

The white line in L absorption spectra of rare earth oxides

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MS received 23 April 1993; revised 17 August 1993

Abstract. The method of curve fitting of the experimentally obtained absorption edge has been developed and successfully adopted to study the precise variation in the density of states responsible for the occurrence of the white line associated with the L_{II} and L_{III} absorption discontinuities of rare earth (RE) in their sesquioxides. The theoretical equation and the curve fitting routine is flexible enough to include all the transitions responsible for XANES as well as other phenomena such as, screening effect, variation in the potential around the metal ion due to surrounding ligand ion, charge transfer etc.

Keywords. Levenberg-Marquardt; Lorentzian; XANES; white line; microdensitometer.

PACS No. 78.70

1. Introduction

The oxides and other compounds of rare earths (RE) have attracted a great deal of attention in recent years [1–5]. Their uses as starting materials for the fabrication of several kind of devices are well-known [6–8]. A lot of work has been reported on the L_{II} and L_{III} X-ray absorption discontinuities of RE metals and their sesquioxides. These studies are known to provide direct method of studying the electronic structure of materials [9–10].

A remarkable feature associated with these discontinuities is the prominent absorption maximum close to the main discontinuity, the so-called white line. This white line can be very clearly seen on the original spectrum recorded photographically.

In the present investigation a systematic study of the intensities of the white line associated with the L_{II} and L_{III} absorption discontinuities in the RE sesquioxides RE_2O_3 (where RE = La, Pr, Nd, Sm, Eu and Gd) has been carried out. A curve fitting routine has been used wherein the experimentally obtained absorption curve has been fitted to a theoretical curve. The nature of the theoretical curve can be expressed by an equation of the type

$$F(Y_i) = \text{arc tangent} + 2 \text{ lorentzians.}$$

where, Y_i corresponds to experimentally observed data points and $F(Y_i)$ to data points obtained from the theoretical equation.

After obtaining a close fit we have calculated and compared the full width at half maximum (FWHM) and area under the curve for the Lorentzians. These Lorentzians correspond to the absorption maxima A and A^* associated with the L_{II} and L_{III} absorption discontinuities. This comparison is useful in evaluating the theoretical equation used in the curve fitting routine.

2. Experimental

The experimental technique involves the following aspects:

- (1) To set and test the performance of the spectrograph
- (2) To obtain the best possible X-ray spectra on film
- (3) Use of standard measurement technique, and
- (4) Use of standard computer programs to derive maximum information from the observations recorded.

In this work a transmission type, focussing X-ray spectrograph of Cauchois geometry of diameter 400 mm, was used. The (100) reflecting planes of a well tested mica crystal were used for obtaining the spectrum. A Chirana X-ray tube with a tungsten target, operated at 18 kV, 15 mA was used as a source of white radiation. Details of the setting of the spectrograph are given in our earlier publications [11, 12].

The performance of the spectrograph was tested by calculating the FWHM of $W\text{L}\alpha_1$ line. Our value of 7.1 ± 0.36 eV is in close agreement with those reported by earlier workers [13].

Different thicknesses of the absorbing screen were tried, and the one which gave the best white line was finally selected for recording the spectrum. Care was taken to maintain the uniformity in the thickness of the absorber.

The spectra were recorded on Agfa X-ray film. Minimum possible exposure was given to the film to ensure that the photodensity S of the film was proportional to the incident X-ray intensity, I . This is the most important criterion when one has to study the relative intensities of the spectra recorded on the film. It was found that for an exposure less than 6 h, the above condition was satisfied. The temperature of the developer and fixer was kept at 15°C. Care was taken not to over-develop the film. The microphotometer records of the spectra were obtained using a Carl-Zeiss microdensitometer, MD 100. We [14] have modified the recording technique which has the following advantages.

- (1) Observations are in a digital format.
- (2) Energies of data points can accurately be determined due to precise knowledge of their positions.
- (3) The process of measurement is fast, accurate and has a high degree of repeat reliability.

Observations, in digital format, have paved way for usage of standard computer programs.

The L_{II} and L_{III} absorption curves of RE in their sesquioxide, within 25 eV from the inflection point, can be considered to be significantly dominated by

- (1) transitions from respective initial levels ($2p_{1/2}$ for L_{II} and $2p_{3/2}$ for L_{III} absorption discontinuities) to the continuum. These are represented by arc tangent curves.
- (2) On this arc tangent curve are superimposed 2 lorentzians corresponding to the transitions to $2t_{2g}$ and $3e_g$ molecular orbital levels from $2p_{1/2}$ for L_{II} and from $2p_{3/2}$ for L_{III} absorption discontinuities.

The contribution of other effects in this region of absorption discontinuity can be considered to be minimum.

The function which we have fitted to the experimentally observed absorption curve

has therefore the following form.

$$\begin{aligned}
 A &= A(1) * (0.5 + 1/3 * 14 * (\text{atan}(E - E_0) / A(2))) \\
 B &= A(3) / (1 + ((E - A(4))^2 / A(5))) \\
 C &= A(6) / (1 + ((E - A(7))^2 / A(8))) \\
 F(Y_i) &= A + B + C
 \end{aligned} \tag{1}$$

where $A(1)$ is the amplitude constant and $A(2)$ is the width of the arc tangent curve. $A(3)$ and $A(6)$ are the square of the amplitudes, $A(4)$ and $A(7)$ are the positions of absorption maxima A and A^* and $2 * A(5)^{1/2}$ and $2 * A(8)^{1/2}$ are the full widths at half maximum of first and second lorentzian respectively. E and E_0 are respectively the energy values of the points on the absorption curve and the inflection point on the discontinuity.

This curve fitting is done by utilizing a least square fit minimization technique. i.e.

$$X^2 = (Y_i - F(Y_i))^2 \tag{2}$$

The program minimizes the value of X^2 by adjusting the values of floating parameters $A(1)$ to $A(8)$ in the equation for $F(Y_i)$.

The above problem being a non-linear fitting one, we have used the Levenberg-Marquardt method. This method is one of the standard directional set methods for function minimization [15]. The program is written in Fortran 77 and was implemented on a 386 based LAN.

The error involved in the measurement of $F(Y_i)$ is

$$F(Y_i) \pm (X^2 / N \text{ data})^{1/2} \tag{3}$$

where $(X^2 / N \text{ data})^{1/2}$ is the root mean square (RMS) deviation. For a good fit it is necessary that the order of the RMS value be significantly low as compared to the order of Y_i . For all the L_{II} and L_{III} absorption curves of RE_2O_3 RMS deviation was of the order of 10^{-2} to 10^{-3} , whereas (Y_i) was of the order 1. The degree of close fit is observed from figure 1(a, b).

The expression for B and/or C in (1) has been given by Weiskoff and Wigner [16] for a spectral line which is close to a classical lorentzian. Making use of this form of spectral line, Richtmyer *et al* [17] have discussed the shape of L_{III} absorption discontinuity of gold. They considered the energy continuum of empty states to be formed of regularly shaped discrete levels of equal widths. They also assumed that the transition probability of the inner electron being raised to all these levels is the same. This model then gives rise to a series of absorption lines of the same intensity with equal half widths. Upon integrating these curves, one obtains an arc tangent energy dependence for the absorption coefficient in the region of discontinuity. This arc tangent energy dependence in (1) is represented by expression A .

According to Nordfors [18], the inflection point in the initial rise of an absorption curve (displaying very nearly an arc tangent dependence in most cases) marks the energy value of the onset of allowed energy levels for the ejected inner electrons.

Materlik *et al* [19] while calculating the L_{III} and L_I absorption in Gd up to 80 eV above E_f , have taken the E_f point to correspond to the inflection point of the initial rising part of the absorption coefficient. The same procedure has been used by previous workers in our laboratory [9, 10]. We have in this work taken the second derivative

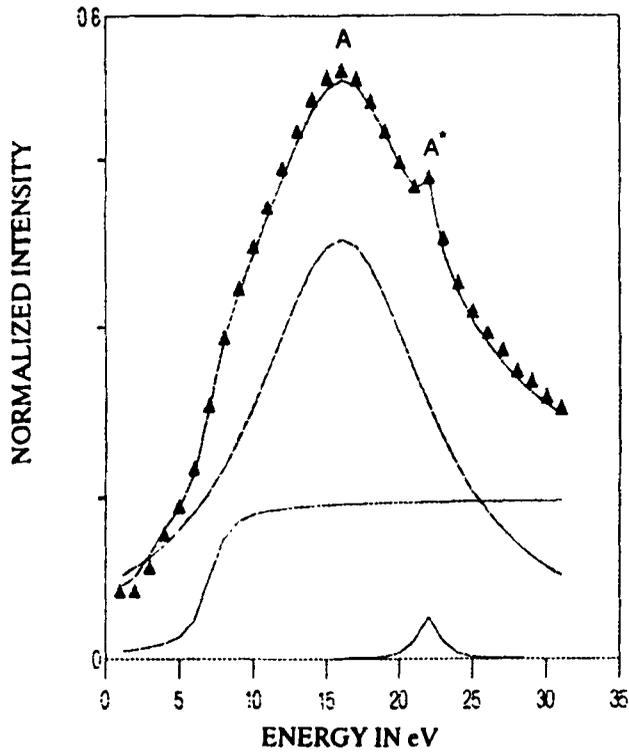


Figure 1(a). L_{II} absorption spectrum of La in La_2O_3 . (—) Experimental value, (\blacktriangle) Theoretical value.

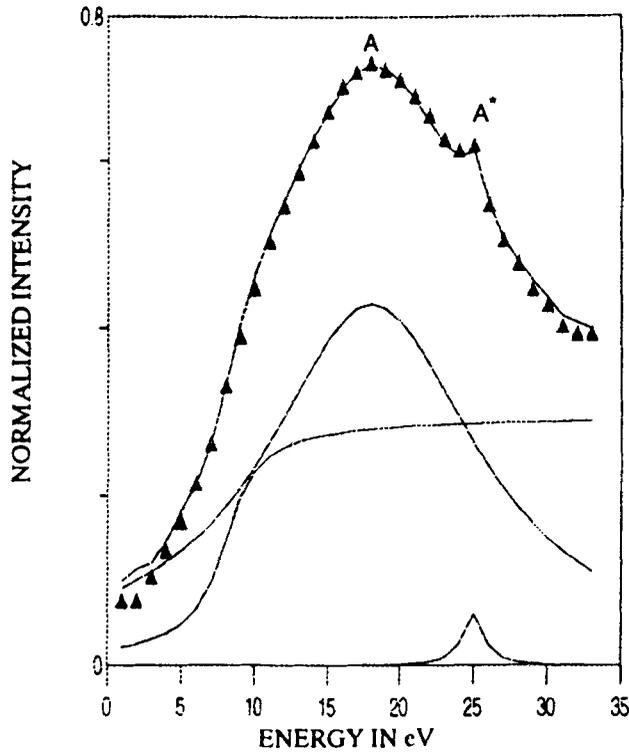


Figure 1(b). L_{III} absorption spectrum of La in La_2O_3 . (—) Experimental value, (\blacktriangle) Theoretical value.

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Table 1. L_{II} absorption discontinuity of RE.

Compound	(Width in eV) [†] A	Area under A	(Width in eV) [†] A^*	Area under A^*
La ₂ O ₃	5.0	4.05	0.57	0.11
Pr ₂ O ₃	5.8	4.67	0.69	0.15
Nd ₂ O ₃	6.3	4.90	0.75	0.18
Sm ₂ O ₃	6.9	5.80	0.88	0.19
Eu ₂ O ₃	8.2	6.53	0.96	0.22
Gd ₂ O ₃	8.8	6.87	1.1	0.25

[†] indicates the widths of lorentzians corresponding to the absorption maxima A and A^* (shown in figure 1(a)) associated with the L_{II} absorption discontinuity of rare earths in their sesquioxides.

Table 2. L_{III} absorption discontinuity of RE.

Compound	(Width in eV) [†] A	Area under A	(Width in eV) [†] A^*	Area under A^*
La ₂ O ₃	5.3	3.33	0.67	0.08
Pr ₂ O ₃	6.1	3.69	0.81	0.14
Nd ₂ O ₃	7.0	4.64	0.89	0.16
Sm ₂ O ₃	7.5	4.95	0.95	0.18
Eu ₂ O ₃	8.4	5.41	1.1	0.20
Gd ₂ O ₃	9.3	6.47	1.3	0.22

[†] indicates the widths of lorentzians corresponding to the absorption maxima A and A^* (shown in figure 1(b)) associated with the L_{III} absorption discontinuity of rare earth in their sesquioxides.

of the absorption curve to obtain precise knowledge of inflection point on these absorption curves. The point E_0 corresponding to the energy of the inflection point on the arc tangent curve was fixed at this particular point. The program was then run to adjust the floating parameters from $A(1)$ to $A(8)$ to get the minimum value of X^2 .

After successful run of the program we could obtain and compare the widths of the Lorentzians corresponding to the main absorption maxima A and A^* for both L_{II} as well as L_{III} absorption discontinuities. We also calculated the area under the Lorentzians corresponding to the main absorption maxima A and A^* for all the absorption discontinuities studied in the present work.

Tables 1 and 2 give the values of Lorentzian width corresponding to the main absorption maxima A and A^* obtained by using the program, for the L_{II} and L_{III} absorption discontinuities.

3. Results and discussion

The experimentally observed L_{II} and L_{III} absorption curves were normalized by calculating $(I_0 - I)/I_0$. Here I is the intensity at different points in the region of absorption edge and I_0 is the intensity of the continuum over which the absorption edge lies. The intensity of the continuum in the narrow energy region of the discontinuity can be presumed to be constant.

The L_{II} and L_{III} absorption curves for La_2O_3 are shown in figure 1(a, b).

We have obtained a secondary maximum A^* on the higher energy side of the absorption maximum A corresponding to the white line. Similar types of absorption edges are obtained for the rest of the rare earth oxides. The features A and A^* associated with the absorption discontinuities can be explained as follows.

The pronounced white line can be attributed to the transition $2p$ to $5d$ [20–22], highly favoured one due to symmetry consideration. This assignment is also supported by the X-ray isochromat studies [23] of gadolinium sesquioxide. These studies indicate the predominance of d character in its conduction band. The plots of the radial density as a function of r for the $4s$, $5s$, $5p$, $5d$ and $6s$ electrons for tri-positive gadolinium atom are given by Freeman *et al* [24]. The plots vividly demonstrate that the half filled $4f$ shell is indeed deeply embedded within the $5s$ and $5p$ shells. The plot also shows that the atomic state, $5d$, is widely separated from the $4f$ state. According to Rohler [25], the information obtained from the L_{II} and L_{III} absorption spectrum is very local. The measurement probes essentially the $5d$ states of the absorbing atom as modified (from the atomic $5d$ states) by the immediate neighbours. As is well-known, in sesquioxides the RE ions are surrounded by oxygen atoms in an octahedral coordination. The molecular energy level diagram for this system is given in figure 2 [26].

It must be mentioned here that the molecular orbital (MO) diagram is only qualitative and is built on the considerations of LCAO and MO formulation with respect to the first coordination. This first coordination, according to Rohler [25], plays an important and significant part in the atomic orbital modification. The MO diagram does not take into account the several complicating effects, such as interelectronic repulsion, spin orbit coupling, the extend of overlap between the orbitals of the absorbing atom and the concerned ligand ions, etc. Although simplistic, such a diagram enables us to interpret the spectral features associated with the L_{II} and L_{III} absorption edges [27].

The molecular orbital levels $2t_{2g}$ and $3e_g$, have a very significant contribution from the $5d$ atomic orbitals of rare earth ions. These molecular orbital levels will thus be highly favoured for the transition from the initial $2p_{1/2}$ and $2p_{3/2}$ levels in the case of L_{II} and L_{III} absorption respectively.

The probability of transition to MO $3a_{1g}$, which has a contribution from $6s$ atomic orbital of rare earth ion, is comparatively less. The transition to the $4t_{1u}$ molecular level, which has a contribution from the $6p$ atomic levels, is forbidden. We can therefore attribute the main absorption maximum A to the transition to molecular orbital level $2t_{2g}$ and the secondary maximum A^* to the transition to the $3e_g$ molecular orbital level in both the L_{II} and L_{III} absorption spectra.

Tables 1 and 2 show that the width of the Lorentzians corresponding to the absorption maxima A and A^* increases as we go down to the series. This can be explained as follows:

In the lanthanides ($57 < Z < 71$) it has been shown [28] that the natural widths of the K, L, M and N levels increase more or less monotonously with the increasing atomic number. We expect the same trend to continue in RE sesquioxides. Also, the increase in the width in sesquioxides can be attributed to the fact that as the atomic number of RE increases the life time of the antibonding molecular orbitals of RE sesquioxide, to which the transitions responsible for the absorption maxima A and A^* take place, decreases.

From tables 1 and 2 one observes that the width of the Lorentzian corresponding

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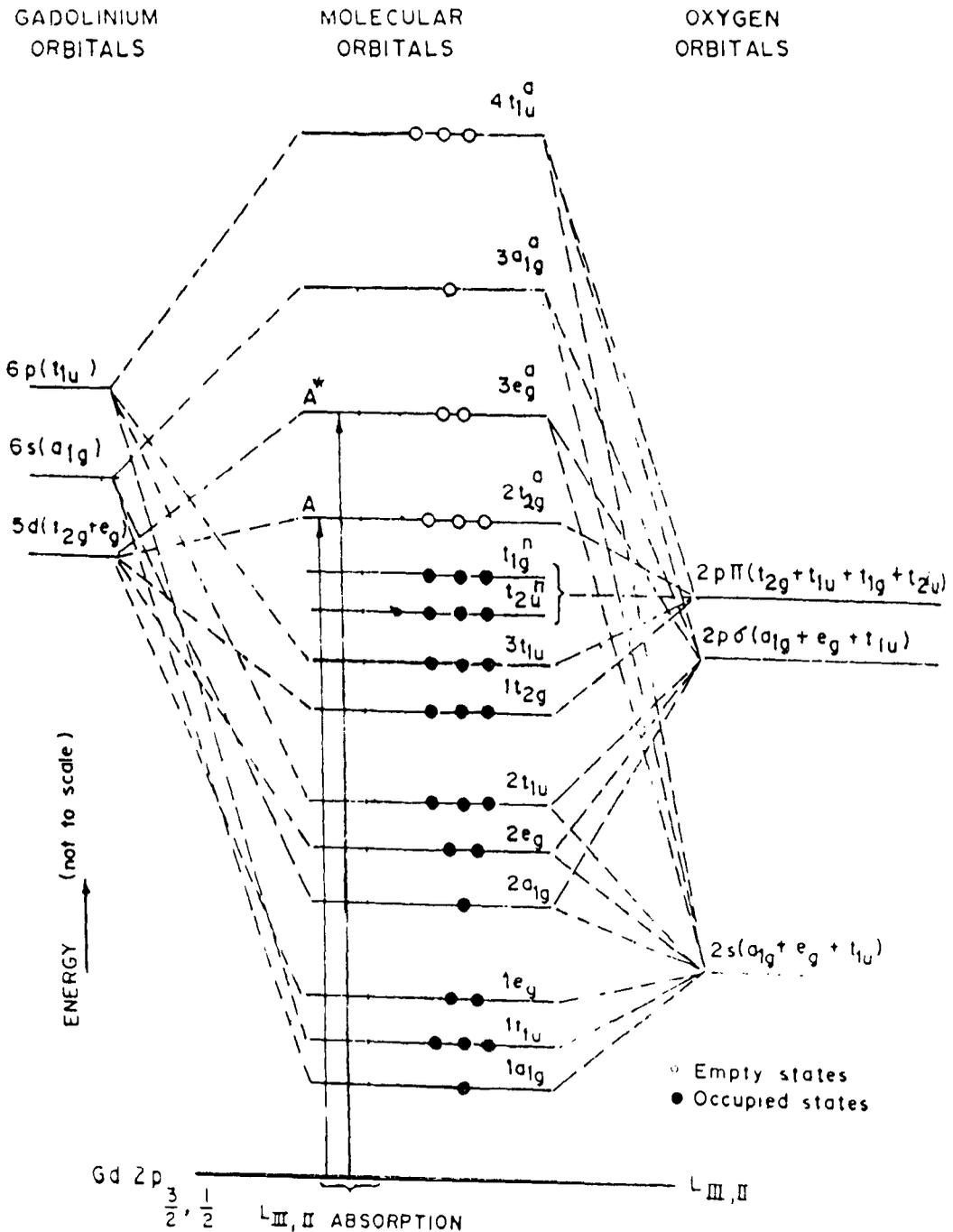


Figure 2. Molecular orbital diagram for Gd_2O_3 .

to absorption maxima A and A^* is less in L_{II} absorption discontinuity compared to the L_{III} absorption discontinuity for the same RE sesquioxide. This may be attributed to the different initial atomic levels ($2p_{1/2}$ for L_{II} and $2p_{3/2}$ for L_{III} absorption discontinuity) from which the electron makes the transition to the molecular orbital energy levels. The above assumption is based on the fact that, transition probability

is the function of the initial as well as the final energy levels. The width of the lorentzian corresponding to these transitions will therefore be affected by the change in these initial levels.

The two peaks, A and A^* , result from the transitions from the inner level $2p_{1/2}$ to the levels $2t_{2g}$ and $3e_g$ respectively for L_{II} and from $2p_{3/2}$ to the same levels $2t_{2g}$ and $3e_g$ for L_{III} . The ratio of the widths and area under the curve of the lorentzians corresponding to the transition to these two levels $2t_{2g}$ and $3e_g$ is thus expected to remain the same for both L_{II} , as well as L_{III} absorption discontinuities. As can be seen from tables 1 and 2 our experimental results corroborate this fact.

4. Conclusion

The agreement between the experimentally observed and theoretically predicted results shows the validity of the theoretical equation as well as the fitting technique used in this work. This technique can be considered as a step towards solving the XANES problem. The theoretical equation is flexible enough to take into account all the transitions responsible for the XANES as well as other phenomena such as, screening effect, variation in the potential around the metal ion due to surrounding ligand ions, charge transfer, etc. The work in this direction is in progress.

Acknowledgement

We are thankful to the University Grants Commission, New Delhi, for financial support.

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