International Journal of Advance Research in Science and Engineering
Volume No.07, Special Issue No.08, March 2018
www.ijarse.com
IJARSE
ISSN: 2319-8354

# Photon induced $L_3$ vacancy alignment study for Gd in the energy range 7.3-8.6 keV

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## ABSTRACT

*The unequal distribution of vacancies in magnetic sub-states of a state with angular momentum j >1/2 leads to vacancy alignment and results in anisotropic distribution of resulting X-rays. In decay of L vacancies,* $L_\alpha$ *and* $L_\ell$ *group of X rays originate only from the filling of* $L_3$ *vacancies. For isotropic distribution of X-rays, the cross-section ratio* $L_\alpha/L_\ell$ *is independent of incident energy and simply becomes equal to the ratio of their radiative decay rates Fs. Thus, alignment of photon induced* $L_3$ *vacancies can be checked from energy dependence of* $L_\alpha/L_\ell$ *cross-section ratios [1]. From our previous measurements on L X-rays for Gd at nine tuned photon energies from synchrotron Beamline-16, Indus-2, India [2] such that three energies each are at intervals 0.1 keV for selective excitations of* $L_1$, $L_2$ *and* $L_3$; $L_2$ *and* $L_3$ *and only* $L_3$ *sub-shell, alignment studies have been made. Certainty and reliability of the measurements were checked from comparison of measured* $L_\alpha$ *and* $L_\ell$ *fluorescence cross-sections with theoretically calculated ones. The alignment parameter* ($A_2$) *and* $A_2'$ *(Coster-Kronig corrected* $A_2$) *were evaluated and their variation with incident energies are interpreted in terms of peculiar electronic configuration of Gd and Coster-Kronig effects on* $L_3$ *vacancies.*

***Keywords:* *Coster-Kronig transitions, L X-ray intensity ratios, Selective sub-shell excitations, Synchrotron photons, X-ray fluorescence.***

## 1. Introduction

$L_3$ level with total angular momentum *j*=3/2 may have unequal vacancy population in magnetic sub states $m_j$=3/2 and 1/2 (Berezhko and Kabachnik [3], Berezhko et al., [4]) leading to vacancy alignment ($A_2$). Both $L_\ell$ and $L_\alpha$ group of L X-ray lines arise only from the feeding of $L_3$ vacancies, produced from direct ionization plus Coster-kronig (CK) transferred vacancies from $L_1$ and $L_2$. Thus, the ratio $L_\alpha/L_\ell$ is free from $L_3$ vacancy population and only depends upon the ratio of their fractional radiative decay rates $F_{3\alpha}/F_{3\ell}$. Radiative decay rates being after ionization effect are independent of incident photon energy and only depend upon atomic number *Z*. This makes $L_\alpha/L_\ell$ ratio independent of incident photon energy. In our lab Bansal et al. [1] determined alignment parameter from incident energy dependence of $L_\alpha/L_\ell$ fluorescence cross-section ratios for elements, Z=66-83 at three tuned synchrotron photon energies for selective excitations of L sub-shells.

Recently, the measurements have been refined for selective L sub-shell excitations in the region Z=62-67 with nine $E_{ij}$ monochromatic photon energies tuned such that three ($j$=1-3) energies at intervals of 0.1 keV in each of the three regions ($i$=1-3); > $EL_1$, >$EL_2$ & < $EL_1$ and >$EL_3$ & <$EL_2$ where $EL_i$ are absorption edge energies of element. Excitation between $L_3$ and $L_2$ edges is free from CK effect while the other two comprise the CK effect due to shifting of $L_2$ and both $L_2$ and $L_1$ vacancies to $L_3$ sub-shell. Gd is central element in the rare-earth region, hence, in the present work the photon induced L X-ray measurements on Gd at nine energies were used to check the alignment of vacancies from incident energy dependence of $L_\alpha/L_\ell$ cross-section ratios.

## 2. Experimental measurements

LXRF measurements for Gd were carried out at microfocus X-ray fluorescence beamline (BL-16) of Indus-2 synchrotron radiation facility in India in ambient air environment [2]. Self supporting target of Gd with thickness 0.0319 $g/cm^2$ was prepared from spec pure powder of $Gd_2O_3$ with styrol ($C_8H_8$) as binder following the method of Mann *et al.* [5]. Monochromatized photons in the energy range 7.3-8.6 keV were incident at 45° to the target surface for its excitation and emitted fluorescent L X-rays were measured at 90° to the incident photon beam with the SDD (Vortex, USA) photon detector having energy resolution ~138 eV at 5.959 keV (Mn $K_\alpha$) X-rays placed at ~30 mm distance from the centre of the target. The recorded spectra of Gd at three incident energies 7.3(>$EL_3$), 8.1(>$EL_2$) and 8.4(>$EL_1$) keV are shown in Fig 1. With only $L_3$ excitation $E_{31}$ (7.3 keV), X-ray groups $L_{\gamma1}$, $L_{\gamma2}$ and most of $L_{\beta1}$ originating from $L_1$ and $L_2$ are absent, at $E_{21}$ (8.1 keV), only peaks from $L_3$ and $L_2$ excitations dominate and $L_{\gamma2}$ originating mainly from $L_1$ is absent while at $E_{11}$ (8.4 keV), all peaks $\ell$, α, β's and γ's are present.

Counts under $L_\ell$ and $L_\alpha$ X-ray peaks ($N_{L\ell/\alpha}$) for each spectrum were collected to evaluate experimental L-shell X-ray cross-section ratios $\sigma^*_{L\alpha}/\sigma^*_{L\ell}$ using relation (Bansal et al., 2017b).

$$\frac{\sigma^*_{Lg}(E_{ij})}{\sigma^*_{L\ell}(E_{ij})} = \frac{N_{L\alpha}(E_{ij})\beta_{L\ell}(E_{ij},e)\varepsilon_{L\ell}(e)}{N_{L\ell}(E_{ij})\beta_{L\alpha}(E_{ij},e)\varepsilon_{L\alpha}(e)} \tag{1}$$

where $\beta$'s are target self absorption correction factor at incident photon ($E_{ij}$) and emitted X-ray energies ($e$) and $\varepsilon_L(e)$ is extrinsic efficiency of detector for a group of X-rays depends upon the transmission of X-rays through the air column between target and detector, detector window, Au contact layer and Si dead layer and their absorption in the detector material calculated as Bansal et al. [6].

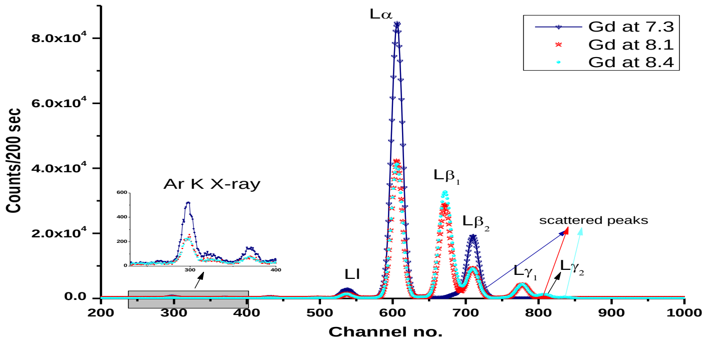

**Fig. 1 L X-ray spectra of Gd recorded at 7.3, 8.1 and 8.4 keV incident energies.**

## 3. Formulations for alignment evaluations

The X-ray fluorescence cross-sections for $L_\ell(L_3\text{-}M_1)$ and $L_\alpha(L_3\text{-}M_{4,5})$, X-rays at incident photon energy $E_{ij}$ for isotropic distribution of X-rays in terms of photo ionization cross-section for $L_i$ sub-shell $\sigma_{Li}$, sub-shell fluorescence yield $\omega_{Li}$, Coster-Kronig transition probabilities $f_{ij}$ and radiative decay rates $F$'s are given as

$$\sigma^*_{L\ell}(E_{ij}) = \left(\sigma_{L3}(E_{ij}) + \sigma_{L2}(E_{ij})\,f_{23} + \sigma_{L1}(E_{ij})\left(f_{13} + f_{12}f_{23}\right)\right)\omega_{L3}F_{3\ell} \qquad (2)$$

$$\sigma^*_{L\alpha}(E_{ij}) = \left(\sigma_{L3}(E_{ij}) + \sigma_{L2}(E_{ij})\,f_{23} + \sigma_{L1}(E_{ij})\left(f_{13} + f_{12}f_{23}\right)\right)\omega_{L3}F_{3\alpha} \qquad (3)$$

and the cross-section ratio, $$\frac{\sigma^*_{L\alpha}(E_{ij})}{\sigma^*_{L\ell}(E_{ij})} = \frac{F_{3\alpha}}{F_{3\ell}} \qquad (4)$$

For anisotropic emission of X-rays from aligned vacancies created by incoming polarized photon beam along z-axis in a x-z reaction plane, Barrea et al. [7] have given the X-ray distribution from $L_3$ state ($j$=3/2) as

$$W\,(\theta,\phi=0^o) = \frac{W_0}{4\pi}\left[1+\alpha_2 A_{20}[P_2(\cos\theta) - \frac{3}{2}\sin^2\theta]\right] \qquad (5)$$

where $W_0$ is the total X-ray emission rate, $\theta$ is the angle between the X-ray and the incoming photon beam, $\phi$ is azimuthal angle and in the x-z reaction plane ($\phi$=0) , $\alpha_2$ is a constant whose value depends upon the total angular momentum $j$ of the initial and final states involved in the X-ray emission. Under dipole approximation, $A_{20}$ is being taken as $A_2$ in the following text.

With $\alpha_2$ ($L_\ell$) = 0.5, $\alpha_2$ ($L_{\alpha1}$) = 0.1, $\alpha_2$ ($L_{\alpha2}$) = -0.4 [3], for $L_\ell$ and $L_\alpha$ (a combination of $L_{\alpha1}$ and $L_{\alpha2}$ lines), the total intensities $W_{L\ell}$, $W_{L\alpha1}$, $W_{L\alpha2}$ proportional to respective XRF cross-sections, $\sigma^*_{L\ell}$ $\sigma^*_{L\alpha1}$ $\sigma^*_{L\alpha2}$ [8] give

$$\frac{\sigma^*_{L\alpha}}{\sigma^*_{L\ell}}(\theta,\phi=0) = \frac{W_{L\alpha1}(\theta,\phi=0)+W_{L\alpha2}(\theta,\phi=0)}{W_{L\ell}(\theta,\phi=0)}$$

$$= \frac{F_{3\alpha1}[1+0.1A_2(P_2\cos(\theta) - \frac{3}{2}\sin^2(\theta))] + F_{3\alpha2}[1-0.4A_2(P_2\cos(\theta) - \frac{3}{2}\sin^2(\theta))]}{F_{3l}[1+0.5A_2(P_2\cos(\theta) - \frac{3}{2}\sin^2(\theta))]} \qquad (6)$$

For no alignment of $L_3$ state vacancies, $A_2$=0 and expression (6) reduces to relation (4).

At emission angles $90^o$ the expression (6) becomes

$$\frac{\sigma^*_{L\alpha}}{\sigma^*_{L\ell}}\left(\theta=90^{O},\phi=0\right)=\frac{(F_{3\alpha1}+F_{3\alpha2})[1-0.2A_2+A_2F_{3\alpha2}/(F_{3\alpha1}+F_{3\alpha2})]}{F_{3\ell}[1+0.5A_2\left(-2\right)]}$$

Taking $F_{3\alpha2}/F_{3\alpha1}=1/9$ for hydrogen like wave functions, on solving one gets;

$$\frac{\sigma^*_{L\alpha}}{\sigma^*_{L\ell}}\left(\theta=90^{O},\phi=0\right)=\frac{(F_{3\alpha1}+F_{3\alpha2})[1-0.1A_2]}{F_{3\ell}[1-A_2]} \tag{7}$$

The ratio $\sigma^*_{L\alpha}\big/\sigma^*_{L\ell}$ is a function of the degree of alignment $A_2$ as well as of the radiative transition probabilities those are energy independent. Thus, the dependence of cross-section ratio on incident energy comes from the alignment of $L_3$ vacancies and leads to $A_2$ evaluations.

## 4. Results and discussion

Experimental cross-section ratios at different incident energies were evaluated using equation (1) and are listed in table 1 along with $F_{3\alpha}/F_{3\ell}$ ratio. The certainty and reliability of the measurements have already been judged from the comparison of measured $L_\alpha$ and $L_\ell$ fluorescence cross-sections with theoretically calculated ones [2].

**Table 1: Evaluated experimental cross-section ratio along with $F_{3\alpha}/F_{3\ell}$, alignment parameter $A_2$ and Coster-Kronig corrected $A_2'$ for Gd.**

| Incident energy (keV) | | $\frac{I^*_{L\alpha}}{I^*_{L\ell}}(E_{ij})$ ($F_{3\alpha}/F_{3\ell}$=24.152) | $A_2$ | $A_2'$ |
|---|---|---|---|---|
| $E_{31}$ | 7.3 | 20.687±1.45 | -0.190±0.013 | -0.19±0.013 |
| $E_{32}$ | 7.4 | 24.713±1.73 | 0.025±0.002 | 0.025±0.002 |
| $E_{33}$ | 7.5 | 24.838±1.74 | 0.031±0.002 | 0.031±0.002 |
| $E_{21}$ | 8.1 | 20.755±1.45 | -0.185±0.013 | -0.171±0.012 |
| $E_{22}$ | 8.2 | 23.706±1.66 | -0.021±0.001 | -0.019±0.001 |
| $E_{23}$ | 8.3 | 25.307±1.77 | 0.05±0.004 | 0.046±0.003 |
| $E_{11}$ | 8.4 | 27.904±1.95 | 0.147±0.010 | 0.123±0.009 |
| $E_{12}$ | 8.5 | 31.679±2.22 | 0.257±0.018 | 0.215±0.015 |
| $E_{13}$ | 8.6 | 24.976±1.75 | 0.037±0.003 | 0.030±0.002 |

The experimental values are with 7% uncertainties calculated from quadrature sum of the uncertainties in counts $N_{L\alpha/\ell}$ (1–4%), targets thickness (<2%) and target self absorption correction factor $\beta_{L\alpha/\ell}$ (<4%) [6]. The plot of experimental cross-section ratios versus energies along with $F_{3\alpha}/F_{3\ell}$ radiative transition probabilities ratios is shown in Fig. 2.

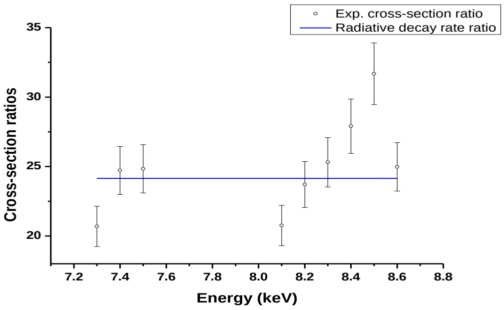

Fig. 2 Variation of experimental cross-section ratios versus energies along with $F_{3\alpha}/F_{3\ell}$ radiative transition probabilities ratios for Gd.

The cross-section ratios are fluctuating around constant ratio $F_{3\alpha}/F_{3\ell}$. Higher deviation at $E_{11}$, $E_{21}$ and $E_{31}$ from $F_{3\alpha}/F_{3\ell}$ indicates the existence of vacancy alignment at near edge energies that almost decreases with energy with exception at energy and $E_{32}$. At energy between $EL_3$ and $EL_2$ edges, anisotropy is expected as only $L_3$ gets excited; between $EL_2$ and $EL_1$ edges and above $EL_1$ edge, the anisotropy is expected to be disturbed due to shifting of isotropic vacancies from ionized $L_2$ and $L_1$ sub-shells to $L_3$ sub-shell because of CK transitions along with direct ionization of $L_3$. Thus, by varying incident energies between L sub-shell thresholds, the effect of CK transitions is being checked. In the present experimental set-up, for dipole distribution of emitted $L_3$ fluorescent X-rays the alignment parameter $A_2$ values were evaluated and are given in table 1. Taking no uncertainties in *F*'s ratio, the errors in $A_2$ values are 7%.

According to Kamiya et al. [8], negative $A_2$ values result if the transfer momentum lies in the incident photon direction and the ionisation of m=0 electrons takes place. Similarly $A_2$ value is positive if the transfer momentum is perpendicular to the photon direction and the ionisation of m=1 electron takes place.

To make $A_2$ values free from the effect of CK transitions, the relation

$$A_2^{'} = \frac{\sigma_{L3}}{[\sigma_{L1}(f_{12}f_{23}+f_{13})+\sigma_{L2}f_{23}+\sigma_{L3}]}A_2 \qquad (7)$$

was used to modify the values of alignment parameter $A_2$ as $A_2'$ those were evaluated using photo ionization cross-section $\sigma_{Li}$ of Scofield [9] and CK transition probabilities $f_{ij}$ of Krause et al. [10] and are also listed in table 1. The value of alignment has reduced after applying CK correction at $L_2$ and $L_1$ excitations while these are same at only $L_3$ excitation shows that CK effect is nil at only $L_3$ excitation. Neglecting the plus / minus sign, $A_2'$ values 0.19 to 0.12 are very much within the limits 0.5 and 0.05 for $L_3$ state [4] and show sufficient alignment at near edge energies $E_{11}$, $E_{21}$ and $E_{31}$ following the decreasing pattern from at $E_{11}$ to $E_{31}$.

As the energies apart from the edges, alignment becomes negligible with $A_2'$ values < 0.05 except at energy $E_{12}$. It shows the successive start of $L_2$ and $L_1$ ionization also impacts the $L_3$ vacancy population towards alignment. Further, to find whether this peculiar alignment character is due to the start of 5*d* filling in Gd, our data from measurements on other elements in rare earth region is to be analyzed.

## 5. Acknowledgement

The Experimental support from synchrotron radiation faculty, RRCAT, Indore and financial assistance from UGC-DAE in the form of project grant (CSR-IC-BL-18/CRS-115/2014-15/1211) are highly acknowledged.

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