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# $L$-shell ionization of atoms and their subsequent decay by radiative and non-radiative transitions

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**Abstract.** The study of the ionization of atoms resulting in vacancies in their inner shells and the subsequent decay of the atomic-vacancy states by x-ray and Auger transitions continue to be an active area of interest. A rapid survey of the theoretical efforts to calculate the transition probabilities involving $L$-subshells in the high-$Z$ atoms is presented. A complete review of the $L_1$-subshell yields for single-vacancy atomic states obtained by various experimental techniques is included. The production of multiple vacancies in the $L$ shell and the role of the spectator vacancies in the decay process is discussed. A detailed case study of determining experimentally the number of multiple vacancies produced, and the x-ray fluorescence yields during ionization by heavy-ion bombardment is presented. It is established that the effect of spectator vacancies is to increase the x-ray fluorescence yields substantially.

**Keywords.** Aromic physics; x-ray transitions; x-ray fluorescence yields.

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## 1. Introduction

In 1972 at Atlanta, Bernd Crasemann said the following in his summary of the international conference on the inner-shell processes: 'It seems to me that the main problems related to a single inner-shell vacancy production and decay now have very nearly been solved, both experimentally and theoretically, and that we have a good basic understanding of ionization and of radiative and Auger transition probabilities and fluorescence yields.... The big challenge, I think, now lies in multiple vacancies. There, experiment has gotten ahead of theory and will have to stay ahead to provide a guide in solving some really complex and fascinating problems: collision mechanisms, transition-energy shifts, the formation of a vast array of satellite lines, and fluorescence yields in the presence of several vacancies'. I would like to take you through a guided tour, through the various stages of our understanding during the last 25 years since these remarks were made. It could be cast in the form of an autobiographical sketch of my own interests, but I will resist the temptation and just let you know that my nuclear physics studies required the knowledge of x-ray fluorescence yields of $L$ subshells and that was how I got interested in this subject. It is safe to generalize that 'the original impetus for the study of the inner shell vacancy atomic states has its origins in the interpretation of a variety of experiments in nuclear and atomic physics.' A precise knowledge of atomic transitions, their transition probabilities and branching ratios became crucial as both theoretical and experimental techniques have advanced. In addition, studies of the inner-shell ionization by proton, electron and photon impact help us to test the various theories of ionization.

Most of the experimental $L$-shell studies concentrate on the measurement of the x-rays emitted following the ionization. When a vacancy is created in an inner-shell, such as $K$, $L$ or $M$ shell, it is quickly filled up by an electron from an outer shell. The excess energy in this transition is delivered as a photon or an Auger electron. The former we refer to as a radiative transition and the latter as non-radiative transition. The Auger process leaves the atom immediately, most of the time, in a double vacancy state, because one electron leaves the atom while another fills the vacancy. Figuritively speaking an inner-shell vacancy bubbles up into an outer shell. Since we will be talking about $L$-shell, with its subshells, we can distinguish those non-radiative transitions that promote the inner shell vacancy into one of the higher subshells of the same shell. These are referred to as Coster–Kronig transitions. There is also a possibility that an initial vacancy can lead to two vacancies in the subshells of the same shell. Such transitions are called super Coster–Kronig transitions. The probabilities of these atomic transitions are expressed in terms of x-ray fluorescence yields $\omega_i$, Coster–Kronig yields $f_{ij}$ and the fractional x-ray transition rates $F_x$, and Auger yield $a_i$. For example $L_1$-subshell x-ray fluorescence yield is defined as the number of $L_1$-subshell characteristic x-rays emitted per $L_1$-subshell vacancy present in a sample element. Both the experimental and theoretical efforts are directed towards obtaining these yields. Since the advent of semiconductor detectors for detecting x-rays in mid-sixties, the experimentalists heavily concentrated on measuring x-ray yields.

The theoretical and experimental work until the early seventies has been thoroughly summarized in two comprehensive review articles [1]. Progress in the measurement of $L$-subshell x-ray and Coster–Kronig yields has been reviewed in several articles subsequently [2, 3].

## 2. $L$-subshell yields of singly ionized atoms

The methods used for measuring the $L$-subshell yields can be divided broadly into two categories, i.e. the singles spectrum method and coincidence methods, to use the language of the experimentalist.

Measurements are scarce for light and medium heavy elements ($Z < 47$). A crystal spectrometer is used to detect the x-rays. Vacancy production is achieved by the impact of electrons and the number of vacancies in each subshell is taken from theoretical estimates of the ionization cross sections [4]. In principle a radioactive source can be used too, as demonstrated in the case of $Z = 45$ [5].

Radioactive decay has been the main source of innershell vacancies and these experiments for measuring $L$-shell yields began almost thirty years ago. The creation of inner shell vacancies takes place copiously in the processes of electron capture decay, internal conversion, and with less frequency in some higher order processes such as internal ionization and shake off and shake up mechanisms. The number of primary $L$ vacancies created is estimated from known theoretical probabilities for these processes.

For elements with high $Z$, the most widely used method is the ($K_\alpha$) – ($L$ x-ray) coincidence technique. Since a $K_{\alpha 1}$ x-ray emitted in the $K$ vacancy decay signals the creation of an $L_3$ vacancy and a $K_{\alpha 2}$ x-ray signals the $L_2$ vacancy, the measurement of $L$ x-rays in coincidence with these $K$ x-rays permit the determination of $\omega_3$, $\omega_2$ and $f_{23}$. The $L_1$ subshell yields are not accessible by similar techniques because $K$ x-rays do not postulate $L_1$ vacancies. However, the internal conversion process in the radioactive decay results in a preponderance of $L_1$ vacancies in certain cases and these sources were used to measure the $L_1$ subshell yields, $\omega_1$, $f_{12}$ and $f_{13}$, after correcting for the presence of $L_2$ and $L_3$ vacancies. Similar opportunities to measure the $L_1$ subshell yields are available when radioactive decay is due to electron capture from $K$ or $L$ shells. In both these situations the theoretical estimates of internal conversion coefficients and orbital electron capture probabilities have to be used in estimating the primary vacancy distribution of $L$ subshell vacancies. In suitable cases where conversion electrons of a specific subshell can be resolved and $L$ x-rays characteristic of each subshell also can be resolved, it is possible to measure a complete set of $L$ shell yields [6].

In principle, measurements of singles spectrum can permit the determination of all the $L$ subshell yields, provided spectra for different known initial vacancy distributions are available. Such measurements were made in the case of a few radioactive decay sources [1]. A breakthrough in such measurements was achieved by using the continuously tuneable, monochromatized synchrotron radiation [7]. Vacancy production by photoionization has certain advantages over other methods. The ionization of a particular subshell can be simply switched on and off by tuning the energy of the primary photons across the absorption edge of the corresponding subshell. When the energy of the primary photons is tuned to atleast three energies each just above the threshold of an $L$-subshell the number of created vacancies is strongly varied. If at each energy the emitted $L$ x-rays (or Auger electrons) are observed with sufficient resolution to separate the contributions from different $L$ subshells, all $L$-subshell yields can be determined. The theory of inner-shell photoionization is well understood [8]. The subshell ionization cross sections are known with comparatively high accuracy and comprehensive tabulations of relativistic Hartree–Slater (RHS) cross sections are available [9]. Several measurements by the synchrotron photoionization method have been performed already [10, 11].

## 3. Theoretical estimates of $L$ subshell yields

Theoretical values of Auger and x-ray transition rates have been calculated with considerable success over the last two decades, even though some problems remain unresolved. Most atomic inner-shell transitions are characterized by high transition energies and involve tightly bound electrons. In the decay of these excited atoms particle emission dominates when it is energetically possible except for $K$ shell of heavy elements. For most atomic transitions the number of Auger and Coster–Kronig channels is very large and radiationless rates are high. Consequently x-ray emission contributes relatively less to the total width. Independent particle models are usually employed to perform atomic inner-shell calculations [1]. There are other sophisticated methods such as diagramatic many-body perturbation theory [12], close-coupling approximation [13] and complex rotation method [14, 15], but they are limited to a few light atoms due to their intrinsic complexity. For highly charged ions with many open shells, effects of both relativity and

**Table 1.** $L_1$ subshell x-ray fluorescence yields, $\omega_1$

| Z/Element | Experimental | | | | Estimates | Theory | |
|---|---|---|---|---|---|---|---|
| | Radioactive decay | Synchrotorn photoionization | Electron impact | Proton impact | Krause (1979) | Chen, Crasemann and Mark (1981) Chen (1991) | Rao and Chen (1996) |
| 56 Ba | | | | | 0.052 | 0.0538 | |
| 57 La | | | | 0.642 ± 0.0077 | | | 0.0586 |
| 59 Pr | 0.060±0.007 | | | | 0.061 | | 0.0671 |
| 60 Nd | 0.0721±0.007 | | | 0.0728 ± 0.0087 | 0.064 | 0.0678 | |
| 62 Sm | | 0.067±0.010 | | | 0.071 | | 0.0807 |
| 63 Eu | 0.06±0.02 | | | | 0.075 | 0.0793 | |
| 66 Dy | | | | 0.109±0.013 | | | 0.0939 |
| 67 Ho | | | | | 0.094 | 0.0964 | |
| 70 Yb | 0.131±0.013 | | | | 0.112 | 0.116 | |
| | 0.126±0.010 | | | 0.136±0.016 | | | |
| 71 Lu | | | | 0.135±0.016 | | | 0.124 |
| 72 Hf | | 0.125±0.008 | | | 0.128 | | 0.129 |
| 73 Ta | 0.140±0.012 | | 0.144±0.014 | | 0.137 | | 0.135 |
| | 0.15±0.02 | | | | | | |
| 74 W | | 0.130±0.008 | 0.123±0.012 | | 0.147 | 0.137 | |
| 75 Re | 0.095±0.020 | | 0.111±0.011 | | 0.144 | | 0.114 |
| 77Ir | 0.152±0.014 | 0.139±0.008 | 0.126±0.013 | | 0.120 | | 0.108 |
| | 0.16±0.014 | | | | | | |
| 78 Pt | 0.124±0.012 | 0.130±0.008 | 0.112±0.012 | | 0.114 | | 0.105 |
| 79 Au | 0.098±0.020 | 0.137±0.008 | 0.121±0.012 | | 0.107 | | 0.0985 |
| 80 Hg | 0.093±0.007 | | | | 0.107 | 0.082 | |
| | 0.132±0.018 | | | | | | |
| 81 Tl | 0.121±0.014 | | | | | | |
| | 0.07±0.02 | | | | 0.107 | | 0.0988 |
| 82 Pb | 0.104±0.019 | 0.145±0.009 | 0.135±0.014 | | 0.112 | | 0.102 |
| | 0.09±0.02 | 0.16±0.04 | | | | | |
| 83 Bi | 0.095±0.05 | | 0.134±0.013 | | 0.117 | 0.0988 | |
| 90 Th | 0.108±0.022 | | | | 0.161 | 0.140 | |
| 92 U | 0.21±0.04 | | | | 0.176 | 0.150 | |
| 96 Cm | 0.25±0.06 | | | | 0.228 | 0.180 | |

**Table 2.** The sources for experimental values listed in table 1 grouped according to the mechanism of $L$ vacancy production.

| $Z$ | *Radioactive decay* |
|---|---|
| 59 | P Venugopala Rao, *Bull. Am. Phys. Soc.* **35**, 1154 (1990) |
| 60 | M V Pantazopoulous and P Venugopala Rao, *Bull Am. Phys. Soc.* (1986) |
| 62 | R Stötzel, U Werner, M Sarkar and W Jitschin, *J. Phys.* **25**, 2292 (1992) |
| 63 | V R Veluri and P Venugopala Rao, Z. Physik **A280**, 317 (1980) |
| 70 | M I Marquis, M C Martins, F Parente, J G Ferreira, *J. Phys.* **B26**, 1263 (1993) |
| | L A McNelles, J L Campbell, J S Yeiger, R L Graham and J S Merritt, *Can. J. Phys.* **53**, 1349 (1975) 73 |
| | P Venugopala Rao, *Bull. Am. Phys. Soc.* (May 1989) |
| | P A Indira, I J Unus, R Stephen Lee and P Venugopala Rao, *Z. Phys.* **A290**, 245 (1979) |
| 75 | L Salguerio, M T Ramos, M L Escrivao, M C Martins and J G Ferreira, *J. Phys.* **B7**, 342 (1974) |
| 77 | M I Marquis, M C Martins, F Parente and J G Ferreira, *J. Phys.* **B26**, 1263 (1993) |
| | P A Indira, J M Palms and P Venugopala Rao, *Z. Phys.* **A284**, 33 (1978) |
| | L Salguerio, M T Ramos, M L Escrivao, M C Martins and J G Ferreira, *J. Phys.* **7**, 342 (1974) |
| 78 | M I Marques, M C Martins and J G Ferreira, *Phys. Scr.* **32**, 107 (1985) |
| 79 | L Salguerio, M T Ramos, M L Escrivao, M C Martins and J G Ferreira, *J. Phys.* **B7**, 342 (1974) |
| 80 | P Venugopala Rao, *Bull. Am. Phys. Soc.* **37**, 1119 (1992) |
| | M I Marques, M C Martins and J G Ferreira, *Phys. Scr.* **32**, 107 (1985) |
| 81 | M I Marques, M C Martins and J G Ferreira, *Portugal. Phys.* **11**, 9 (1980) |
| | R E Wood, J M Palms and P Venugopala Rao, *Phys. Rev.* **187**, 1497 (1969) |
| 82 | Mustafa Tan, R A Braga, R W Fink and P Venugopala Rao, *Phys. Scr.* **25**, 536 (1982) |
| | P Venugopala Rao, J M Palms, R E Wood, *Phys. Rev.* **A3**, 1568 (1971) |
| 83 | R W Fink and H U Freund, *Phys. Rev.* **C3**, 1701 (1971) |
| | A Maio, J P Riberio, A Barroso and F B Gil, *J. Phys.* **B8**, 1216 (1975) |
| 90 | L Salguerio, M T Ramos, M L Escrivao, M C Martins and J G Ferreira, *J. Phys.* **B7**, 342 (1974) |
| 92 | J C McGeorge, D W Nix and R W Fink, *Z. Phys.* **255**, 335 (1972) |
| 96 | J C McGeorge and R W Fink, *Z. Phys.* **250**, 293 (1972) |
| | *Photoionization* |
| 72–82 | U Werner and W Jitschin, *Phys. Rev.* **A38**, 4009 (1999) |
| 82 | A Kodre, M Hribar, B Aljec and J Pahor, *Z. Phys.* **A290**, 245 (1981) |
| | *Electron impact* |
| 73–83 | J Q Xu, *Phys. Rev.* **A43**, 4771 (1991) |
| | *Proton impact* |
| 57–71 | J Q Xu and X J Xu, *Phys. Rev.* **A49**, 2191 (1994) |

configuration interaction may be quite important. The multiconfiguration Dirac-Fock method is currently the most general scheme to incorporate these effects and hence it becomes the most widely used method in calculating the transition rates for highly charged ions [16, 17].

In the calculation of these transition rates, the creation of a hole state is assumed to be separate from the decay process. In this two-step process, the post-collision interaction between the primary electron and Auger electron is neglected. The coupling between electron and photon continua is usually neglected. Hence the Auger and x-ray transition

**Table 3.** Coster–Kronig, Auger and radiative widths (eV) and yields for $L_1$ vacancy states.

| Z | Widths | | | | Yields | | | |
|---|---|---|---|---|---|---|---|---|
| | $CK_{12}$ | $CK_{13}$ | Auger | Radiative | Total | $f_{12}$ | $f_{13}$ | $\omega_1$ |
| 57 | 0.760 | 1.232 | 1.524 | 0.219 | 3.735 | 0.203 | 0.330 | 0.0586 |
| 59 | 0.800 | 1.242 | 1.571 | 0.260 | 3.873 | 0.207 | 0.321 | 0.671 |
| 62 | 0.814 | 1.349 | 1.641 | 0.334 | 4.138 | 0.197 | 0.326 | 0.0807 |
| 66 | 1.062 | 1.615 | 1.722 | 0.456 | 4.855 | 0.219 | 0.333 | 0.0939 |
| 71 | 0.978 | 1.841 | 1.817 | 0.654 | 5.290 | 0.185 | 0.348 | 0.124 |
| 72 | 0.962 | 1.936 | 1.839 | 0.701 | 5.438 | 0.177 | 0.356 | 0.129 |
| 73 | 0.986 | 1.978 | 1.860 | 0.752 | 5.576 | 0.177 | 0.355 | 0.135 |
| 75 | 1.002 | 3.768 | 1.901 | 0.861 | 7.532 | 0.133 | 0.500 | 0.114 |
| 77 | 0.871 | 5.295 | 1.947 | 0.982 | 9.095 | 0.0958 | 0.582 | 0.108 |
| 78 | 0.905 | 6.013 | 1.968 | 1.048 | 9.934 | 0.0911 | 0.605 | 0.105 |
| 79 | 0.894 | 7.333 | 1.992 | 1.117 | 11.336 | 0.0789 | 0.647 | 0.0985 |
| 81 | 0.715 | 8.810 | 2.036 | 1.267 | 12.828 | 0.0557 | 0.687 | 0.0988 |
| 82 | 0.784 | 9.038 | 2.057 | 1.349 | 13.228 | 0.0593 | 0.683 | 0.102 |

rates are calculated independently. The frozen orbital approximation is frequently invoked by assuming the orthogonality between the initial and final one-electron wave functions. This assumption then leads to the transition matrix elements which depend only on the wavefunctions of the active electrons. An excellent review and summary of the calculation of x-ray and Auger transition rates can be found in the review article by Chen [18].

Comparison with theoretical calculations shows very good agreement for the $L_2$ and $L_3$ subshell yields [3]. Agreement between theory and experiment is not very good in the case of $L_1$ subshell. As pointed out by Jitschin, the Coster–Kronig yields for this subshell appear to be overestimated by the theory. These are quantities which are indirectly measured in all these experiments. It is the x-ray fluorescence yield which is directly measured in many cases. The existing experimental data for $\omega_1$ is summarized in the following three tables. Table 1 lists all the theoretical [19, 20] and experimental results. The values listed under the column 'Estimates' are taken from the semi-empirical fit by Krause [21]. This set obviously requires some revisions in view of the new set of experimental and theoretical values available now. Table 2 lists all the sources from which this data is gathered. Table 3 lists the theoretical values of widths and yields for the subshell recently reported by Rao and Chen [20].

The experimental data confirm the characteristic trend of the theoretical values. However in the region of $Z = 74$ to 79, where additional Coster–Kronig transitions become energetically possible, the agreement between theory and experiment needs to be improved. The values obtained from radioactive-decay and proton-impact sources follow the trend of the theoretical values. The results obtained from both photoionization and electron impact sources indicate an increasing trend in the values as $Z$ increases, in a region ($Z = 74$ to 79) where the theoretical estimates show a decreasing trend. Experiments that can lead to more accurate determination of $\omega_1$, are very desirable.

**Table 4.** Average $L$ x-ray yields from double $L$-vacancy states.

| $Z$ | Measured quantity | Method | Increase over single vacancy yields |
|---|---|---|---|
| 49 | $(\omega_{LL})/(\omega_{eL}) = 1.16 \pm 0.10$ | ($Lx$–$Lx$) and ($Lx$-conversion electron) coincidences [22] | 14% |
| 73 | $(\omega_{LL})/(\omega_{K\alpha L}) = 1.31 \pm 0.09$ | ($Lx$–$Lx$) and ($Lx$–$K\alpha$) coincidences [23] | 33% |
| | $\omega_{LL} = 0.275$ (estimated from the measured values of $\omega_{L_iL_i}$) | $K$ Auger electron-$Lx$ coincidences [24] | <10% |
| 80 | $(\omega_{LL})/(\omega_{K\alpha L}) = 1.20 \pm 0.08$ from the decay of Au 198 | ($Lx$–$Lx$) and ($Lx$-$K\alpha$) coincidences [25] | 20% |
| 80 | $(\omega_{LL})/(\omega_{K\alpha L}) = 1.17 \pm 0.07$ from the decay of Tl-204 | ($Lx$-$Lx$) and ($Lx$-$K\alpha$) coincidences [25] | 17% |
| 81 | $(\omega_{LL})/(\omega_{K\alpha L}) = 1.15 \pm 0.07$ from the decay of Hg-203 | ($Lx$-$Lx$) and ($Lx$-$K\alpha$) coincidences [25] | 15% |
| 82 | $\omega_{LL} = 0.410 \pm 0.029$ | $K$ Auger electron-$Lx$ coincidence [26] | 10% |

$\omega_{LL}$ is the average $L$ x-ray yield per vacancy from the double $L$-vacancy states created during the $K$ Auger electron emission. $\omega_{K\alpha L}$ is the average $L$ x-ray yield per vacancy from the single $L$-vacancy states created during the emission of $K_\alpha$ x-ray emission.

## 4. $L$ x-ray emission from double $L$-vacancy atoms

$K$-$LL$ Auger transitions leave the atoms in states of two $L$ shell vacancies. Their decay proceeds partly through a cascade of transitions resulting in the emission of two $L$ x-rays. By determining the rate of coincidences between these two $L$ x-rays, the $L$ x-ray emission probability of the double $L$-vacancy states is obtained. Table 4 lists the available average $L$ x-ray yields from double $L$-vacancy states measured using the radioactive sources. These values are compared with the estimated yields derived using single-vacancy atomic-state transition probabilities.

Two possible explanations can be offered for the 15 to 20 per cent increase in the average $L$ x-ray yield from the double $L$-vacancy states: (1) The presence of the spectator vacancy can alter the sensitive Coster–Kronig transition probabilities and can indirectly alter the radiative yields. (2) There is a possibility that more than two $L$ vacancies can be created in the $K$ Auger electron emission because of correlation effects. This would increase the ($L$ x-ray)–($L$ x-ray) coincidence rates. For example at $Z = 80$, if the 15% increase in the observed value is attributed to the presence of $KLLL$ transitions, approximately 3% of the total $K$ Auger electron emission may include $KLLL$ Auger transitions.

## 5. Multiple-vacancy atomic states and their decay

The effects of multiple ionization which are the norm rather than exception in heavy-ion induced ionization, are not well understood. The presence of multiple ionization and its effect on $K$-shell vacancy state decay was recognized early. The energy shifts and the changes in the transition rates of $K$ x-rays due to the presence of the spectator vacancies are easily identified. The situation is different in the case of $L$ x-ray spectra. The resolution of $L$ x-ray detectors, even with the state of the art techniques, is not sufficient to identify the transitions from the multiply ionized states. There is a dearth of theoretical know-how that can predict the x-ray yields from multiple vacancy states.

One of the most powerful descriptions of the inner-shell ionization by charged particles was developed by Brandt and coworkers [27–31]. It was formulated in the framework of the perturbed stationary state (PSS) theory which is based on the first Born approximation. The most recent version of this theory (ECPSSR) includes the effects of Coulomb deflection of the projectile on the target nucleus, the distortion of the state of the atomic electron (change of the binding energy and polarization of the electron cloud), the relativistic nature of the electron, and the energy loss of the projectile during the ionization process.

One of the questionable points of this theory is the binding energy correction. The fact that the change in the binding energy of the inner-shell electron due to the presence of the projectile is calculated using the stationary perturbation theory means that full adiabaticity of the perturbed atomic states is assumed. This is valid only at low collision velocities where the electron can adjust its state to the eigenfunction of the total Hamiltonian at every moment. The effect of non-adiabaticity increases with increasing collision velocity. Sarkadi [32, 33] has shown that the effect is comparable to that of polarization and electron capture.

Theoretical models, which predict the inner-shell ionization probabilities have been tested extensively using the measured $K$ x-ray production cross sections. On the other hand comparison between theory and experiment could not be carried out with the same confidence in the case of $L$-shell ionization particularly the heavy-ion induced ionization.

The multiple vacancy production in the $L$-shell ionization caused by charged particles were noted by several workers. Olsen *et al* [34] studied the $L$ x-ray spectra from proton, alpha-particle, and oxygen bombardment of Sn. They have established the presence of the satellite transitions resulting from multiple $M$-shell vacancies. They noted that the relative intensities of these satellites are of the correct order of magnitude for a direct simultaneous Coulomb ionization mechanism. Bissinger *et al* [35] studied the Au $L$ x-ray spectra produced by $^{16}O$ beam of 12–50 MeV. Their observed energy shifts indicate that multiple ionization is occurring. Burkhalter *et al* [36] have observed satellite peaks, belonging to the $L_\alpha$- and $L_{\beta 1}$-lines of Ge bombarded by $^4He$. Using the Hartree-Fock-Slater calculations, they found that energies of these peaks correspond to the $L_\alpha$- and $L_{\beta 1}$-satellite transitions in which multiple $3d$-vacancies are present. They also observed the germanium satellite lines, induced by $^{20}Ne$, which have energies corresponding to multiple $(3d)^n$ plus $N$-shell vacancies where $n$ has values of 4, 5 and 6. Li *et al* [37] have compared the experimental ratios, $\sigma_{L3}/\sigma_{L2}$ and $\sigma_{L1}/\sigma_{L2}$ for heavy elements ($Z_2 = 73$–92) bombarded by $^1H$, $^4He$, $^{12}C$, $^4He$ and $^{16}O$ ($Z_1 = 1$ to 8) with the predictions of the plane-wave Born approximation (PWBA), the semiclassical (SCA) and binary encounter (BEA) approximations. These ratios are lower than the theoretical predictions when the projectile energies are below 2 MeV/u and are higher for heavy projectiles. To test if these deviations are due to multiple ionization of the outer shells $(M, N, O, \ldots)$, they compared the experimental ratios of $L_1/L_\alpha$, $L_{\beta 2,15}/L_\alpha$ and $L_{\beta 1}/L_{\gamma 1}$ to the theoretical values obtained from Scofield's work [38] and concluded that the simultaneous $L$-plus $M$-shell, or $L$-plus $N$-shell multiple ionization effects are small.

Sarkadi and Mukoyama [24] noted the presence of multiple ionization in the case of heavy ion-bombardment in their studies of the $L$-shell ionization of gold by proton, alpha particle, carbon, nitrogen, oxygen projectiles in the energy range of 0.4 to 3.4 MeV. Rao *et al* [39] investigated the $L$-shell ionization in Ho, Er, Tm, W, Tl, Pb, and Bi by 20 MeV carbon ions and 37.5 MeV silicon ions. They have attributed the observed energy shifts of the $L_\alpha, L_{\gamma 1}$ and $L_{\gamma 4}$ x-rays to the presence of $M$-shell spectator vacancies. $L_\alpha/L_\gamma$ intensity ratios were compared with the theoretical predictions of the PWBA and BEA using single-vacancy $L$-shell yields. The disagreement with theories for $Z > 74$ was considered to be an indication of the multiple ionization.

Bhattacharya *et al* [40] measured $L$-subshell ionization cross sections of 0.9 to 1.8 MeV and concluded that the PWBA (with all the corrections included) does not agree well with the experiment.

Jitshin *et al* [41] have given extensive comparisons between existing ionization theories and experimental data for the $L$-subshell ionization cross section ratios in gold bombarded by protons, alpha particles, lithium, berillium, carbon, oxygen, silicon, and sulphur ions with energies ranging from 0.23–6.7 MeV/u and noted considerable multiple ionization of higher shells.

Jesus *et al* [42] reported experimental proton-, deutron- and alpha-induced $L$ x-ray production absolute cross sections for gold, lead and uranium in the incident projectile energy range 0.2–0.9 MeV/u. The intensity ratios of different $L$ x-ray transitions produced by the same projectile seem to show that the usually accepted single-vacancy state values of $L$-shell yields are unable to produce agreement with theory.

It is clear from this brief survey that the effects of multiple ionization could be significant in the heavy-ion induced $L$-shell ionization. The most obvious effects are (a) the shifts in the energies of $L$ x-ray lines due to the presence of the satellite lines and (b) the change in the values of $L$-shell yields.

Saris and Onderdelinden [43] have shown experimentally that $\omega_{L2,3}$ of the argon atom increases by a factor of two as the incident energy of the projectile $Ar^+$ is doubled. The high degree of ionization created in the atom obviously diminishes the Auger transition probability and enhances the radiative probability. Larkins [44] introduced a method to determine the fluorescence yield of the $2p$ subshell in the defective atom. As the number of spectator vacancies present in the $3p$ subshell of the atom increased, the value of $\omega_{L2,3}$ could change by more than an order of magnitude.

The observation of changes in energies is difficult because individual satellite lines were not resolved with the Si(Li) detectors or even crystal spectrometers. Instead a group of satellite lines corresponding to each of the diagram lines appears in a single broadened peak which represents the envelope of the photo peaks of the constituent lines. The centroid of this group shifts to an energy higher than that of the diagram line. The increase in energy is referred to as 'energy shift'. This energy shift is obviously a measure of the state of ionization of the atom. In their work on alpha-particle induced ionization, Olsen *et al* [34] have noted the presence of satellites in $L_{\beta 6}$, $L_{\beta 2,15}$, $L_{\gamma 1}$ and $L_{\gamma 2,3}$ x-rays of tin. Centroid energy shifts in gold lines induced by oxygen-ion bombardment have been noted by Bissinger *et al* [35]. Rao *et al* [39] have also observed energy shifts in $L$ x-rays from high $z$ targets bombarded by carbon and silicon ions. Schonfeldt [45] has measured energy shifts of the projectile lead $L$ x-rays resulting from bombarding a variety of targets. He deduced the number of spectator vacancies in the Pb atoms by comparing the energy shifts with the calculated shifts.

Uchai *et al* [46] reported the results of an investigation of $L$ x-ray spectra from seven elements in the $70 \leq Z \geq 90$ range. Thin metal targets were bombarded with 107 MeV $Ag^{6+}$. From the observed $L$ x-ray energy shifts and $L$ x-ray emission rates, the $L$-shell ionization cross section ratios were deduced by adopting procedures that permit an estimation of the degree of multiple ionization and the values of the x-ray and Coster-Kronig yields in the presence of spectator vacancies. They showed that the branching ratios of $L$-subshell characteristic x-ray transitions are substantially altered by the presence of spectator vacancies. The observed $L$ x-ray intensity ratios are consistent with Scofield rates, provided that these rates are multiplied by simple scaling factors. They deduced that the heavy-ion bombardment resulted in about 7 vacancies in the $M$ shell, about 20 vacancies in the $N$ shell and about 7 vacancies in the $O$ shell in addition to the single vacancy in the $L$ shell. They have also established that the highest energy line in the $L_\gamma$ series can be identified as an $L_1{-}O_{4,5}$ transition proceeding in the presence of numerous multiple vacancies.

The multiple vacancies in the $M$ and higher shells created during the ion-atom collision may not be all filled prior to radiative filling of the $L$ vacancy, and therefore act as spectators during $L$ x-ray emission As a result, the binding energies of all levels increase because of less screening of the nuclear charge. Because the binding energies of the inner shells shift more than those of the outer shells, the difference in binding energies between two particular levels widens with a consequent increase in the energy of the emitted x-ray. The energies of 10 $L$ x-rays ($L_\iota$, $L_{\alpha 1}$, $L_{\alpha 2}$, $L_{\beta 1}$, $L_\eta$, $L_{\gamma 1}$, $L_{\gamma 2}$, $L_{\gamma 3}$, $L_{\gamma 4}$ and $L_{\gamma 4'}$) are calculated for the seven elements (Yb, Ta, W, Pt, Au, Pb and Th) studied in this work. These energies are found with a Dirac-Fock computer program [39] as differences of configuration-average total energies for various configurations up to 11 spectator vacancies in the $M$ shell. The energy shift of an $L$ x-ray for a particular configuration is determined by subtracting from its transition energy the corresponding value for the configuration with no $M$ vacancies. The observed energy shifts in eV for the case of gold are 204 for $L_\iota$, 169 for $L_\alpha$, 212 for $L_{\beta 1}$, 577 for $L_{\gamma 1}$, 546 for $L_{\gamma 2,3}$, 874 for $L_{\gamma 4,4'}$.

An average energy shift can be obtained by summing the energy shifts of all configurations and dividing by the sum of the $M$ vacancies. For the Au $L_\alpha$ line, for example the calculated average energy shift per $M$ vacancy is 26 eV. From this value and the experimentally observed shift of 169 eV, it is concluded that approximately seven $M$ shell vacancies (denoted as $V_M$) are present in addition to the single $L$ vacancy during the $L$ x-ray emisson in Au. The energy shifts due to vacancies in $N$ and $O$ shells are neglected because the average shifts per vacancy for the Au $L_\alpha$ line are only 0.5 and 0.25 eV, respectively.

The measured intensity ratios characteristic of transitions to the $L_1$, $L_2$ and $L_3$ subshells are compared with Scofield values. The $L_\alpha/L_\iota$ ratios – for which both transitions filling the $L_3$ vacancy originate from the $M$ shell are only slightly smaller than the Scofield values, an observation which was also made earlier by Sarkadi and Mukoyama [24]. The situation is quite different with the branching ratios for transitions from different shells. The measured $L_{\beta 1}/L_{\gamma 1}$ ratios are about 60% higher than the Scofield values. Qualitatively, this result implies that more vacancies are present in the $N$ shell than in the $M$ shell. The $L_{\gamma 2,3}/L_{\gamma 4,4'}$ ratios similarly suggest that fewer vacancies present in the $O$ shell than in the $N$ shell.

**Table 5.** $L_1$ subshell x-ray fluorescence yields in the presence of spectator vacancies.

| Z/Element | Population of spectator vacancies | | | Yields with spectators | Yields with no spectators: Estimates Krause (1979) | Yields with no spectators: Theory Chen, Crasemann and Mark (1981) |
|---|---|---|---|---|---|---|
| $L_1$ subshell x-ray fluorescence yields in the presence of spectator vacancies. | | | | | | |
| 70 Yb | 9 | 24 | 6 | 0.191 | 0.112 | 0.116 |
| 73 Ta | 8 | 20 | 5 | 0.186 | 0.137 | 0.135 |
| 74 W | 7 | 21 | 6 | 0.196 | 0.147 | 0.137 |
| 78 Pt | 7 | 20 | 7 | 0.229 | 0.114 | 0.105 |
| 79 Au | 7 | 20 | 7 | 0.236 | 0.107 | 0.0985 |
| 82 Pb | 7 | 21 | 8 | 0.301 | 0.112 | 0.102 |
| 90 Th | 5 | 15 | 9 | 0.141 | 0.161 | 0.141 |
| $L_2$ subshell x-ray fluorescence yields in the presence of spectator vacancies. | | | | | | |
| 70 Yb | 9 | 24 | 6 | 0.410 | | 0.222 |
| 73 Ta | 8 | 20 | 5 | 0.405 | | 0.258 |
| 74 W | 7 | 21 | 6 | 0.418 | | 0.270 |
| 78 Pt | 7 | 20 | 7 | 0.476 | | 0.321 |
| 79 Au | 7 | 20 | 7 | 0.479 | | 0.334 |
| 82 Pb | 7 | 21 | 8 | 0.526 | | 0.373 |
| 90 Th | 5 | 15 | 9 | 0.601 | | 0.479 |
| $L_3$ subshell x-ray fluorescence yields in the presence of spectator vacancies. | | | | | | |
| 70 Yb | 9 | 24 | 6 | 0.392 | | 0.210 |
| 73 Ta | 8 | 20 | 5 | 0.384 | | 0.343 |
| 74 W | 7 | 21 | 6 | 0.391 | | 0.255 |
| 78 Pt | 7 | 20 | 7 | 0.434 | | 0.306 |
| 79 Au | 7 | 20 | 7 | 0.438 | | 0.320 |
| 82 Pb | 7 | 21 | 8 | 0.473 | | 0.360 |
| 90 Th | 5 | 15 | 9 | 0.535 | | 0.463 |

To estimate the vacancies in the $N$ and $O$ shells, a scaling procedure in which the Scofield rates are multiplied by a factor to take the energy shifts [45] into account and by an appropriate scaling factor $(n_s - V_s)/n_s$ to account for the missing electrons [44], where $n_s$ is the number of electrons in the neutral atom and $V_s$ is the number of spectator vacancies in the multiply ionized atom for the $s$ shell ($s = M.N.O\ldots$). For gold cited above, where seven $M$ vacancies are estimated, the measured $L_{\beta 1}/L_{\gamma 1}$ ratio yields an estimate of 20 $N$ vacancies ($V_N$) through the application of this scaling procedure. In turn this $V_N$ value and the measured $L_{\gamma 2,3}/L_{\gamma 4,4'}$ ratio imply seven $O$-shell vacancies for Au. For gold $n_M = 18$, $n_N = 32$ and $n_O = 18$.

The scaling procedure used above to estimate the number of missing electrons or vacancies, is applied to the available theoretical non-radiative and radiative transition rates for singly ionized atoms, and the $L$-shell x-ray fluoresence yields for atoms with multiple vacancies. Table 5 lists these values for the three subshells along with the values for the single-vacancy states taken from Krause's semi-empirical fit [21] and the theoretical calculations by Chen *et al* [19]. It is quite clear that the presence of several spectator vacancies resulted in substantial increase of the x-ray fluorescence yields in almost all the cases studied. To date Uchai's work [48] is the most complete treatment of multiple ionization effects on the $L$ shell vacancy state decay.

## 6. Conclusion

The big challenge to understand the effect of multiple vacancies on the $L$-subshell transitions is under way. It is firmly established that the spectator vacancies alter not only the energies of the diagram lines but also the transition rates. Only scaling procedures are available now to estimate the transition rates for multiple vacancy states and theoretical procedures to calculate them directly are yet to be formulated. The experimentalists are still ahead of theory.

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