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L_1 ABSORPTION EDGE OF THE $4f$ HEAVY RARE-EARTH METALS

B.D. SHRIVASTAVA

School of Studies in Physics, Vikram University, Ujjain–456010, India

AND S.K. JOSHI*

Physics Department, Government Arts and Science College, Ratlam–457001, India

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The wavelengths of the L_1 absorption edges of the $4f$ heavy rare-earth metals (^{65}Tb to ^{71}Lu) have been measured using a 40 cm curved crystal spectrograph of the Cauchois-type in the transmission mode. The measured values have been found to fit nicely in the modified Moseley diagrams. The absence of the white lines at the L_1 edges of the rare earths in metallic form and its occurrence in their compounds has been discussed.

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1. Introduction

A look at the X-ray wavelength tables compiled by Bearden [1] shows that few investigations had been carried out on the L_1 edge of the rare earths from ^{65}Tb to ^{71}Lu. In fact till the preparation of these tables, only single measurements were available for all these elements except for ^{66}Dy for which two measurements were available. These measurements are quite old and many of them were made by low resolution spectrographs. The latest X-ray wavelength tables compiled by Cauchois and Senemaud [2] have adopted all the wavelengths from the tables of Bearden except for two changes. They have reported the value of wavelength of ^{68}Er L_1 edge as 1276.97 XU (= 1.27965 Å) instead of 1267.97 XU (= 1.27063 Å), though both the tables have mentioned it to have been taken from the same reference i.e., Sakellaridis [3]. It appears that there is a printed error in the tables of Cauchois and Senemaud [2] as Sakellaridis [3] has reported the wavelength as 1267.97 XU (= 1.27063 Å). Another change is that Cauchois and Senemaud have

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*To whom the correspondence should be addressed: 2, Senior M.I.G., Mhow Road, Ratlam–457001, India.

adopted a new wavelength for ^{70}Yb L_1 edge which was reported by Nigam et al. [4].

After the publication of the tables of Cauchois and Senemaud, Chetal and Sarode [5] studied the rare earths and reported measurements on L_2 and L_3 absorption edges, but did not report any measurement on L_1 absorption edge. Also, Garg and Jain [6] made measurements on L_2 and L_3 edges along with L_1 absorption edge in the rare earths, but their measurements were made on compounds and not on metals.

Thus, it is clear that concentrated efforts have not been made to measure the wavelength of L_1 absorption edges in these rare earths in the metallic state, though many studies have been made on L_2 and L_3 edges. Hence, it was considered worthwhile to investigate the L_1 edge in these rare earths in the metallic state again.

2. Experimental

A 40 cm curved crystal transmission spectrograph, with a mica crystal cut to reflect from (100) planes, was used for recording photographically the absorption spectra. In the region of interest, the dispersion of the spectrograph was about 0.012 Å mm^{-1}.

Metals of 99.9% purity, supplied by M/s. Rare Earth Products Ltd., Lancashire, UK, were used in the present investigation. The absorbing screens were prepared by uniformly spreading the metals in powder form on a cellophane tape and covering it with another piece of tape. After several trials, optimum thickness of the absorption screen, which gave sharpness of contrast in the spectrogram, was found to be about 10 mg cm^{-2} for these metals. This value is slighty higher for all the metals than that calculated from Sandstrom's formula [7].

A Machlett sealed off tungsten target tube was used as the source of continuous X-rays for recording all the absorption discontinuities of these metals. Another Machlett sealed off tube with copper target was, however, used to record Tb L_1 and Tm L_1 edges, because these edges lie near the tungsten emission lines. We also tried to record Gd L_1 edge but could not do so even with the copper target tube, as the W L_{α_1} line masked it completely. The tungsten lines appeared with diminished intensity in the spectra recorded with the copper target tube, due to the deposition of tungsten from the hot tungsten filament on the copper anticathode. Taking into consideration the optimum conditions for obtaining good spectrograms, the X-ray tubes were operated at 16 kV and 10 mA. The exposure time ranged between 15–20 hours on Agfa Curix M1 X-ray films.

Measurements of the absorption edges were made with a Carl–Zeiss microphotometer. The position of the absorption edge was fixed by taking the point of inflection on the absorption curves. The emission lines of copper, nickel, iron and tungsten, present on the spectrograms, were used as reference lines. Their wavelengths were taken from the X-ray wavelength tables of Cauchois and Senemaud [2]. At least three selected spectrograms were used for measurements and each spectrum was measured at three heights. Thus, the values reported herein are the averages of at least nine measurements.

3. Results and discussion

Table I gives the wavelengths of the L_1 absorption edges of the rare earths ^{65}Tb to ^{71}Lu as measured by us. It also includes the wavelengths reported by different authors and those adopted by Bearden [1] and Cauchois and Senemaud [2].

TABLE I

Wavelengths of the L_1 absorption edges of rare earths ^{65}Tb to ^{71}Lu. The conversion formula $\lambda(\text{Å}) = 0.0010021017 \times \lambda(\text{XU})$ has been taken from Ref. [2]. It has been used to convert all the previously reported XU values into Ångström values.

Elem.	Wavelengths reported by different authors (Å)	Ref.	Wavelengths adopted by		Present work
			Bearden [1] (Å)	Cauchois & Senemaud [2] (Å)	Wavelengths (Å)
^{65}Tb	1.42236	[8]	1.42238	1.42236	1.42248
^{66}Dy	1.36766	[9]	1.36927	1.36837	1.36950
	1.36837	[10]			
^{67}Ho	1.31906	[11]	1.31906	1.31906	1.31918
^{68}Er	1.27063	[29]	1.27066	1.27965	1.27101
^{69}Tm	1.22508	[12]	1.22506	1.22508	1.22504
^{70}Yb	1.18187	[13]	1.18187	1.18237	1.18197
	1.18237	[4]			
^{71}Lu	1.14019	[13]	1.14019	1.14019	1.14015

As an illustration, the three absorption edges L_1, L_2 and L_3 of the rare-earth metal Ho are shown along white lines at L_2 and L_3 edges in Fig. 1.

The L_1 absorption edges of the heavy rare-earth metals have not been found to have the preabsorption structure which has been observed in the case of L_2 and L_3 absorption edges of Gd to Tm [14].

3.1. L_1 absorption edges of ^{65}Tb to ^{71}Lu

The L_1 edges of the heavy rare earths are observed to be faint as compared to the L_2 and L_3 edges which are sharp and distinct. However, under optimum conditions of spectrograph setting, absorber thickness and exposure time, these L_1 edges have been made measurable up to a reliable degree of accuracy in the present investigation. Prior to the present work, only Jain [15] had attempted to measure the white lines at the L_1 absorption edges in the thiosalicylic acid (TSA), ethyl thiosalicylic acid (ETSA) and methylsalicylic acid (MTSA) complexes of Sm, Tb and Dy and in the oxides of these elements, but he did not report any measurement on the L_1 edges in the metallic state.

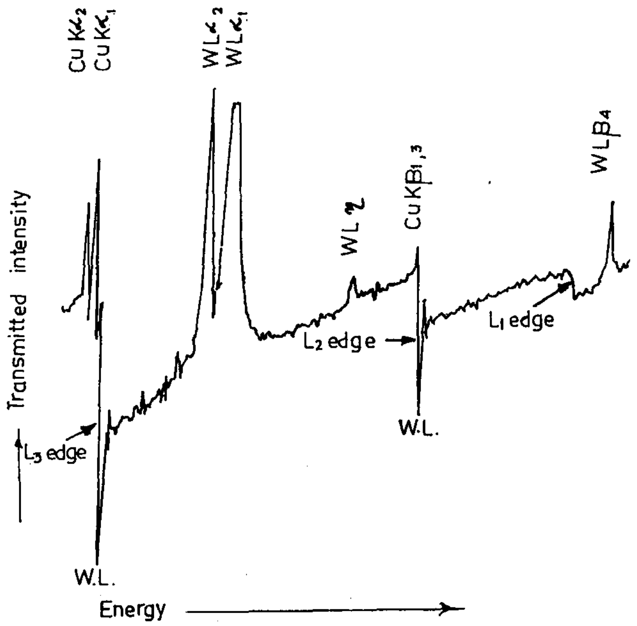

Fig. 1. L-absorption spectrum of Ho.

A perusal of Table I shows that the values of the L_1 edges obtained in the present work are in close proximity to those reported by earlier workers and also to those adopted by Bearden [1] and Cauchois and Senemaud [2].

The primary method for evaluating measured values of the absorption limits is through utilisation of the modified Moseley diagrams. Bearden [1] has extensively used the modified Moseley diagrams, constructed by Matthews [16], for compiling the values of wavelengths of absorption limits in his tables of X-ray wavelengths. He has found these modified Moseley diagrams most helpful in fixing the weights to be assigned to the various data, and in deciding which values to reject. The modified Moseley diagrams have also been very useful in forming a rough error estimate for each limit. In a few cases he has recommended the value determined solely by the interpolated figure obtained from the modified Moseley diagram. The modified Moseley diagram of Matthews for these rare-earth metals is reproduced in Fig. 2. The method to construct these modified Moseley diagrams is as follows:

— An inverse wavelength, or wave number, $\tilde{\nu}$ in Å^{-1} is calculated for each measurement, using the published wavelengths.

— The average slope of $\sqrt{\tilde{\nu}}$ versus atomic number Z for each of the K, L and M absorption limits is then calculated for groups of 8 to 18 elements and the equation for a straight line, roughly approximating the variation of experimental points, is determined for each group. The grouping of the elements is decided largely by the outer electronic configuration of the atoms. In most cases, the elements in a group have vacancies in the same or adjacent electronic subshells.

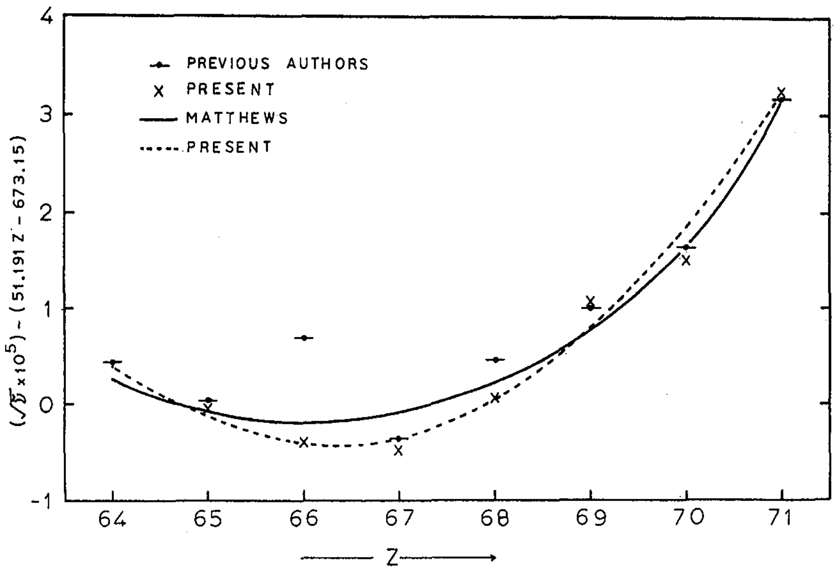

Fig. 2. Modified Moseley diagram for L_1 absorption limits.

— To obtain the modified Moseley diagrams, these deviations from a straight line of the experimentally determined values for $\sqrt{\bar{\nu}}$ have been plotted versus Z. Fitting of the curves to the resulting points is done visually, taking into account the reliability of the data and the variations of the electronic configuration with the increasing atomic number.

The modified Moseley diagrams constructed by Matthews [16] and used by Bearden [1] for compilation of X-ray wavelengths for these rare-earth metals is shown in Fig. 2. The results of the present investigation are also plotted in the same diagram (Fig. 2). In order to plot the modified Moseley diagram for the present results on the same scale as used by Matthews, the values $\sqrt{\bar{\nu}}$ obtained from Å^{-1} values have been multiplied by a factor of $\sqrt{1/1002.1017}$. It is readily observed that the present values of L_1 absorption limits fit nicely on a curve which has the same shape as that of the curve of Matthews. It is also observed that the fitting of the points on the present curve is much better than on the curve of Matthews. Thus, the present results are more accurate and reliable than the previous measurements.

3.2. White lines at L_1 *absorption edge*

In our studies on the L_1 absorption edge of the rare earths ^{65}Tb to ^{71}Lu, we did not observe any white line at the L_1 edge. It is important to mention here that in a separate study we have been able to record the white lines at L_2 and L_3 edges of these rare-earth metals. The cause of the white line has qualitatively been understood as due to a high density of final states or due to exciton effects [17, 18]. The difference between the L_1 and $L_{2,3}$ edges arises because L_1 edge initiates from the $2s$ state while $L_{2,3}$ edges initiate from the $2p$ state. These edges thus probe the density of final states with different symmetries. The L_1 edge (as does the K edge) probes the p-symmetric portion of the density of the final states, while the $L_{2,3}$ edges probe the s- and d-symmetric portions.

We have explained the occurrence of the white line at the L_2 and L_3 edges and its absence at the L_1 edge of these metals on the basis of the theoretically determined density of states in the following manner.

The density of states for the rare-earth metals has been calculated [19–24] theoretically by Augmented Plane Wave (APW) and Relativistic Augmented Plane Wave (RAPW) methods. The general features of the band structure are:
— A very narrow $4f$ band located a few electron volts below the bottom of the conduction band;
— The bands near the Fermi surface being of mixed s–d character, originating from atomic $5d$ states and relatively flat;
— The d bands originating from the $5d$ states contributing a high density of states in the vicinity of Fermi energy.

The absorption coefficient for the X-rays is given as [25]:

$$\mu(E) \propto P(E)N(E), \qquad E > E_{\mathrm{f}},$$

where $P(E)$ is the transition probability from a L level to the unfilled part of the conduction band and $N(E)$ is the density of the states of this band. As the histograms representing the theoretically determined density of states show that there is a high density of states for the $5d$ bands above the Fermi energy and the density of states at the peak above the Fermi energy is maximum, Dubey and Shrivastava [26] argued that according to the above equation this strong peak for the $5d$ bands above E_{f} should give rise to a strong absorption maximum, or the white line at the $L_{2,3}$ absorption edges (the transition probability being assumed to be a slowly varying function of energy near the absorption edge [27]). Since the transitions from the $2p$ states to the $5d$ bands are allowed, while those from the $2s$ states to the $5d$ bands are forbidden by optical dipole selection rules, the existence of the white line at the L_2 and L_3 edges of the rare-earth metals (Tb to Lu) can be assigned to an allowed transition from the $2p$ states to the unfilled part of $5d$ bands and the white line peak can be correlated with the strong peak above the Fermi level in the theoretical density of state curve for the $5d$ bands. The absence of the white line at the L_1 edge for these metals corresponds to the forbidden dipole transition from the $2s$ states to the $5d$ bands.

Garg and Jain [6, 15] have reported the existence of white lines at the L_1 absorption edges in the thiosalicylic acid (TSA), ethylthiosalicylic acid (ETSA) and methyl thiosalicylic acid (MTSA) complexes of Sm, Tb and Dy and oxides of these elements. Further the white lines reported by Jain [15] are broad and they have been seen only in compounds of these metals and not in pure metals. Chandra [28] has also reported the presence of white lines at the L_1 edges of several compounds of Sm, Gd, Tb and Dy and their absence in the metallic state. The white line at L_1 edge indicates the presence of a large density of p-symmetric final states in rare-earth compounds while the absence of white lines at the L_1 edges of the rare-earth metals suggests a lack of high density of p-symmetric states above the Fermi level in them. The possible explanation for the presence of white lines in compounds is as follows: On compounds formation, the interatomic distances for the metal atoms increase resulting in the dehybridization of the wave function. This dehybridization narrows down the *p*-band giving rise to high density *p* states. The transition of the electron from the initial L_1 states to these high density *p* states gives a white line at the L_1 edge in the rare-earth compounds. These compounds also have a high density of vacant *d* states and hence they show white lines at all the $L_{2,3}$ edges similtaneously.

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