The work presented in this thesis deals with the investigation of the effect of processes initiated after creation of primary vacancies on L and M shell X-ray emission.

In all the measurements/investigations involving basic phenomenological study as well as application of X-ray emission, the primary interaction processes and cross-sections thereof are interpreted in terms of energies, intensities and other characteristics of the X-ray lines or group of lines emitted as a result of the initiating process. The process of X-ray emission follows the various vacancy rearrangement processes within the atomic subshells initiated after the creation of primary vacancies in the inner shells. The X-rays resulting from the primary vacancies contain information on the concerned process responsible for creation of vacancy [1]. However, it is seen that in all shells above K shell, some processes, faster in time, alter the initial primary vacancy distribution in different subshells of a shell before these vacancies are filled either through X-ray emission or Auger process. In L, M and higher shells, primary vacancies may be altered by the non-radiative Coster-Kronig and Super-Coster-Kronig transitions which are much faster in time (nearly $10^{-17}$ seconds) in comparison to the time involved in normal shell to shell transitions. Similar is the case when the energy of incident radiation or the transition energy
of the vacancy creating radioactive process is higher than the lower
shell/subshell (say K shell) and the X-ray line/group being
measured is of higher shell (say L shell). Then the lower to higher
subshell transitions (say K to L) being faster in time will alter the
primary subshell vacancy status of the higher shell (say L shell).
Due to these processes, in measurements involving inner shells, the X-
ray energies and intensities do not reveal true characteristics of the
primary vacancies and the contribution of processes initiated after the
primary interactions have to be properly taken care of. Further, when L subshell of an atom is ionized by protons with incident energy greater
than the K shell binding energy of the element, the vacancies produced
in the subshell of that atom include the direct vacancies produced by the
proton impact and the indirect vacancies produced due to inter-shell K to
L and the intra-shell L to L and L to L transfer (Coster-Kronig
transfer) of vacancies. Thus, in experiments involving
measurement/determination of alignment related parameters, the
measured values of L X-ray intensities used to determine these
parameters are to be corrected/modified for processes responsible for
creation of unaligned vacancies in the L sub shell (indirect processes).

In the work done in past, these contributions to the primary
vacancies have either been eliminated/controlled experimentally [2-5] or
accounted for otherwise by different workers under their typical
experimental conditions only. Very little work has been done for a
detailed insight into the contribution of the vacancies initiated after the primary interaction processes leading to X-ray emission.

Rani et al. [6] have investigated the effect of CK transitions on L₃ subshell X-ray fluorescence cross-sections for some elements in the range 41 ≤ Z ≤ 92. They have indicated up to 63% enhancement of the XRF cross-sections. Allawadhi et al. [7] have investigated the effect of CK transitions on average L shell fluorescence yields. Their findings indicate that, in the absence of CK transitions, the fluorescence yields have been found to be strongly energy dependent, but the extent of compensation provided by CK transitions at different energies is adjusted in such a way so as to make the average L shell fluorescence yields independent of the incident photon energies. Oz et al. [8-9] and Ertugrul [10] have reported the measurements of CK enhancement factors of some elements in the range 66 ≤ Z ≤ 92. Oz et al. report about 20-30% enhancement for L₄ and L₅ X-ray groups, while Ertugrul has reported an enhancement of about 0.93 times for Au L₃ X-rays. Sogut [11] has reported the variation of enhancement effect of CK transitions on L₃ X-rays of Ba, La & Ce compounds. He has inferred that the variation of L₃ X-rays of La and Ce compounds is more than that of Ba. The only investigation for studying the effect of CK transitions on the anisotropy of X-ray emission following Au L shell photoionization has been made by Yamaoka et al. [12]. They have observed small dilution of anisotropy of L₃ X-rays due to the CK transfer of vacancies.
These preliminary investigations show that the above-mentioned contributions in the primary vacancy distribution results in the change of the spectral distribution of the emitted X-ray line/group resulting in change in the values of different X-ray emission parameters. Moreover, it has been emphasized by Bambynek et al. [13] that detailed knowledge of radiationless transition processes is necessary for the interpretation of a large variety of measurements in nuclear and atomic physics. For example, the transition energy in nuclear electron-capture decay and the multi-polarity of internally converted nuclear $\gamma$-transitions can often be determined by measuring relative X-ray intensities and applying pertinent subshell fluorescence yields to derive primary vacancy distributions. A number of more subtle effects of nuclear origin require a precise knowledge of the properties of atomic transitions for their interpretation. One example is "internal ionization" or ejection of atomic electrons during nuclear decay, usually studied by detecting characteristic X-rays of the daughter atom in coincidence with $\beta$-particles [14].

A brief account of the various excitation and de-excitation parameters related to the L and M shell along with their to-date status has been given in the first chapter.

Accurate values of charged particle induced X-ray production cross-sections are required to analyze various experimental situations related to PIXE analysis, thin film monitoring and sample analysis of
various materials etc. If the energy of incident projectile is less than the K shell binding energy of the target element, the L shell X-rays emitted under different L-X-ray groups will be attributed by the following two factors:

1. X-rays resulting from the direct interaction of the incident charged particles with the electrons in three subshells.
2. Change in the primary vacancy distribution of the three subshells brought out by the relatively faster intra-shell Coster-Kronig (CK) transfer of vacancies

On the other hand, if the energy of the incident charged particles exceeds that of the K shell binding energy of the target element, another factor will come into play. In this case, an additional set of vacancies will originate in the different L subshells due to shift of K shell vacancies to the three L subshells. This alteration of L subshell vacancies will change the attributes of the L shell X-ray spectra resulting in the change in X-ray production cross-section. The effect of intra-shell Coster-Kronig transfer among the three subshells of the L shell and that of the inter-shell transfer of K shell vacancies to the three L subshells on the L subshell X-ray production cross-sections for three incident projectiles viz. protons, deuterons and He ions in the energy range 100 keV to 10 MeV in intermediate and high Z elements has been investigated in the chapter 2. The comparison of the X-ray production cross-sections determined using different values of subshell parameters has also been
undertaken with the available experimental data.

The values of L subshell X-ray intensity ratios for protons, deuterons and He ion are not only important for interpretations of PIXE experiments, but also help in the electron structure studies of the materials [15]. The accurate determination of these ratios for heavy elements is important for their wide use in the field of non-destructive testing, medical research and trace elemental analysis using PIXE. When the vacancies are produced on irradiation of the target of an element by charged particles, the vacancy distribution among the subshells depends upon the mechanisms of excitation of the L subshell electrons and the nature and energy of the incident particles. In the case of L and higher shells, when the Coster-Kronig channels are energetically available, the vacancies in the more tightly bound L$_1$ & L$_2$ subshells predominantly shift to L$_3$ subshell, thus making a significant alteration in the initial vacancy distribution prior to the L X-ray or the Auger electron emission. Another process that may affect the L subshell vacancy distribution is the K to L$_i$ subshell vacancy transfer (inter-shell). In the second chapter, the variation in L subshell X-ray Intensity Ratios due to Coster-Kronig & Inter-shell vacancy transfer has been studied for the X-rays induced by protons, deuterons and He ions with energies ranging from 100 keV to 10 MeV in elements with 40 $\leq$ Z $\leq$ 92.

Over the years, the work relating to the K- and L-shell ionization processes has provided good insight in to the phenomenon of X-ray
emission and the related parameters, but, very little information is available on the M-shell processes. The studies on the M-shell ionization provide more insight into the collision process [16] since it possesses five subshells, giving rise to a more complex spectra than that of the K shell or even the L shell which have one or three subshells respectively. Survey of literature shows that very little experimental and theoretical work has been carried out relating to the M X-rays and related parameters. Further, since M shell has five subshells, the alteration in vacancy distribution due to the secondary vacancy creation in various subshells is expected to play a more significant role in modification of X-ray emission parameters. The determination of M subshell X-ray production cross-sections is also more complicated in comparison to K shell and L \textsubscript{i} subshells due to subsequent processes altering the primary vacancy distribution. The contribution of all these processes has to be taken into account for accurate evaluation of the M subshell X-ray production cross-sections. In the fourth chapter, the formulation to calculate the different charged particle induced M subshell production cross-sections has been worked out and the contribution of vacancy transfer by the M subshell Coster-Kronig transitions has been studied for elements with $70 \leq Z \leq 90$ for proton induced X-ray emission.

The Calculations of Cooper and Zare [17] predict that after ionization of atomic inner shells, the vacancy state has equal population of different magnetic substates irrespective of its angular momentum i.e.
the vacancy state is non-aligned. The fluorescent X-rays emitted subsequently are, therefore, expected to be isotropic in spatial distribution and unpolarized. However, the later calculations of Flugge et al. [18] predict the other way round and show that if the angular momentum $j$ of the vacancy state produced after ionization is greater than $1/2$ (i.e. $L_3$, $M_3$, $M_4$ and $M_5$), it has unequal population of magnetic substates and is, therefore, aligned. The X-rays emitted on the decay of aligned vacancy states are expected to be anisotropic in spatial distribution and plane polarized. Similarly, when an ion collides with an atom, the ionization probability of states with $j \geq 3/2$ depends upon the orbital orientation relative to the beam direction [19]. Magnetic substates corresponding to different values of $m_j$ are differently populated. This alignment leads to anisotropic emission and polarization of X-rays. The anisotropy can influence the results of measurements of the X-ray production cross-sections in ion-atom collisions. When $L_3$ sub shell of an atom is ionized by protons with energy above the K shell binding energy of the element, the secondary processes responsible for creation of unaligned vacancies in the $L_3$ sub shell (indirect vacancies) result in the modification of the alignment related parameters, which must be corrected for in the experimental interpretations. In the chapter 5, this dilution in $L_3$ subshell vacancy alignment by processes initiated after primary ionization by protons has been estimated by calculating the Dilution Factors for some elements with $45 \leq Z \leq 53$. 