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Self-Absorption Effects in the Soft X-Ray M_α and M_β Emission Spectra of the Rare Earth Elements

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The M_α and M_β emission spectra and the M_{IV} and M_{V} absorption spectra have been studied for the rare earth elements. It is conclusively shown that the complicated multiplet structure observed in the emission spectra is not real emission structure but is, instead, produced by sample self-absorption. This is demonstrated by observing the emission spectra over wide variations in take-off angle and bombarding-electron energies and finally by comparing the detailed structure of both the emission and absorption spectra. The M_{IV} and M_{V} absorption structure completely overlaps the M_α and M_β emission lines which are each found to have but one intensity maximum when obtained under conditions of minimum self-absorption. Some of these spectra have never been shown previously, while others have been studied in detail by several investigators. Points of agreement and disagreement with previous work are mentioned and the wavelengths of the emission lines and absorption edges are listed for all of the lanthanides. It is concluded that $4f \rightarrow 3d$ electron transitions are reversible in these elements.

I. INTRODUCTION

The rare earths are a unique series of elements insofar as they have an inner shell of electrons which is not full. The $3d$ and $4d$ shells of the first and second transition series elements are also unfilled but they are admixed to some extent with the valence band permitting the d electrons to become involved in chemical bonding. In the rare earth elements (lanthanides), however, the unfilled $4f$ shell is truly an inner shell and the $4f$ electrons play little part in chemical bonding.[1,2] This accounts for the almost identical chemical properties of the rare earths and also forms the basis for some unusual phenomena observed in their M_α and M_β x-ray emission spectra which fall in the 7.6–14.9-Å wavelength region.

The M_α ($4f \rightarrow 3d\frac{5}{2}$, or $M_{\text{V}}N_{\text{VI,VII}}$) and M_β ($4f \rightarrow 3d\frac{3}{2}$, or $M_{\text{IV}}N_{\text{VI}}$) emission spectra of the rare earths represent transitions involving the unfilled shell. Theoretically, one would expect the emission lines resulting from such transitions to be complicated multiplets because of coupling between the incomplete $4f$ shell and the singly ionized M_{IV} or M_{V} shell.[3] Apparent confirmation of this general idea was first shown some 40 years ago by Van der Tuuk[4] and a short time later by Lindberg.[5] Both were able to resolve the broad M_α line into several components for most of the rare earths. The M_β line was also resolved into more than one component, but in general was not as complicated as M_α. Hirsch[6] explained the extra M_β structure as double-jump satellites and concluded that the M_α satellites vanished at erbium, the rest of the multiple splitting being part of the main M_α band. Apparently it was felt that experimental results were fully explained and there was no further reason to seriously question the complicated multiplet structure observed for M_α. No other complete study of these rare earth emission spectra has appeared since Lindberg's work some 36 years ago.[5]

In 1945 Rule[7] studied the $M_{\text{IV,V}}$ absorption spectra of samarium and observed a curious correspondence between wavelengths of points on his absorption curves with the emission lines of Lindberg.[5] Lindberg had, in fact, obtained the M_{V} absorption line for two of the rare earths (Yb and Er) and considered them to correspond to the "$M_{\alpha\text{III}}$" and "$M_{\alpha\text{IV}}$" emission lines. Later, Zandy[8] confirmed Rule's observation of correspondence between points on the absorption and emission spectra of samarium, but was not sure just what physical significance should be attached to such correspondence. Zandy also obtained the $M_{\text{IV,V}}$ absorption spectra of Eu, Nd, and Pr but was unable to observe any correspondence between emission and absorption spectra. The $M_{\text{IV,V}}$ absorption spectra had also been obtained for a few other rare earths by Stewardson and Lee[9] (erbium) and Lee, Stewardson and Wilson[10] (thullium and erbium) but no comparison was made with emission spectra. Then in 1956 a reinvestigation of the erbium $M_{\text{IV,V}}$ absorption spectrum by Stewardson and Wilson was published.[11] The absorption spectrum was compared to the $M_{\alpha,\beta}$ emission lines and revealed a complete overlap in wavelength between the respective emission and absorption lines. It was also observed that the multiplet structure of the erbium emission spectrum became more distinct as higher electron-beam potentials were used. Stewardson and Wilson then concluded that the erbium emission multiplet structure of both M_α and M_β was not real, but was produced by

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[1] D. N. Trifonov, *The Rare Earth Elements* (Pergamon Press, Inc., New York, 1963).

[2] N. E. Topp, *The Chemistry of the Rare Earth Elements* (Elsevier Publishing Co., Inc., New York, 1965).

[3] I. B. Borovskii and T. M. Golovner, Dokl. Akad. Nauk (USSR) **88**, 233 (1953).

[4] J. H. Van der Tuuk, Z. Phys. **44**, 737 (1927).

[5] E. Lindberg, Nova. Acta Reg. Soc. Sci. Upsaliensis **7**, 7 (1931).

[6] F. R. Hirsh, Phys. Rev. **38**, 914 (1931).

[7] K. C. Rule, Phys. Rev. **68**, 246 (1945).

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

[9] E. A. Stewardson and P. A. Lee, Proc. Phys. Soc. (London) **64A**, 318 (1951).

[10] P. A. Lee, E. A. Stewardson and J. E. Wilson, Proc. Phys. Soc. (London) **65A**, 668 (1952).

[11] E. A. Stewardson and J. E. Wilson, Proc. Phys. Soc. (London) **69A**, 93 (1956).

self-absorption in the target material, the true emission being a broad single line probably accompanied by true satellites.

Our intention in this paper is to show that the multiplet structure of both M_α and M_β observed for all of the lanthanide rare earths is caused entirely by self-absorption effects and attempt to show, as far as possible, the true appearance of the emission spectra. This entails a detailed investigation of both emission and absorption spectra, many of which have not previously been shown in the literature.

II. EXPERIMENTAL TECHNIQUES

A. Instrumentation

The flat crystal vacuum spectrometer used for this investigation has been described previously.[12] Characteristic emission spectra are produced by electron-beam bombardment of the target material which is mounted on a four-sided rotatable brass anode. For absorption studies the continuum from a platinum or gold target was used. A special anode assembly was constructed for part of the self-absorption studies and it has the capability of being rotated perpendicular to the entrance soller slit, making the take-off angle continuously variable between 0° and 70°.

The detector is a thin-window, flow-proportional counter using an argon–methane (P-10) flow gas at a reduced pressure (120 Torr). All recording electronics, including the pulse-height discriminator, were commercial Picker equipment except for a low-noise Tennelec preamplifier. The resultant rate meter scans and the curves shown in the figures have a mean deviation of $\pm 2\%$.

Several different crystals were used to disperse the radiation, a particular crystal being chosen to provide the best possible dispersion of a given wavelength interval. The following crystals were used in this study: EDT ($2d = 8.8030$ Å) for lutetium, ytterbium, and thullium; ADP ($2d = 10.639$ Å) for erbium, holmium, dysprosium, terbium, and gadolinium; ammonium tartrate ($2d = 14.152$ Å) for europium, samarium, neodymium, praseodymium, and cerium; sucrose ($2d = 15.121$ Å) for lanthanum.

A special eight-position sample wheel was used to hold the absorption film specimens and placed directly in front of the detector slit. This wheel could be rotated to any one of the eight positions from outside the vacuum. This enabled us to obtain both the emission and absorption spectrum from the same element during the same run. Normal operating vacuum was $1\text{–}3 \times 10^{-6}$ Torr.

The $M_{\alpha,\beta}$ spectra of the rare earths cover the 7.6–14.9 Å region and several wavelength standards were used throughout the region to measure energy positions of the rare earth spectra. The standards used were AlK_{α_3} (8.2820 Å) and K_{α_4} (8.2718 Å) from Al_2O_3; MgK_{α_3} (9.8209 Å) and K_{α_4} (9.8078 Å) from MgO, and CuL_{III} (13.330 Å) from Cu metal.[13]

B. Sample Preparation

All of the rare earth emission spectra were run, where possible, from both metal and oxide specimens. The oxides were all in the form of fine powder which were mixed into a slurry with acetone or methanol and spread directly on the anode surface. Metallic samples were prepared by vacuum evaporation of metal chunks onto aluminum foil and some were run in the form of thin rolled sheet. A few of the metals, especially europium, were quite difficult to keep from oxidizing and it is doubtful that the spectra obtained from them are truly characteristic of the metal. For those elements where metallic spectra could be obtained, only the spectrum of ytterbium showed any change between metal and oxide. The spectra shown in Figs. 1–9 are from the oxides.

Absorption specimens were prepared by vacuum evaporation of metal or oxide chunks onto aluminum foil (2.0 mg/cm^2) or onto an extremely thin Formvar film. The rare earth thickness varied between approximately 0.05 and 0.2 mg/cm^2.

III. RESULTS AND DISCUSSION

The rare earth M_α and M_β emission spectra obtained at 10 kV are shown in Fig. 1. It is rather difficult to compare these spectra with those which have been obtained previously since all of the earlier work was done using photographic film as the detector. Most of the work includes tables of wavelength values of the M_α and M_β components but it is often difficult to visualize just how a spectrum looks from a table of wavelength values. It appears, however, that our wavelength positions agree quite well with those listed by Lindberg.

Since Lu has a filled $4f$ shell one would expect the Lu M_α and M_β spectra to be quite similar to that of the next higher elements Hf, Ta, etc., which, indeed, it is. As seen in Fig. 1, the Lu spectrum consists of two sharp lines, each with some high-energy satellite structure. The next lower atomic number element, Yb, has one $4f$ vacancy and this causes a change in the emission spectrum. Both M_α and M_β become broader and their relative intensity changes significantly; also the M_α line now shows an extra component. At Tm the spectrum changes even more and so on down the series as the $4f$ shell begins to empty out. Notice that when going from lutetium down through samarium the M_α band shows more and more multiplet structure and becomes weaker and weaker with respect to M_β. The M_β

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[12] D. W. Fischer and W. L. Baun, Spectrochim. Acta **21**, 443 (1965).

[13] W. L. Baun and D. W. Fischer, *Advances in X-Ray Analysis* (Plenum Press, Inc., New York, 1965), Vol. 8.

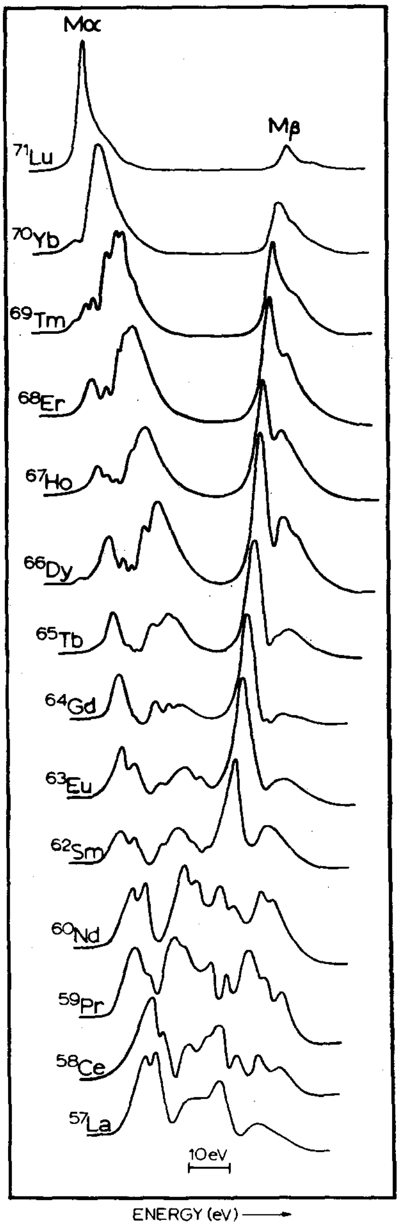

FIG. 1. M_α and M_β emission spectra of the rare earth elements obtained with electron-beam potential of 10 kV and 30° take-off angle.

band, on the other hand, does not become so complicated in structure but appears as a main M_β with a high-energy "satellite" which becomes more and more separated from the main component. Hirsh,[6] in fact, found that these extra high-energy peaks followed very nicely the expected Moseley relationship for M_β satellite lines. The M_α satellites appeared to vanish at erbium and from there on down the structure was all attributed to the main M_α band. Notice that at Nd the spectra again change so that for the bottom four elements it is difficult to pick out by sight the individual M_α and M_β structures. From the spectra shown in Fig. 1 one can follow what appears to be a systematic change from element to element. Theoretical predictions of multiplet structure arising from multiple 4*f* vacancies seem to be beautifully confirmed.[3]

When we first observed these spectra, we were duly impressed but upon closer inspection some inconsistencies were found. Reasonably good values of the energy separation between the M_{IV} and M_V levels can be obtained from the L_{α_1} and L_{α_2} lines which were studied by Sakellaridis[14] and others. The M_α and M_β lines should be separated by this same amount. In order to obtain these expected energy spreads it is necessary to use the strongest M_β component and the longest wavelength M_α component which in some cases is the weakest in intensity of any of the multiplets. One cannot help but notice the puzzling difference in behavior of the M_α and M_β emission groups. M_β remains relatively simple with the apparent main component and high-energy satellite. M_α, on the other hand, appears to split into as many as six components. It is also difficult to explain why the M_α emission as shown in Fig. 1 is so much weaker in intensity than M_β for elements such as Tb, Gd, Eu, and Sm. One would expect the M_α/M_β intensity ratio to decrease because of the depopulation of the N_{VII} levels with decreasing atomic number but the ratios shown in Fig. 1 are too low to be accounted for on this basis alone.

These inconsistencies became somewhat clarified as the result of an investigation which produced the spectra shown in Figs. 2 and 3. These figures show the DyM_α and M_β emission spectra obtained with various

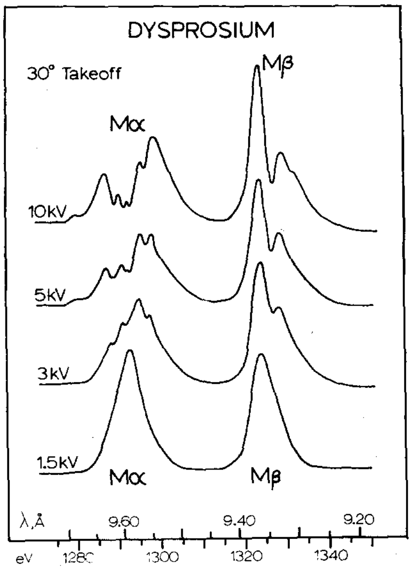

FIG. 2. Dysprosium M_α and M_β emission spectra obtained at various electron-beam energies with constant 30° take-off.

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[14] P. Sakellaridis, Compt. Rend. **236**, 1244 (1953).

electron-beam energies and take-off angles. Notice that as the beam voltage is increased and/or the take-off angle is decreased the multiplet structure becomes more distinct and M_α becomes weaker with respect to M_β. Thus the spectral details and intensity ratios are dependent on the effective depth from which the x-rays emerge from the target material. The obvious conclusion is that the multiple components of M_α and M_β are being produced by self-absorption effects as first proposed by Stewardson and Wilson for erbium.[11] The rest of the rare earths show similar results when subjected to the same variations in electron-beam voltage and take-off angle as shown for dysprosium in Figs. 2 and 3.

For every element the multiplet structure was most pronounced under conditions of high electron-beam voltage and/or very low take-off angle. Under conditions of minimum self-absorption, the spectra are found to consist of a single line for both M_α and M_β as shown in Fig. 4. These spectra were all obtained with bombarding-electron energies of 200–300 V in excess of M_{IV} threshold from the same specimens and during the same run as the spectra shown in Fig. 1. Compare these two figures and notice the very striking difference in the spectra especially from elements such as Nd, Pr, and Ce. The spectra in Fig. 4 may still be slightly affected by self-absorption, especially in relation to the relative intensities of M_α and M_β, but they should be very close to being the "true" emission spectra. It would be better to use electron-beam voltages even closer to M_{IV} threshold than we used to obtain these spectra but, in our case, the intensity would be too low to obtain reliable line profiles. The wavelength values of the M_α and M_β intensity maxima of Fig. 4 are listed in Table I. These wavelengths are in fairly good agreement with those listed by Bearden[15] who averaged Lindberg's multiplet component measurements[5] by using a modified Moseley diagram. When a Moseley plot is made of the values in Table I, very straight lines are obtained for both M_α and M_β.

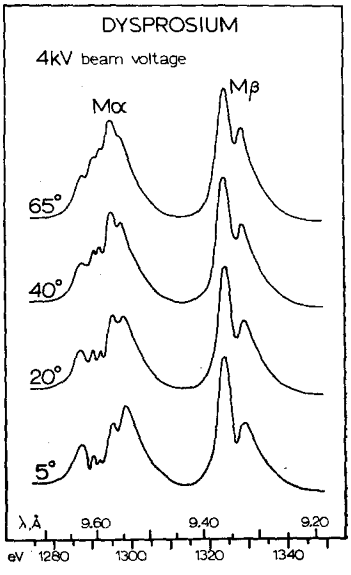

FIG. 3. Dysprosium M_α and M_β emission spectra obtained at various take-off angles with constant 4-kV electron-beam voltage.

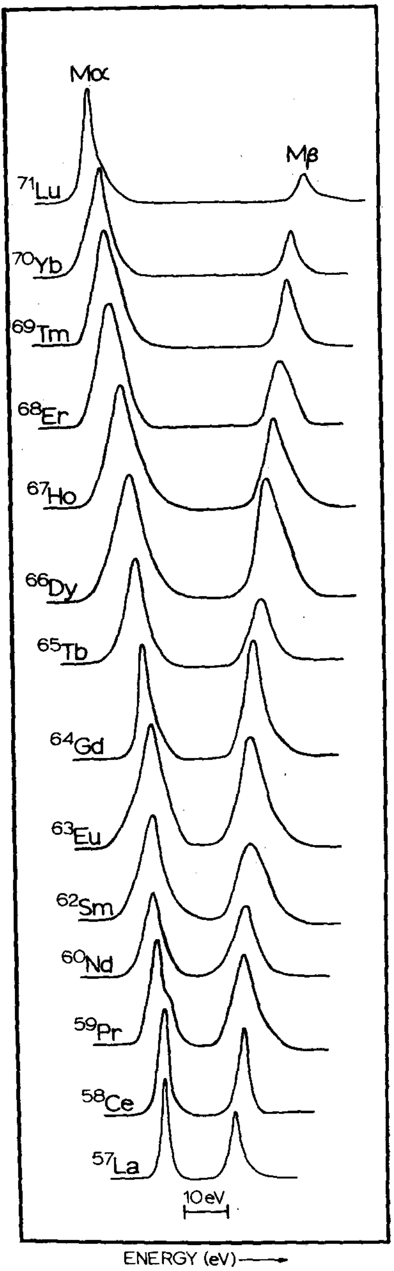

FIG. 4. M_α and M_β emission spectra of the rare earth elements obtained under minimized self-absorption conditions. Electron-beam voltage was 200–300 V in excess of M_{IV} threshold with high take-off angle.

To illustrate even more clearly that these gross dis-

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[15] J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

TABLE I. Wavelengths of rare earth M_α and M_β emission lines obtained with minimized self-absorption conditions.

Element	$M_\alpha(M_\text{V}N_\text{VI,VII})$ λ(Å)	$M_\alpha(M_\text{V}N_\text{VI,VII})$ (eV)	$M_\beta(M_\text{IV}N_\text{VI})$ λ(Å)	$M_\beta(M_\text{IV}N_\text{VI})$ (eV)
La	14.859 ±0.005	834.38 ±0.30	14.573 ±0.005	850.75 ±0.30
Ce	14.078	880.66	13.786	899.32
Pr	13.339	929.45	13.056	949.60
Nd	12.667	978.76	12.399	999.91
Sm	11.485	1079.49	11.249	1102.14
Eu	10.955	1131.72	10.736	1154.81
Gd	10.469	1184.26	10.249	1209.68
Tb	10.014	1238.07	9.787	1266.78
Dy	9.589	1292.94	9.359	1324.71
Ho	9.193	1348.63	8.959	1383.86
Er	8.822	1405.35	8.584	1444.32
Tm	8.475	1462.89	8.238	1504.98
Yb	8.141	1522.90	7.912	1566.99
Lu	7.837	1581.98	7.600	1631.31

tortions in M_α and M_β are caused by self-absorption, the M_IV and M_V absorption spectra of all of the rare earths were obtained and are shown in Fig. 5. About half of these spectra have been shown in the literature[7–11,16] and our agreement with them is quite good. All of the earlier work was done using photographic-film recording while the spectra in Fig. 5 were obtained with a flow proportional counter. These spectra cover exactly the same wavelength region as the M_α and M_β emission lines (i.e., 7.6 to 14.9 Å).

TABLE II. M_IV and M_V absorption-edge positions for rare earth elements.

Element	M_V edge λ(Å)	M_V edge (eV)	M_IV edge λ(Å)	M_IV edge (eV)
La	14.875 ±0.008	833.5 ±0.4	14.595 ±0.008	849.5 ±0.4
Ce	14.065	881.5	13.783	899.5
Pr	13.350	928.7	13.080	947.9
Nd	12.703	976.0	12.411	996.1
Sm	11.518	1076.4	11.254	1101.6
Eu	10.975	1129.7	10.740	1154.4
Gd	10.497	1181.1	10.231	1211.8
Tb	10.041	1234.7	9.778	1267.9
Dy	9.627	1287.8	9.355	1325.3
Ho	9.227	1343.7	8.956	1384.3
Er	8.845	1401.7	8.580	1444.9
Tm	8.514	1456.2	8.229	1506.6
Yb	8.179	1515.8	···	···

Notice, in Fig. 5, the progressive change in the spectra as one goes down through the rare earth series. The M_IV absorption is quite weak in Yb and slowly increases in intensity with respect to M_V as the 4*f* shell becomes more empty. As was noted by earlier investigators, the spectra themselves are quite different in appearance from the "edge" structure normally observed in x-ray absorption spectra. These might be better described as "line" absorption.

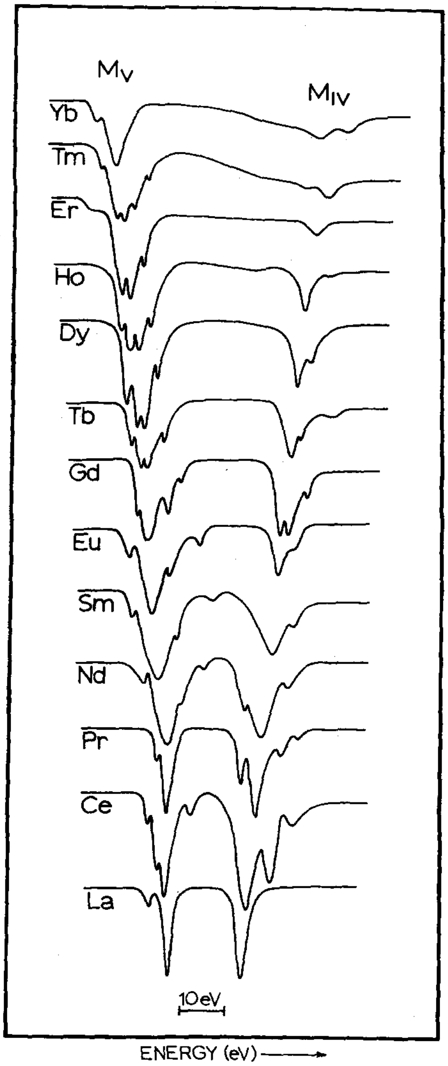

FIG. 5. M_IV and M_V absorption spectra of the rare earth elements.

The M_IV and M_V edge positions are listed in Table II. A Moseley plot of these values produces two straight lines which are only slightly displaced from those of the M_α and M_β emission lines. These values were measured at the midpoint of the edge on the low-energy side of the absorption "line."

If the M_IV and M_V absorption spectra are placed in exact register with the M_α and M_β emission spectra of

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[16] K. C. Williams, Proc. Phys. Soc. (London) **87**, 983 (1966).

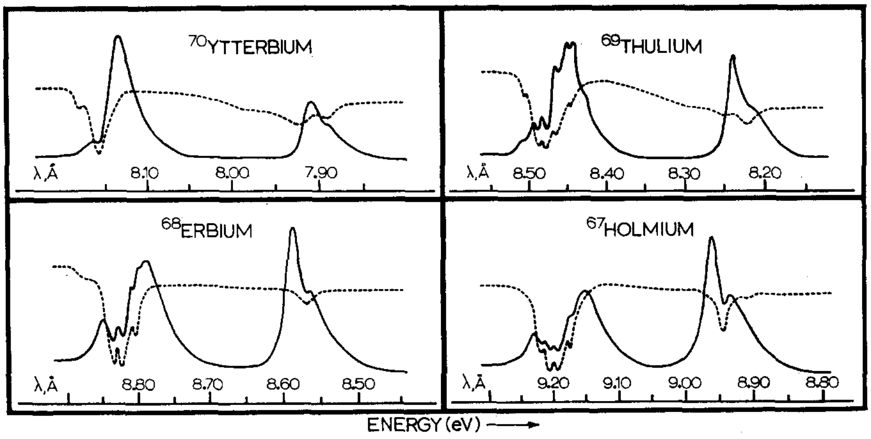

FIG. 6. Correspondence between $M_{\rm IV}$ and $M_{\rm V}$ absorption spectra (dashed curve) and M_α, M_β emission spectra at 10 kV (solid curve) for Yb, Tm, Er, and Ho.

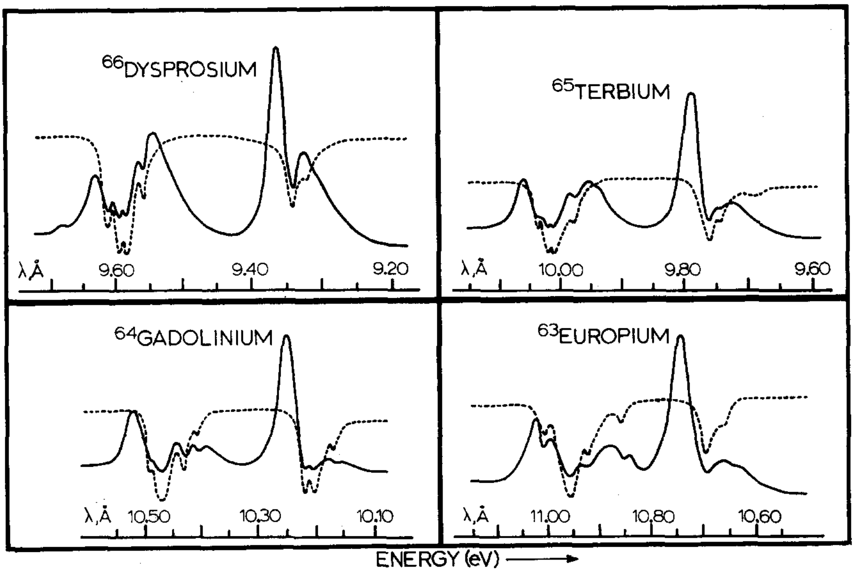

FIG. 7. Correspondence between $M_{\rm IV}$ and $M_{\rm V}$ absorption spectra (dashed curve) and M_α, M_β emission spectra at 10 kV (solid curve) for Dy, Tb, Gd, and Eu.

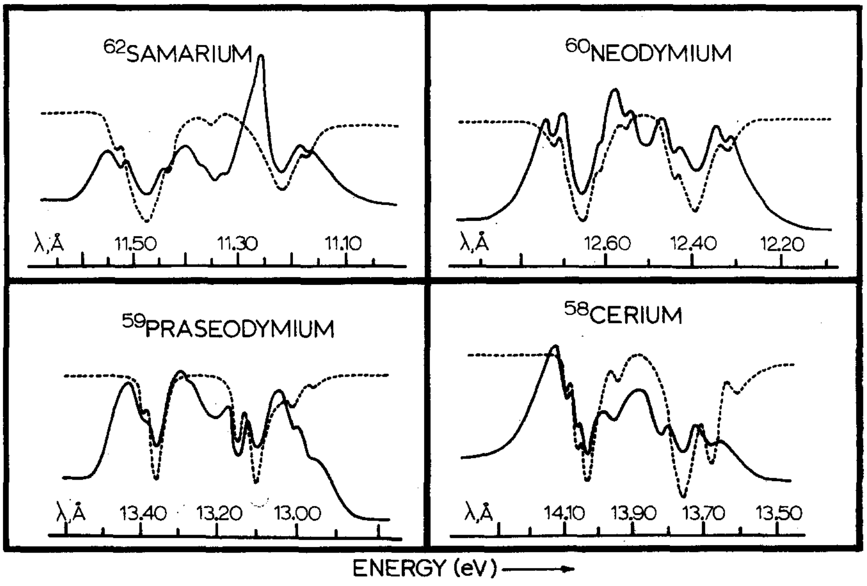

FIG. 8. Correspondence between $M_{\rm IV}$ and $M_{\rm V}$ absorption spectra (dashed curve) and M_α, M_β emission spectra at 10 kV (solid curve) for Sm, Nd, Pr and Ce.

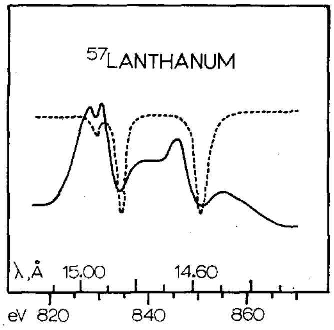

FIG. 9. Correspondence between M_{IV} and M_V absorption spectra (dashed curve) and M_α, M_β emission spectra at 10 kV (solid curve) for lanthanum.

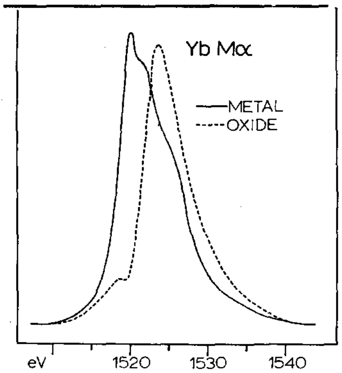

FIG. 10. Differences in M_α emission line from +2 and +3 valence states of ytterbium.

Fig. 1 for each of the elements, the results shown in Figs. 6, 7, 8 and 9 are obtained. For all of the thirteen elements the M_{IV} absorption completely overlaps the M_β emission. Also, in every case, the absorption structure is precisely mirrored in the emission spectra. In fact, for most of these elements one could obtain a virtually complete $M_{IV,V}$ absorption spectrum just by studying the $M_{\alpha,\beta}$ emission spectrum at widely different beam potentials. Certainly, these results show that the multiple structure observed on M_α and M_β is not real emission structure at all. It is definitely absorption-structure.

The fact that the emission and absorption spectra fall at the same energy positions indicates, as first suggested by Lindberg[5] and later by Stewardson and Wilson,[11] that the $M_{IV}N_{VI}$ and $M_VN_{VI,VII}$ transitions are quite reversible. This is perhaps shown most strikingly in the case of lanthanum (Fig. 9) which in its normal state has no 4*f* electrons.[1,2] On this basis one would not expect to see LaM_α or M_β emission lines. It is found, however, that these lines can be produced quite easily under electron-beam bombardment (Figs. 1 and 4). We must, therefore, be injecting electrons into the 4*f* level by an absorption process. Electrons from the M_{IV} or M_V shells (and to lesser extent, the $N_{IV,V}$ shells) are absorbed into the 4*f* shell and can then fall into the M_{IV} or M_V vacancy. All of the $M_{IV,V}$ spectra shown in Fig. 5 must represent absorption into the unfilled 4*f* sites and not the normal "edge" absorption into the continuum of states.

Except for Eu and Yb, neither the $M_{\alpha,\beta}$ emission nor the $M_{IV,V}$ absorption spectra appear to be significantly influenced by chemical combination. Eu and Yb are apparent exceptions because they show divalent properties as metals but become trivalent when oxidized.[1,2] Williams showed that the two different valence states of Eu result in significantly different $M_{IV,V}$ absorption spectra.[16] We have not been able to keep Eu in a pure metallic state long enough to obtain either emission or absorption spectra from it because it oxidizes too rapidly, even under vacuum. We have, however, succeeded in obtaining the $M_{\alpha,\beta}$ emission spectra from the +2 and +3 states of Yb, the M_α line being shown in Fig. 10. When going from metal to oxide this line shifts to higher energy and changes considerably in shape. This change seems to confirm the general idea that the Yb 4*f* shell is filled in the metal but has one vacancy in the oxide.[16] The Yb spectra shown in Figs. 1, 4, and 5 are from the oxide in order to be consistent with the rest of the series.

IV. CONCLUSIONS

The results shown here indicate conclusively that the rare earth M_α and M_β emission spectra are seriously distorted by self-absorption. It is further proved that the complicated multiplet structure observed for M_α and M_β is not the true emission structure. The true spectrum consists of single lines for both M_α and M_β with some overlapping high-energy satellite structure. In a way, the general idea that the multiple emission components are caused by the unfilled 4*f* shell is correct. This multiplicity actually occurs in the absorption spectrum, however, and not in the true emission spectrum. The complete overlap of the emission and absorption spectra indicate that the $M_{IV}N_{VI}$ and $M_VN_{VI,VII}$ transitions are reversible for the lanthanide elements.

The striking distortion caused by self-absorption points up the dangers of putting too much faith in emission spectra without also investigating the conditions under which the spectra were obtained. Self-absorption can also significantly affect valence emission band spectra[17,18] and give one a completely false impression of the actual band shapes and energy positions. Many of the disagreements in the literature concerning band shapes, band widths, etc., can be traced to the failure of the investigators to take possible self-absorption effects into consideration.

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[17] H. P. Hansen and J. Herrera, Phys. Rev. **105**, 1483 (1957).
[18] R. J. Liefeld, Bull. Am. Phys. Soc. **10**, 549 (1965).