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The M Emission Spectrum of ^{68}Erbium

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Abstract: The M emission spectrum of ^{68}Er was reinvestigated using wavelength dispersive spectrometry, with a TAP diffracting crystal. By recording the spectra using the second-order reflection, an improved energy resolution was achieved, which is necessary to resolve the M_5O_3 line from the neighboring α M_5N_7 transition. In addition to the five lines/bands tabulated in the classical paper of Bearden, a number of further lines were observed. These are M_1N_3, M_3O_1, M_2N_1, M_5O_3, M_3N_1, and M_4N_3. For all the lines with an energy below the M_5 absorption structure (M_5O_3, M_3N_1, M_4N_3, and ζ M_5N_3), an increasing relative intensity with increasing energy of the exciting electrons, E_0, was observed. This dependence has its origin in the fact that these lines are normally absorbed whereas Mα (M_5N_7) and Mβ (M_4N_6) are additionally affected by anomalous line-type absorption.

Key words: X-ray spectrometry, electron microprobe analysis, wavelength dispersive spectrometry (WDS), erbium, M emission spectrum, relative intensities

Introduction

Recently, when reinvestigating the M emission spectra of the elements $55 \leq Z \leq 58$ with wavelength dispersive spectrometry (WDS), a total of 34 M lines were observed (Dellith & Wendt, 2004), of which only 13 are contained in Bearden's classical compilation (Bearden, 1967). In that work, for each rare earth (RE) element only 4 or 5 M lines/bands are tabulated. In contrast, 9 M lines are given for the element ^{50}Sn and 16 for ^{73}Ta. Therefore, when starting the present reinvestigation, we assumed that the M emission spectra of the RE elements were only incompletely known.

Historically, the M emission and absorption spectra of the RE elements have been studied for a very long time. The understanding of the complicated emission structure of Mα (M_5N_7) and Mβ (M_4N_6) was the main interest in these early investigations. A milestone was achieved in 1956 (Stewardson & Wilson, 1956) when these authors showed that the true emissions of Er Mα (M_5N_7) and Mβ (M_4N_6) are broad single lines and that the observed structures are produced by self-absorption in the target material. A dozen years later it was shown that this so-called anomalous line-type absorption is responsible for all the structures observed in the Mα (M_5N_7) and Mβ (M_4N_6) emissions of the elements ^{57}La to ^{70}Yb (Fischer & Baun, 1967).

In practice, the analyst is only able to correctly identify an observed peak if all the lines that are detectable with a given type of X-ray spectrometer are known. Otherwise, the danger of misinterpreting an unknown line as one caused by an impurity is high. For a correct identification, the knowledge of both the position of a line and its relative intensity is needed. Table 1 summarizes what was known when starting the present reinvestigation. The positions were taken from Bearden's above-cited paper and the relative intensities from the popular ASTM tables (White & Johnson, 1970). From spectra taken by energy dispersive spectrometry (EDS), it was shown that the relative intensity given in the ASTM tables for the line ζ M_5N_3 of the RE elements is too low by 3–4 orders of magnitude (Wendt & Christ, 1985), a finding that was corroborated by later WDS measurements (Lábár & Salter, 1991). However, even this relatively new paper does not contain any indication as to whether the M spectra of the RE elements consist of more lines than those given in Table 1.

Materials and Methods

The measurements were carried out using a JXA 8800 L microprobe (JEOL). The take-off angle of this microprobe is 40°. A TAP crystal with $2d = 25.757$ Å was used as the dispersing element. The energy of the exciting electrons, E_0, was varied in the range $2.5 \leq E_0 \leq 25$ keV. All spectra were taken in the pulse height analysis mode. The voltage of the gas flow proportional counter and the gain of the pulse amplifier were selected in such a manner that the mean pulse height was 4 V. For the spectra taken in first-order reflection, the lower level of the discriminator was set to 2 V

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Table 1. Compilation of Data that Were Known before Starting the Present Reinvestigation of the M Emission Spectrum of ^{68}Er

Line/Band	Position (eV)	Relative Intensity (%)	Absorption Energy (eV)	
M_2N_4	1632	—	M1	2207
M_3N_5 (γ)	1643	1	M2	2006
M_4N_6 (β)	1443	45	M3	1812
M_5N_7 (α)	1406	100	M4	1453
M_5N_3 (ζ)	1090	0.01	M5	1409

The position data stem from Bearden (1967), the relative line intensities from White and Johnson (1970), and the absorption energies from Bearden and Burr (1967). The absorption energies were rounded to the nearest full electron volt.

and the window width to 4 V. For spectra taken in second-order reflection, the optimum discriminator setting is somewhat different. To suppress the background, which has its origin in bremsstrahlung of low energy, the lower level was set to 3 V and the window width to 2 V. A comparison of the central part of the spectra taken at E_0 = 20 keV in first-and second-order reflection is shown in Figure 1. The numbers given in the figure refer to lines summarized in Table 2. The disadvantage of spectra taken using second-order reflection is the loss of intensity, by approximately a factor of 40, compared to spectra taken in first order. Nevertheless, the detail in second-order reflection spectra is greatly improved due to the higher energy resolution. Only in this manner were we able to identify line number 8 without doubt as the M_5O_3 line. In contrast, Lábár and Salter attributed this peak to be part of the Mα (M_5N_7) emission structure.

A full spectrum, taken in first-order reflection at E_0 = 12 keV, is shown in Figure 2a. In Figure 2b the same spectrum is shown with an ordinate scale magnified by a factor of 5.7. In addition, the linear background approximation is shown. In our approximation, the relative net peak heights of the peak maxima are used as a measure of the relative intensities.

The ^{68}Er standard used was nominally a 99.9% pure metal. Like the other RE elements, erbium is a material of high reactivity. Even a freshly polished sample, which was inserted as quickly as possible into the microprobe, was covered by an oxide layer the thickness of which was estimated to be of the order of 10 nm. Consequently, spectra taken from a carbon-coated pressed Er_2O_3 powder were compared with those taken from a freshly polished metal standard. Even when using second order, no indication of any line shift was observed. This result is in agreement with the findings of Fischer and Baun that, except for ^{63}Eu and ^{70}Yb, neither the Mα,β emission (M_5N_7, M_4N_6) nor the $M_{4,5}$ absorption spectra appear to be significantly influenced by chemical combination.

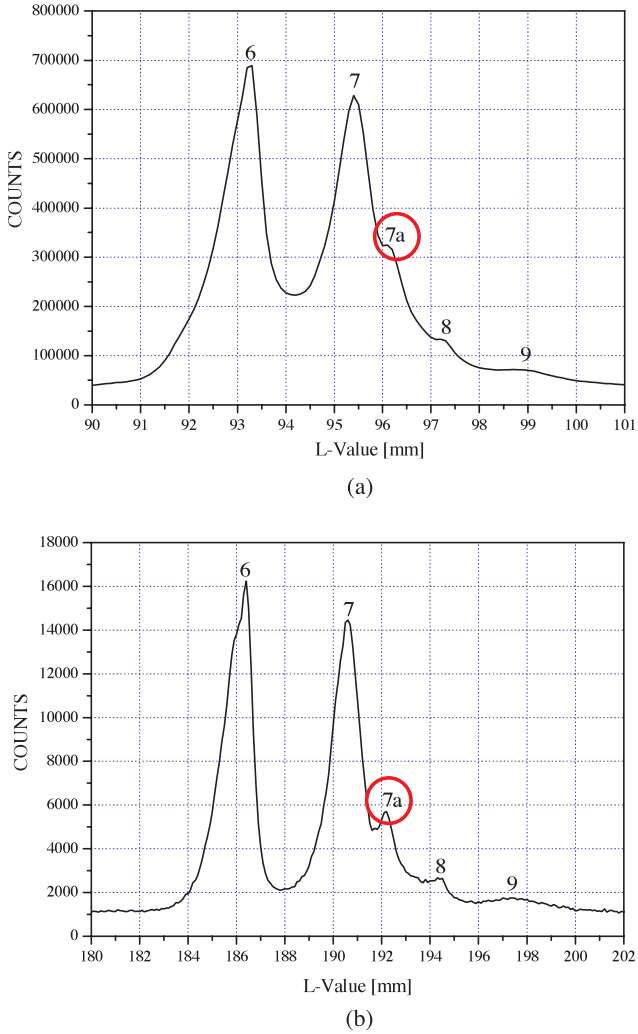

Figure 1. Central part of the Er M spectrum taken at E_0 = 20 keV using (**a**) first-order and (**b**) second-order reflection. The numbers refer to the transitions as given in Table 2. On the *x*-axis the L value is given, which indicates the distance between the X-ray source and the analyzing TAP crystal. As a first approximation the L value increases linearly with the wavelength λ.

Results and Discussion

The results of our search for Er M peaks are summarized in Table 2. With the exception of peak number 8 (Er M_5O_3), all peaks were observed when using first-order reflection. The maximum intensity of the Mα (M_5N_7) peak was observed at an energy that depends on the energy of the exciting electrons, E_0. In Figure 3, two spectra, taken at E_0 = 2.5 keV and E_0 = 20 keV in second-order reflection, are shown together. At E_0 = 2.5 keV, the Mα band (M_5N_7) appears as a single broad line with a peak maximum at 1407 eV. At E_0 = 20 keV, Mβ (M_4N_6) is somewhat higher than Mα (M_5N_7). The maximum of Mα (M_5N_7) now appears at 1413 eV. The

Table 2. Correlation between the Numbers Given in the X-ray Spectra and the Observed X-ray Lines

No.	Designation	Position (eV)	Intensity
1	M_1N_3	1900	Very weak
2	M_2N_4	1830	Weak
3	M_3O_1	1763	Very weak
4	M_3N_5 (γ)	1642	Medium
5	M_2N_1	1557	Very weak
6	M_4N_6 (β)	1446	Very strong
7	M_5N_7 (α)	1407…1413	Very strong
8	M_5O_3	1386	Medium
9	M_3N_1	1364	Medium
10	M_4N_3	1133	Weak
11	M_5N_3 (ζ)	1091	Strong

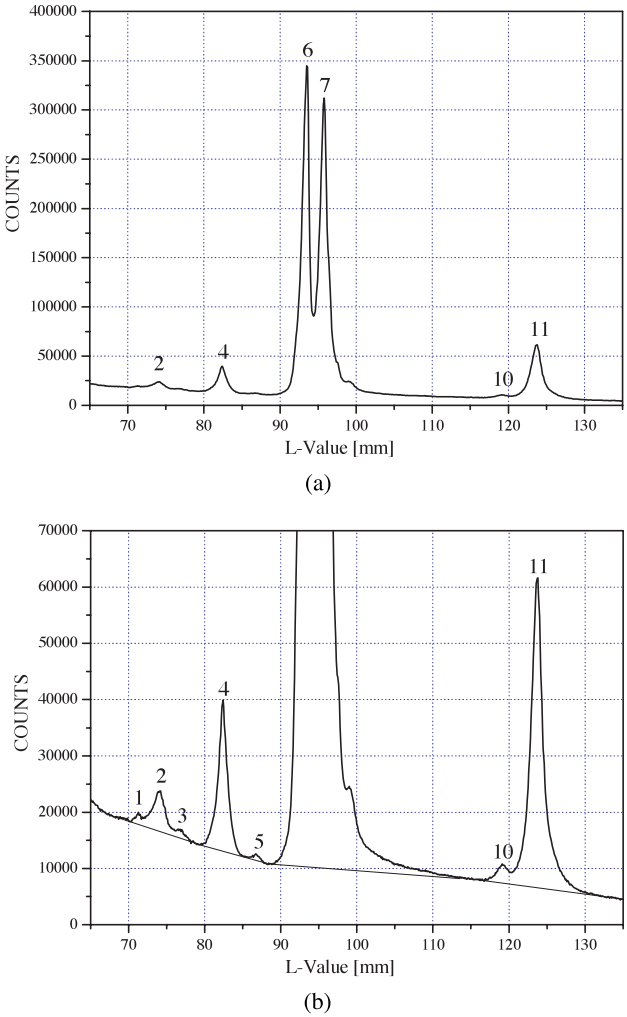

Figure 2. Full M emission spectrum of ^{68}Er taken at $E_0 = 12$ keV using first-order reflection. The numbers refer to the transitions given in Table 2. In **b** the ordinate scale is magnified by a factor of 5.7 compared with **a**. Here, the linear background approximation is shown, which was used to determine the linear net peak heights.

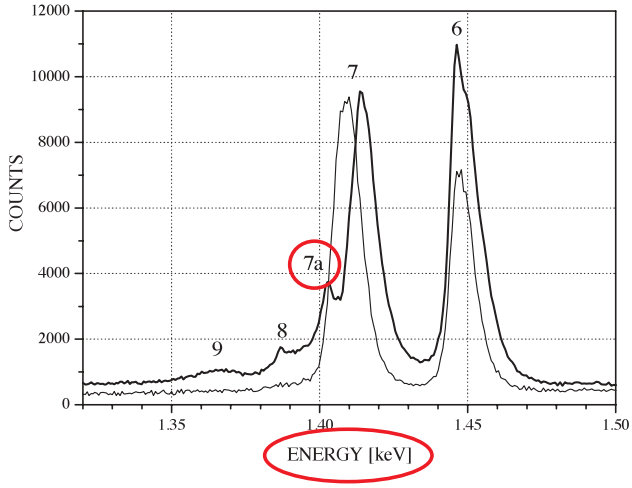

Figure 3. Comparison of two spectra taken using second-order reflection at $E_0 = 2.5$ keV (thin line) and at $E_0 = 20$ keV (thick line). The spectra were scaled to nearly the same gross height of the Mα (M_5N_7) peak (number 7).

origin of this line shift is in the strong line-type absorption of Mα (M_5N_7). Peak number 7a is part of the Mα (M_5N_7) emission, whereas peak number 8 is definitely not.

In Table 2 only qualitative estimates for the relative intensities are given. This is due to the fact that the relative intensities depend more or less strongly on E_0. Quantitative results will follow below. Very weak means that the relative net peak height (r.n.p.h.) is $\leq$0.5% of the strongest M peak. Weak means that it is $\leq$2%. Medium is used when the r.n.p.h. is $\leq$10%, strong when $\leq$25%, and very strong when approximately 100%.

The net peak intensities of Mα (M_5N_7), Mβ (M_4N_6), and Mζ (M_5N_3) are shown versus E_0 in Figure 4. As one can

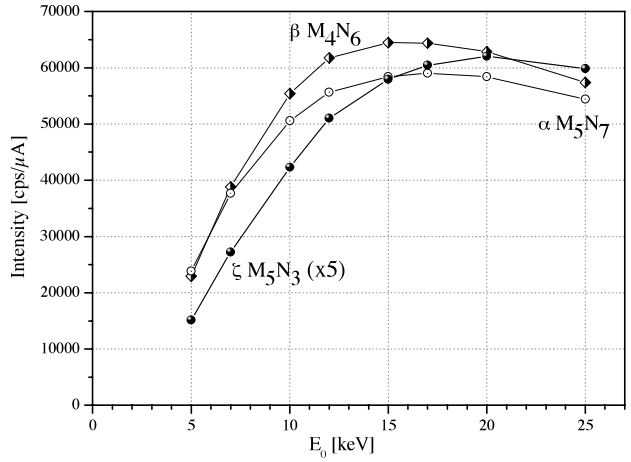

Figure 4. E_0 dependence of the net peak intensities of Mα (M_5N_7), Mβ (M_4N_6), and Mζ (M_5N_3). For the purposes of comparison the true Mζ (M_5N_3) values were multiplied by a factor of 5.

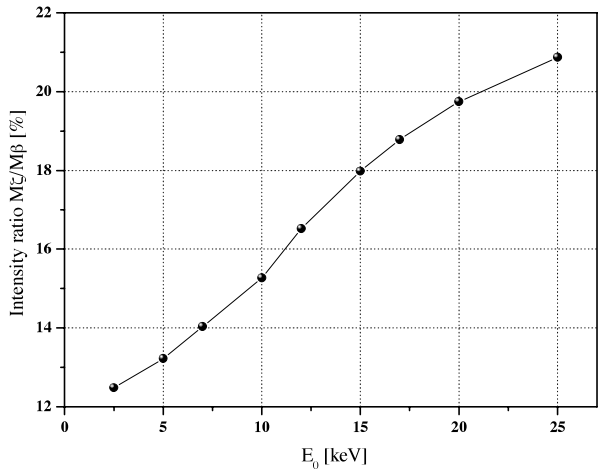

Figure 5. E_0 dependence of the intensity ratio Mζ (M_5N_3)/Mβ (M_4N_6).

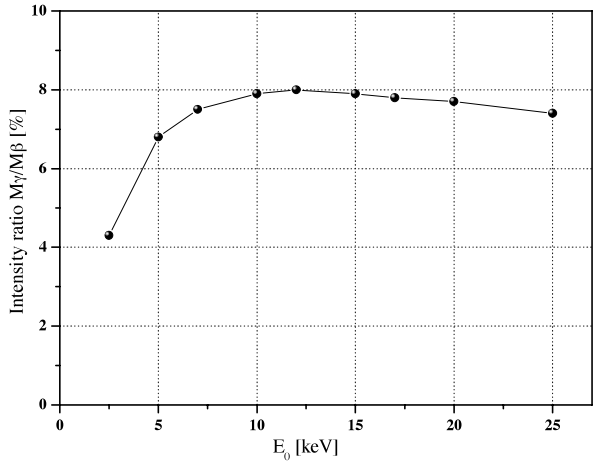

Figure 6. E_0 dependence of the intensity ratio Mγ (M_3N_5)/Mβ (M_4N_6).

see, Mα (M_5N_7) and Mβ (M_4N_6) have a similar E_0 dependence with a maximum near 15 keV. In contrast, Mζ (M_5N_3) goes through a maximum at approximately 20 keV, which means that Mζ (M_5N_3) is less strongly absorbed than Mα (M_5N_7) and Mβ (M_4N_6).

The E_0 dependence of the net peak intensity ratio Mζ (M_5N_3)/Mβ (M_4N_6) is shown in Figure 5. Again, the increase of this ratio with increasing E_0 reflects the weaker absorption of Mζ (M_5N_3) compared with Mβ (M_4N_6). The M_4N_3 line behaves like Mζ (M_5N_3) but is weaker by a factor of approximately 18. In addition, M_3N_1 and M_5O_3 show a E_0 dependence similar to that of Mζ (M_5N_3) but are absorbed somewhat less than Mζ (M_5N_3) because of their higher line energy. Approximately, M_5O_3 is about half as intense as Mζ (M_5N_3), and M_3N_1 half as intense as M_5O_3.

In Figure 6, the E_0 dependence of the net peak intensity ratio Mγ (M_3N_5)/Mβ (M_4N_6) is shown. The line M$\gamma \equiv M_3N_5$ refers to a M_3 vacancy whereas Mβ (M_4N_6) refers to a M_4 vacancy. The decrease of Mγ (M_3N_5)/Mβ (M_4N_6) with decreasing E_0 has its origin in the higher electron binding energy of M_3 electrons compared with that of M_4 electrons; see Table 1. The plateau-like behavior for high E_0 can be explained by assuming that both the lines are absorbed in nearly the same manner. The E_0 dependence of M_2N_4/Mβ (M_4N_6) is very similar to that observed for Mγ (M_3N_5)/Mβ (M_4N_6), but M_2N_4 is less intense than Mγ (M_3N_5) by a factor of 4.

The position of the line M_2N_4 is definitely not 1632 eV as given by Bearden (1967), but 1830 eV; see Table 2. The uncertainty of our measurements did not exceed ± 2 eV.

In Figure 3, one can see that Mα (M_5N_7) is higher than Mβ (M_4N_6) at $E_0 = 2.5$ keV and that the reverse is the case at $E_0 = 20$ keV. The E_0 dependence of Mβ (M_4N_6)/Mα (M_5N_7) obtained from all our measurements in first-order reflection is shown in Figure 7. For the analysis, linear net peak heights were used as the measure of the intensities.

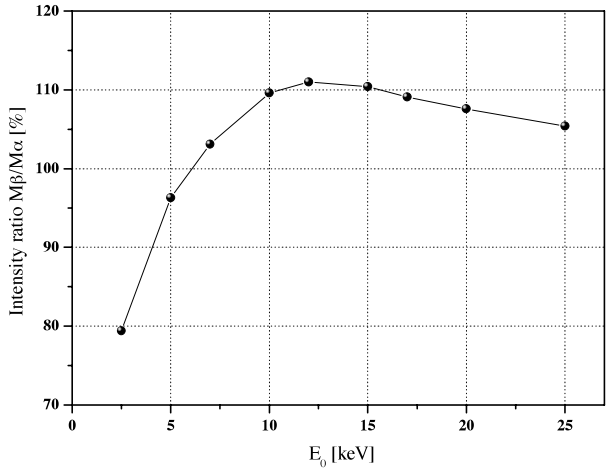

Figure 7. E_0 dependence of the intensity ratio Mβ (M_4N_6)/Mα (M_5N_7).

Lábár and Salter (1991) determined the intensities by integration over the whole lines. In their first-order spectra they were not able to identify M_5O_3 and M_3N_1 as separate lines and assigned them to be Mα (M_5N_7). Probably, this is the main reason for the fact that their values for Mβ (M_4N_6)/Mα (M_5N_7), given in Figure 22b of their paper, are somewhat below ours in Figure 7.

Conclusions

As in the case of the lightest RE elements, where we observed more M lines than tabulated by Bearden (Dellith & Wendt, 2004), also for ^{68}Er more M lines were observed. The knowledge of these lines is important if the purity of an

Er-containing sample has to be analyzed at an electron energy $\leq$10 keV. The energy of the L_3 edge of Er is 8358 eV. Therefore, the L lines cannot be effectively excited at $E_0 \leq$ 10 keV, with the consequence that the M emission spectrum must be used. For example, the position of the line M_4N_3 (1133 eV) was not known before the present reinvestigation. Therefore, the danger of misinterpreting this line as ^{63}Eu Mα (M_5N_7) was high because this line was expected at 1131 eV (Bearden, 1967).

Low E_0 excitation has the advantage of an improved spatial resolution compared to high E_0 excitation. But to make use of this advantage, the soft X-ray spectra should be studied more carefully.

Acknowledgments

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