CHAPTER 4

INCIDENT PHOTON ENERGY AND Z DEPENDENCE OF 
L X-RAY RELATIVE INTENSITIES

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4.1 INTRODUCTION

The radiative decay of the L_(i=1–3) sub-shell vacancies results in emission of X-ray series comprising several lines in each case. Accurate data on the relative intensities of these L X-ray lines for different elements at different incident photon energies are of considerable importance for investigation of atomic inner-shell photoionization processes as well as for a variety of applications. For quantitative elemental analysis of different types of samples using X-ray emission techniques (EDXRF and PIXE), the interpretation of complex spectra comprising overlapping X-ray lines arising from a multi-elemental sample requires the accurate knowledge of relative intensities of different X-ray lines for all the elements.

The L X-ray relative intensities can be deduced from the X-ray production (XRP) cross sections which, in turn, can be evaluated using physical parameters, namely, photoionization cross sections, fluorescence and Coster-Kronig (CK) yields, X-ray emission rates and vacancy transfer probabilities. The theoretical production cross sections for the L_1, L_α, L_β and L_γ X-ray groups were reported long back by Puri et al. [1] for different elements with 36≤Z≤92 at incident photon energies ranging E_{L_1}<E_{inc}<200keV. From these tabulations only the gross intensity ratios, I_1/I_{Lα} (j = 1, β, γ), can be deduced, however, for most of the applications including elemental analysis the knowledge of relative intensities for different resolved X-ray components/lines originating from the individual L_(i=1–3) sub-shells are required. Moreover, the intensity ratios for some of the L_k X-ray components are expected to exhibit abrupt discontinuities in the atomic regions where the cut-off or onset of certain intense Coster-Kronig transitions occur. Similar discontinuities in the values of intensity ratios for given element are expected at incident photon energies in vicinity of the K-shell ionization threshold energy. A thorough literature search
revealed the non-availability of any tabulation of intensity ratios for the resolved L X-ray components/lines produced following photoionization.

In view of the above facts, it was felt necessary to have a comprehensive tabulation of intensity ratios for different resolved L X-ray components as a function of incident photon energy and atomic number (Z).

Accordingly, in this chapter, the L_(i=1-3) sub-shell X-ray intensity ratios, \( \frac{I_{Lk}}{I_{La_1}} \) (for \( k = 1, \eta, \alpha_1, \beta_1, \beta_{2,15}, \beta_{3,4}, \beta_{5,7}, \beta_6, \beta_{9,10}, \gamma_1, \gamma_6, \gamma_{2,3}, \gamma_4 \)) have been evaluated for elements with 36≤Z≤92 at incident photon energies ranging \( E_{L1}<E_{inc}<200\text{keV} \) using currently considered to be more reliable theoretical sets of different physical parameters. At incident photon energies above the K-shell ionization thresholds of an element, the contribution to the production of different L X-ray lines due to the additional L_(i=1-3) sub-shell vacancies created following decay of the primary K-shell vacancies have also been included in the present calculations. In addition, the L\( \alpha_1 \) X-ray production cross sections for different elements at various photon energies have been tabulated so as to facilitate the evaluation of production cross sections for different resolved L X-ray components from the tabulated intensity ratios.

### 4.2 BASIC FORMALISM

The production cross sections (\( \sigma_{Lk}^X \)) for the Lk X-rays at incident photon energy, \( E_{inc} \), can be evaluated using the equations

\[
\sigma_{Lk}^X = \sigma_{L1}^{i} \omega_1 F_{ik}
\]  

where \( F_{ik} \) (i=1-3) represents the fractional emission rate for the Lk \( [k = \beta_3, \beta_4, \beta_{9,10}, \gamma_{2,3}, \gamma_4 \text{ (for i=1)}; k = \beta_1, \eta, \gamma_{1,5}, \gamma_{6,8} \text{ for (for i=2)}; k = 1, \alpha_1, \alpha_2, \beta_{5,7}, \beta_6, \beta_{2,15} \text{ (for i=3)}] \)
groups of X-rays and \( \omega_i (i=1-3) \) represents the \( L_i \) sub-shell fluorescence yields. The \( \sigma^i_{Li} \) denote the total number of vacancies in the \( L_i (i=1-3) \) sub-shells including those transferred through the CK transitions and can be calculated using the equation

\[
\sigma^i_{Li} = \sigma^p_{Li} + \sum_{k<i} \sigma^i_{Lk} f_{ki}
\]  

(4.2)

where \( \sigma^p_{Li} (i=1-3) \) represent the \( L_i \) sub-shell photoionization cross sections and the \( f_{ki} \) (\( f_{12}, f_{13}, f_{23} \)) are the \( L_i \) sub-shell CK transitions probabilities. At incident photon energies above the K-shell ionisation threshold energy (\( E_K \)) of an element (\( E_K < E_{inc} < 200 \text{keV} \)), the number of additional \( L_i (i=1-3) \) sub-shell vacancies \( (N_{Li}) \) created following decay of a primary K-shell vacancy can be calculated as

\[
N_{Li} = \sigma^p_{K} \eta_{KL}, \quad (i=1-3)
\]  

(4.3)

where \( \sigma^p_{K} \) represents the K-shell photoionization cross section at a given incident photon energy and the \( \eta_{KL}, (i=1-3) \) represent the probability for production of the \( L_i (i=1-3) \) sub-shell vacancies following decay of a primary K-shell vacancy.

The intensity ratios,

\[
\frac{I_{Lk}}{I_{La1}} (k = l, \eta, \alpha, \beta, \gamma) \quad (k=2,3,5,7,9,10,1) \]  

(4.4)

can be deduced from the \( L_k \) XRP cross sections as

\[
\frac{I_{Lk}}{I_{La1}} = \frac{\sigma^x_{Lk}}{\sigma^x_{La1}}
\]  

The details of different physical parameters used for present calculations are given below.

### 4.2.1 X-ray Emission Rates

The calculations of \( L_i \) sub-shell X-ray emission rates for single vacancy states based on two different Independent Particle Approximation (IPA) models are
available in Literature [2–4]. The first set is based on the Dirac-Hartree-Slater (DHS) model [2] and the second one is based on the Dirac-Fock (DF) model [3,4]. In the former model, the potential is assumed to be equal for the initial and final states of the atom undergoing transitions. In the latter model, the potential is assumed to be different for initial and final states and hence exchange and overlap effects were included.

The DHS model based emission rates were tabulated by Scofield [2] for all elements with $5 \leq Z \leq 104$ and included the most intense dipole transitions as well as less intense transitions of E2, E3, and M1 multipoles. The DF model based values were tabulated by Scofield [3] for 21 elements in the atomic region $18 \leq Z \leq 94$ and included dipole transitions only. Later on, Campbell and Wang [4] reported a complete set of L$_i$($i=1–3$) sub-shell X-ray emission rates for all the elements with $18 \leq Z \leq 94$, interpolated from the DF model based values tabulated by Scofield [3]. Recently, Puri [5] reported the fitted values of these interpolated emission rates, for different transitions, as a function of atomic number (Z). It has been shown experimentally [6,7] that in case of heavy elements the L X-ray emission rates based on the DF model [3,4] are more reliable than those based on the DHS model [2].

### 4.2.2 Fluorescence and Coster-Kronig Yields

Three sets of the L$_i$($i=1–3$) sub-shell fluorescence ($\omega_i$) and Coster-Kronig ($f_{ij}$) yields are available in literature. Puri et al. [8] reported a comprehensive set of the $\omega_i$ and $f_{ij}$ yields for all the elements with $25 \leq Z \leq 96$ evaluated using the Dirac-Hartree-Slater (DHS) model based X-ray emission rates [2] and the non-radiative transition rates interpolated from the DHS model based data [9] available for limited elements considering the onset and cut-off of different CK transitions in accordance with the
CK transition energy calculations [10]. Krause [11] tabulated a set of semi-empirical fitted values of $\omega_i$ and $f_{ij}$ yields for all elements with $12 \leq Z \leq 110$ based on the experimental data available till 1979. Campbell [12] provided a set of recommended values of the $\omega_i$ and $f_{ij}$ yields based on experimental data available till 2003 for the elements with $62 \leq Z \leq 96$ and recently reported [13] the revised set of recommended values only for the $L_1$ sub-shell fluorescence and Coster Kronig yields, bearing uncertainties $\sim 15\text{-}30\%$, for all elements with $64 \leq Z \leq 92$ except for $Z=75$ and 76. In case of the $L_2$ and $L_3$ sub-shell fluorescence yields, the recommended values [12] are same as the DHS values [8] and the recommended values of CK yield, $f_{23}$, differ from the DHS values up to $\sim 30\%$. In case of the $L_1$ sub-shell yields ($f_{12}$, $f_{13}$ and $\omega_1$), the agreement between the DHS values and the recommended values [12] is not so good (5\text{-}10\%) with exceptionally significant differences ($\sim 50\%$) for elements in vicinity of atomic numbers where cut-off / onset of certain intense CK transitions occur.

### 4.2.3 Photoionization Cross Sections

The $L_i$($i=1$-3) sub-shell photoionization cross sections based on the relativistic Hartree-Fock-Slater (HFS) model are available for all the elements with $Z=1$-101 in the energy range 1-1500 keV [14]. In detailed comparisons [15-18], the theoretical photon absorption cross sections obtained by adding these photoionization cross sections for all sub-shells/shells and small contribution of photon scattering were found to exhibit good agreement with the measured mass attenuation cross sections.

### 4.2.4 Vacancy Transfer Probabilities

At incident photon energies above the K-shell ionization thresholds of an element ($E_{\text{inc.}}>E_K$), a significant number of additional $L_i$($i=1$-3) sub-shell vacancies
are created following decay of the K-shell vacancies. To estimate these additional vacancies, knowledge of the K-shell to L\textsubscript{i} (i=1-3) sub-shell vacancy transfer probabilities, $\eta_{\text{KL}}$ (i=1-3), is required. These probabilities calculated using radiative [2] and radiationless [9] transition rates based on the DHS model for all the elements with Z=18 to 96 were reported by Puri et al.[19]. These DHS model based probabilities [19] were found to be in good agreement with the measured values [20].

4.3 COMPUTATIONAL PROCEDURE AND DISCUSSION

The $\gamma$-ray production cross sections have been evaluated for elements with 36$\leq$Z$\leq$92 at incident photon energies ranging $E_{\text{L1}}<E_{\text{inc}}<200$keV using the DF model based X-ray emission rates [3,4,5], the RHFS model based photoionization cross sections [14] and the DHS model based L\textsubscript{i} (i=1-3) sub-shell fluorescence and Coster-Kronig yields [8], in Eq. (4.1) and Eq. (4.2). At incident photon energies above the K-edge of an element ($E_{K}<E_{\text{inc}}<200$keV), the L\textsubscript{k} XRP cross sections were calculated using Eqs. (4.1) and (4.2) by replacing $\sigma_{i}^{p}$ (i=1-3) with ($\sigma_{i}^{p}+N_{\text{KL,i}}$). The number, $N_{\text{KL,i}}$, representing the additional L\textsubscript{i} (i=1-3) sub-shell vacancies created following decay of the primary K-shell vacancies have been evaluated using the RHFS model based photoionization cross sections [14] and the DHS model based K to L\textsubscript{i} sub-shell vacancy transfer probabilities, $\eta_{\text{KL}}$ (i=1-3) [19], in Eq. (4.3). The $\gamma$-ray intensity ratios, $I_{\text{Lk}}/I_{\text{Lalpha}}$ (thr.) (k=1, $\eta$, $\alpha$, $\beta_{1}$, $\beta_{2,15}$, $\beta_{3,4}$, $\beta_{5,7}$, $\beta_{6}$, $\beta_{9,10}$, $\gamma_{1,5}$, $\gamma_{6,8}$, $\gamma_{2,3}$, $\gamma_{4}$), have been deduced from present calculated L\textsubscript{k} XRP cross sections using Eq. (4.4) and are listed in Table 4.1. Further, the gross ratios $I_{\text{Lj}}/I_{\text{Lalpha}}$ (j=$\beta$ and $\gamma$) have also been deduced from the evaluated XRP cross sections and are listed in Table 4.1. In order to facilitate the
evaluation of production cross sections for the k\textsuperscript{th} X-ray components from the tabulated intensity ratios, the values of $\sigma_{L_\alpha}^X$ for different elements with $36 \leq Z \leq 92$ at incident photon energies ranging $E_{L,1} < E_{\text{inc}} < 200 \text{keV}$ have been given in last column of the Table 4.1.

The intensity ratios, $I_{L_k} / I_{L_{\alpha 1}} (\text{thr.})$ ($k = 1, \alpha_2, \beta_{2,15}, \beta_{5,7}, \beta_6$) exhibited dependence on the atomic number ($Z$) and for a given element these ratios are found to be independent of the incident photon energy. It may be noted that all these X-ray components including the $L\alpha_1$, originate following decay of the $L_3$ sub-shell vacancies. Therefore, these ratios depend only on the X-ray emission rates and are independent of the $L_i (i=1-3)$ sub-shell fluorescence and CK yields and the photoionization cross sections.

The intensity ratios, $I_{L_k} / I_{L_{\alpha 1}} (\text{thr.})$, for ($k = \eta, \beta_1, \beta_3, \beta_4, \beta_{9,10}, \gamma_{1,5}, \gamma_{6,8}, \gamma_{2,3}, \gamma_4$) X-ray components exhibited dependence on both, the incident photon energy as well as atomic number ($Z$). It may be noted that the ($L\beta_{3,4}, L\beta_{9,10}, L\gamma_{2,3,4}$) and the ($L\eta, L\beta_1, L\gamma_{1,5}, L\gamma_{6,8}$) X-ray components, respectively, originate following decay of the $L_1$ and $L_2$ sub-shell vacancies and hence forth are referred to as the $L_{1-2}$-sub-shell X-rays. For a given element, the calculated ratios for the $L_{1-2}$-sub-shell X-rays were found to vary smoothly with the incident photon energy for $E_{\text{inc}} < E_K$ and exhibited an abrupt significant decrease at $E_{\text{inc}}$ just above the $K$-shell ionization threshold energy ($E_K$) and thereafter again varies smoothly with photon energy. A typical plot depicting the variation of $I_{L_k} / I_{L_{\alpha 1}} (\text{thr.})$ ($k = \beta_3, \gamma_{1,5}$), with the incident photon energy for $\gamma_3\text{Yb}$ is shown in Fig.4.1. The observed trend of intensity ratios with incident photon energy can be understood as follows. In fact, at incident photon energies above the $K$-shell ionization threshold energy ($E_{\text{inc}} > E_K$), the $L_{i} (i=1-3)$ sub-
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Figure 4.1: Plot of intensity ratios, $I_{L\beta}/I_{L\alpha_1}$ ($k=\beta_3$ and $\gamma_1,3$), for $^{70}\text{Yb}$ as a function of incident photon energy. The solid lines corresponds to the DHS values and dotted lines represent the intensity ratios calculated using $L_i(i=1-3)$ sub-shell fluorescence and CK yields recommended by Campbell [12,13].

Shell vacancies are created by direct ionization as well as through decay of the primary K-shell vacancies. It is noteworthy here that for $E_{\text{inc}}>E_K$ the major contribution (80-85%) to the total number of L-shell vacancies comes from the additional vacancies produced following decay of the K-shell vacancies. Secondly, the maximum number of additional vacancies are created in the $L_3$ sub-shell and minimum in the $L_1$ sub-shell as is evident from the values of the K to $L_i(i=1-3)$ sub-shell vacancy transfer probabilities: $\eta_{KL_3}:\eta_{KL_2}:\eta_{KL_1}:: 1:0.66:0.21$ for $Z=36$, and $\eta_{KL_3}:\eta_{KL_2}:\eta_{KL_1}:: 1:0.64:0.045$ for $Z=92$.

The present calculated intensity ratios for the $L_2$- and $L_1$-sub-shell X-rays also exhibited abrupt jumps in their values in vicinity of the elements where cut-off/onset of certain intense CK transitions are located. For example, the $L_1$-$L_3\text{M}_{4,5}$ CK transitions are not allowed energetically for elements with $50\leq Z\leq 74$ [10], which
causes significant change in the values of $L_1$ sub-shell fluorescence ($\omega_h$) and CK ($f_{13}$ and $f_{12}$) yields and hence intensity ratios for X-ray components originating following decay of $L_1$ and $L_2$ sub-shell vacancies. Similarly, cutoff of the $L_1$-$L_2$N$_1$ CK transitions occur in vicinity of $Z=67$ [10], which causes a change in the $f_{12}$ values and hence intensity ratios for X-ray components originating following decay of the $L_2$ sub-shell vacancies. A typical plot depicting the variation of ratios, $I_{L_k}/I_{L\alpha 1}$ (thr.) for ($k = \beta_3$ (originating from the $L_1$ sub-shell) and $\gamma_{1,5}$ (originating from the $L_2$ sub-shell)), evaluated at 20 keV incident photon energy with the atomic number ($Z$) is shown in Fig 4.2. The abrupt change in the intensity ratios at $Z=50$ and $Z=75$ for both the $L\beta_3$ and $L\gamma_{1,5}$ X-ray components and at $Z=68$ for the $L\gamma_{1,5}$ X-ray component is evident from this figure. In addition, another abrupt change in these intensity ratios is observed in this figure at $Z=42$, which is because of the fact that for elements with $36 \leq Z \leq 41$ the incident photon energy of 20 keV happen to be above the K-edge of these elements and for the elements with $Z \geq 42$ (for $^{42}$Mo the K-edge energy is 20.146 keV) this photon energy is below the K-edge of all these elements.

The X-ray intensity ratios deduced using the $L_i$($i=1$-$3$) sub-shell fluorescence and CK yields recommended by Campbell [12,13], denoted as $I_{L_k}/I_{L\alpha 1}$ (camp), are compared with the $I_{L_k}/I_{L\alpha 1}$ (thr.) values in Fig. (4.1) and Fig. (4.2). The ratios, $I_{L_k}/I_{L\alpha 1}$ (camp) ($k=\beta_3, \gamma_{1,5}$), are found to differ from the $I_{L_k}/I_{L\alpha 1}$ (thr.) values by up to 15%. Similar differences were observed in case of other $L_2$ and $L_3$ sub-shell X-ray components. It may be emphasized here again that the $\omega_h$ and $f_{ij}$ yields recommended by Campbell [12, 13] bear large uncertainties ~15-30%. 

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Figure 4.2: Plot of intensity ratios, $I_{\gamma_1}/I_{\alpha_1}$ and $I_{\gamma_1}/I_{\alpha_1}$, at 20 keV incident photon energy as a function of atomic number (Z). The solid lines correspond to the DHS values and dotted lines with symbols represent the intensity ratios calculated using $L_i$ sub-shell fluorescence and CK yields recommended by Campbell [12,13].

4.4 CONCLUSIONS

Summarizing, accurate systematic measurements of the relative intensities of the resolved L X-ray components for different elements as function of incident photon energies are highly desirable to test the reliability of presently tabulated theoretical intensity ratios. Further, it may be noted that different $L_i$ sub-shell physical parameters presently used to deduce the X-ray intensity ratios were calculated using the independent particle models, which completely ignore many-particle interactions such as electron-electron Coulomb correlations. These independent particle models are found to be inadequate in handling, particularly, the CK transitions and were found to overestimate the $L_1$ sub-shell CK transition rates [21]. Therefore, more refined theoretical predictions of the CK transition rates incorporating the many particle interactions in the existing models along with better understanding of solid-state effects are also highly desirable.
REFERENCES

