shell.¹⁷ But the samples used in this work were either metallic or oxides (not free atoms) and rare-earth atoms in metallic or oxidized states are expected to have the same electronic configuration and are generally trivalent.⁹ If so the emission spectra from both metals and oxides should be the same and one expects no significant change in the value of the ratio A'/A. The apparent irregularity at ₆₄Gd may be due to the fact that Gd is the only rare-earth element having a $4f^75d6s$ ground-state configuration rather than the usual $4f^N6s^2$.

Figure 5 presents the energy separation ΔE as a function of atomic number for both the $L\beta_{2,15}$ and the $L\gamma_1$ complexes. Both oxides and metals seem to have the same functional dependence on Z, and the two lines seem to get closer together as Z increases. It should be mentioned that although within experimental error, the value of ΔE for the $L\beta_{2,15}$ complexes is larger for the oxides than for the metals at low-Z values, and the situation is reversed for higher-Z elements.

Although all the data were satisfactorily fitted by the sum of two Lorentzians, it is quite possible that the studied structures consist of more than two discrete emission lines; that is, each of the 4d levels splits into more than two sublevels. This seems to be especially true for elements of low atomic number (Fig. 7).

Line structures very similar to those reported here have been known for some time to occur in the transition elements. Various workers have proposed several explanations for this line splitting. The work of Tsutsumi¹⁸ showed that the line splitting could not be due to multiple ionization. He elaborated on a splitting caused by the Coulomb exchange interáction between the hole in the 3p



FIG. 7. $L\gamma_1$ complex of (a) ${}_{59}$ Pr and (b) ${}_{60}$ Nd showing in addition to the main diagram line, the possible existence of two emission lines (arrows).

TABLE III. Relative transition probabilities A'/A and energy separations ΔE as given by Eqs. (3) and (5), respectively. The same results apply to both the $L\beta_{2,15}$ and the $L\gamma_1$ transitions.

Atomic number	Symbol	Spin of $4f$ electrons, S	A' /A	Δ <i>Ε</i> (eV)
59	Pr	37	0.60	8.2
60	Nd	2	0.67	10.7
61	Pm	52	0.71	13.3
62	\mathbf{Sm}	ž	0.75	16.1
63	Eu	$\frac{7}{2}$	0.78	18.9
64	Gd	$\frac{7}{2}$	0.78	20.2
65	Tb	5	0.71	15.6
66	Dy	2	0.67	12.9
67	Но	3	0.60	10.5
68	Er	ĩ	0.50	8.1
69	Tm	$\frac{1}{2}$	0.33	5.5
70	Yb	ŏ	0.00	2.8

level and the electrons in the partially filled 3dlevel of the transition elements. His results gave order of magnitude agreement only. Nefedov¹⁹ introduced spin-orbit coupling with some success, while Ekstig et al.²⁰ performed a much more detailed analysis including configuration interaction and considering the entire transition sequence but with only qualitative success. Since the spin-orbit splitting of the 4d level is too small to explain the observed splitting and the exchange interaction of the 4d hole with the partially filled 4f level in the rare earths must surely be present, it is of interest to see whether this might explain the observed results as reported in this paper. Tsut- $\operatorname{sumi}^{\scriptscriptstyle 18}$ has shown that the energy separation is given by

$$\Delta E = J(2S+1), \tag{3}$$

where J is the exchange integral and S is the total

- ¹L. G. Parratt, Phys. Rev. 50, 1 (1963).
- ²J. A. Bearden, and C. H. Shaw, Phys. Rev. <u>48</u>, 18 (1935).
- ³T. Snyder, Phys. Rev. 59, 689 (1941).
- ⁴E. E. Wainstein, C. R. (Dokl.) L'Acad. Sci URSS <u>40</u>, 102 (1943).
- ⁵S. I. Salem, C. W. Schultz, B. A. Rabbani, and R. T. Tsutsui, Phys. Rev. Lett. 27, 477 (1971).
- ⁶G. K. Wertheim, A. Rosencwaig, R. L. Cohen, and
- H. J. Guggenheim, Phys. Rev. Lett. 27, 505 (1971).
- ⁷T. M. Zimkina, V. A. Fomichev, S. A. Gribovskii, and I. I. Zhukova, Fiz. Tverd. Tela <u>9</u>, 1447 (1967); Fiz Tverd Tela <u>9</u>, 1490 (1967) [Sov. Phys.-Solid State <u>9</u>, 1128 (1967); Sov. Phys.-Solid State <u>9</u>, 1163 (1967)].
- ⁸R. Haensel, P. Rabe, and B. Sonntag, Solid State Commun. 8, 1845 (1970).

spin of the partially filled 4f shell. J can be expressed in terms of Slater integrals

$$J = \frac{3}{35}G^{1}(4d4f) + \frac{4}{105}G^{3}(4d4f) + \frac{10}{231}G^{5}(4d4f).$$
(4)

The ratio of the transition probabilities are given by the level multiplicity only;

$$A'/A = S/(S+1).$$
 (5)

Using these three equations and taking Hartree-Fock Slater integrals as computed by Mann,²¹ we have obtained the values presented in Table III. These results may be compared with the observed values as summarized in Tables I and II.

It is clear that this simple theory is inadequate for the rare earths. Although the calculated and observed ratios of the transition probabilities have much the same Z dependence, the theoretical values are too large. (This was also the case in Tsutsumi's study of the transition elements). The predicted energy separation fits rather well for half-filled 4f shells ($_{64}$ Gd) but is considerably too small for the other elements. Since Tsutsumi studied only elements with nearly half-filled 3dshells (Mn, Fe, and Co) his agreement with observation does not differ from ours.

We must conclude that, although this 4d-4f exchange effect is surely present, it cannot be the sole cause of the splitting of the 4d levels. This observed splitting must still be regarded as not understood.

ACKNOWLEDGMENTS

We would like to acknowledge the assistance of Dr. G. E. Kalbus in the preparation of the oxide samples, and the constructive suggestions of Dr. J. I. Zink. The authors wish to thank the Long Beach California State College foundation for Summer grants which aided in the completion of this work.

- ⁹J. L. Dehmer, A. F. Starace, U. Fano, J. Sugar, and J. W. Cooper, Phys. Rev. Lett. 26, 1521 (1971).
- ¹⁰Jack Sugar, Phys. Rev. B 5, 1785 (1972).
- ¹¹C. S. Fadley and D. A. Shirley, Phys. Rev. A <u>2</u>, 1109 (1970).
- ¹²C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, Phys. Rev. Lett. <u>23</u>, 1397 (1969).
- ¹³P. Sakellaridis, J. Phys. Radium <u>16</u>, 422 (1955).
- ¹⁴S. I. Salem, D. C. Clark, and R. T. Tsutsui, Phys. Rev. A 4, 2390 (1972).
- ¹⁵S. I. Salem, R. T. Tsutsui, and B. A. Rabbani, Phys. Rev. A <u>4</u>, 1728 (1971).
- ¹⁶J. A. Bearden, Rev. Mod. Phys. <u>39</u>, 78 (1967).
- ¹⁷F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, A Comprehensive Text, 2nd edition (Wiley,

- New York, 1966), p. 1052. ¹⁸K. Tsutsumi, J. Phys. Soc. Jap. <u>14</u>, 1696 (1959); J. Phys. Soc. Jap. <u>25</u>, 1418 (1968). ¹⁹V. I. Nefedov, J. Struct. Chem <u>5</u>, 603 (1964); J. Struct.
- Chem. 7, 672 (1966).
- ²⁰B. Ekstig, E. Kallne, E. Noreland, and R. Manne, ²¹J. B. Mann, Los Alamos Report No. LA-3690, 1967
- (unpublished).