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L-shell Ionization of Sn and Gd by 20–100 keV Electron Impact

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Abstract

Measurements have been made of the relative X-ray production cross-section ratios L_α/L_γ, L_α/L_β and L_α/L_l using electrons of energy from 20 to 100 keV incident on thin targets of tin and gadolinium. The experimental ratios obtained are compared with theoretical values. Modification of these ratios due to the formation of double-vacancy atomic states has been calculated, but this effect on its own is not sufficient to account for the discrepancy between the L_α/L_l theoretical and experimental results for tin.

1. Introduction

In recent years much attention has been focused on L-shell ionization by electron impact. Experimental data for the high Z elements Au, Pb and Bi are quite extensive (Schlenk *et al.* 1977; Genz *et al.* 1979; Hoffmann *et al.* 1979; Pálinkás and Schlenk 1980; Shima *et al.* 1981), covering a wide range of electron energies. Despite the energy loss associated with thick targets, two measurements, one relative and one absolute, of the L-shell ionization cross sections of tungsten have been made at electron energies near the L-shell threshold (Chang 1979; Salgueiro *et al.* 1980). Hippler *et al.* (1981) overcame these energy loss problems by measuring the L-shell ionization cross sections using a gas target, specifically argon, at similar electron energies.

Two areas have been of particular interest in studying L-shell ionization by electron impact:

(1) the electron energy dependence of the X-ray production cross-section ratio L_α/L_β;

(2) the Z dependence of the emission rates of the L_α to L_l X-rays.

Genz *et al.* (1979) reviewed the L_α/L_β data for Au, Pb and Bi in the light of the theory of Scofield (1978) and, although the discrepancies between data and theory are attributed to multiply ionized atomic states, no attempt was made to determine how these states affect the ratio. As both the L_α and L_l X-rays result from transitions to the L3 subshell, the ratio of their intensities should be independent of the excitation process, provided that multiple ionization does not occur. Johnston *et al.* (1981) reviewed data for the X-ray emission ratio L_α/L_l for various ionization processes for a range of elements with target atomic number Z between 63 and 90.

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For Z below 73, the data arising from ionization by particle bombardment fell below both the theoretical predictions of Scofield (1974) and the X-ray fluorescence data. Consequently Johnston *et al.* proposed that, for atomic excitation following electron and proton bombardment, multiple ionization significantly alters the L_α/L_l ratio for Z below 73. Again no estimate of the extent of this effect was given.

In the present paper, X-ray production cross-section ratios L_α/L_l, L_α/L_β and L_α/L_γ are determined for thin targets of tin and gadolinium at electron energies between 20 and 100 keV. Comparison is made with the intensity ratios derived from the L-shell ionization theories of Gryzinski (1965) and Scofield (1978). The effect of double-vacancy atomic states on the intensity ratios has been calculated using equations given by Gryzinski, and is discussed in the light of the discrepancies described above.

The ratio of the double- to single-ionization cross section varies approximately as Z^{-2} and so the low Z elements will maximize the double-ionization contribution. However, the differences between the energies of L X-rays decrease with decreasing Z so that resolution of the peaks becomes more difficult. The tin target ($Z = 50$) was chosen as a compromise between these two competing factors. On the other hand, the gadolinium target ($Z = 64$) was selected for comparison with the data by Johnston *et al.* (1981).

2. Experimental Details

Targets of tin and gadolinium, of thickness $9\cdot2$ and $7\cdot2\ \mu\mathrm{g\,cm^{-2}}$ respectively, were bombarded with electrons from a Jeol CX100 electron microscope at energies of 20, 40, 60, 80 and 100 keV. The samples were prepared by evaporation of a metal layer on a thin carbon film ($2\cdot5\ \mu\mathrm{g\,cm^{-2}}$) previously evaporated on a woven nylon grid.

The imaging properties of the electron microscope permitted careful alignment and control of the size of the beam spot. In this manner, background radiation was minimized by focusing the beam on small areas of the sample (typically $10^{-5}\ \mathrm{cm^2}$). The carbon backing, whilst only slightly increasing the background radiation (being of low Z), gave strength to the metal film which was made thin deliberately so as to minimize electron energy loss. Indeed for both Sn and Gd the calculated electron energy loss, using the formula of Heitler (1954), was less than $0\cdot3\%$ of the initial electron energy for all the energies studied. Many of the components of the microscope which were initially constructed of copper were replaced with nylon, reducing, but not entirely eradicating, the K X-ray contribution of copper to the L X-ray spectra.

The characteristic atomic de-excitation L X-ray spectra were observed with a Kevex Mark V Si(Li) detector; the specified energy resolution of this detector was 148 eV FWHM at $5\cdot9$ keV. The X-rays were detected at 90° to the incident electron direction and 36° to the target normal. The measurements presented are taken to be representative of the total X-ray production cross section since the anisotropy in the emission of the L_α, L_β, L_γ and L_l X-rays has been found to be zero within experimental errors (Hoffmann *et al.* 1979).

3. Analysis

An example of an acquired spectrum is shown in Fig. 1. This spectrum features a continuous background with the characteristic X-ray peaks superimposed. The majority of the background is produced by bremsstrahlung photons originating within the metallic film and carbon backing, although some photons arise from scattering of the electron beam within the microscope column. The background was subtracted by fitting a single third-order polynomial to a number of data points on either side of the L X-ray spectrum and then interpolating as shown by the solid line in Fig. 1.

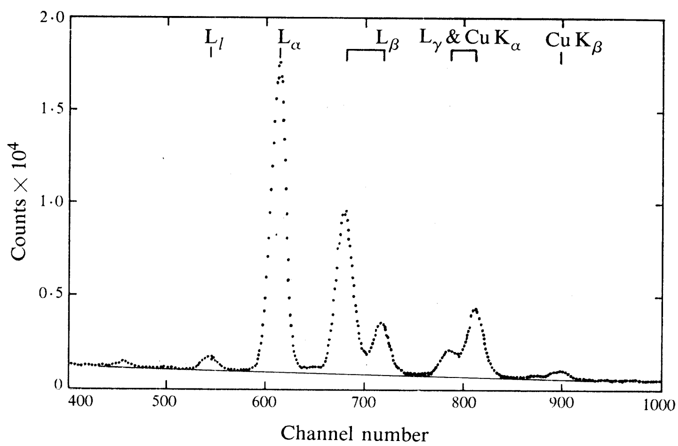

Fig. 1. Gadolinium L X-ray spectrum at 100 keV electron bombardment, showing the characteristic spectral peaks and the background which was subtracted as described in the text.

The areas under the spectral peaks were then evaluated by fitting gaussians to the background-subtracted pulse-height data; the L_α and L_l X-ray peaks were each fitted with a single gaussian whilst the L_β and L_γ groups were fitted by gaussians centred on the most intense transitions in each group. The FWHM of the fitted gaussians (typically 148 eV for Sn and 168 eV for Gd) were consistent with the system resolution. The relative efficiency of the detector was calculated using a method derived from the work of D. D. Cohen (1981, personal communication). The resultant uncertainties in the final experimental ratios, produced by the uncertainty in the detector efficiency, are relatively small as the detector efficiency varies little over the energy range of the X-rays considered in any one particular intensity ratio.

4. Theory

X-ray Production Cross Sections

The derivations of the relative L X-ray production cross-section ratios, assuming a single atomic vacancy, are based upon two L- and K-shell ionization theories, namely, the classical theory of Gryzinski (1965) using the binary encounter approximation (BEA), and the theory of Scofield (1978) using the relativistic form of the first-order Born approximation (RBA) together with a Hartree–Slater central potential. Since Scofield calculated the ionization cross sections down to only 50 keV, an extrapolation based upon his polynomial fit was performed to enable comparisons with the 20 and 40 keV data presented.

The L X-ray production cross sections are derived from the K-shell and L-subshell ionization cross sections using the relations

$$\sigma_l = \omega_{L3} \Gamma_{3l} \sigma_{L3}^{h} / \Gamma_3 , \tag{1}$$

$$\sigma_\alpha = \omega_{L3} (\Gamma_{3\alpha_1} + \Gamma_{3\alpha_2}) \sigma_{L3}^{h} / \Gamma_3 , \tag{2}$$

$$\sigma_\beta = \omega_{L3} \Gamma_{3\beta} \sigma_{L3}^{h} / \Gamma_3 + \omega_{L2} \Gamma_{2\beta_1} \sigma_{L2}^{h} / \Gamma_2 + \omega_{L1} \Gamma_{1\beta} \sigma_{L1}^{h} / \Gamma_1 , \tag{3}$$

$$\sigma_\gamma = \omega_{L2} \Gamma_{2\gamma} \sigma_{L2}^{h} / \Gamma_2 + \omega_{L1} \Gamma_{1\gamma} \sigma_{L1}^{h} / \Gamma_1 , \tag{4}$$

where ω_{Li} denotes the fluorescence yield for the Li subshell, $\Gamma_{i\lambda}$ the decay width of the $i\lambda$ characteristic X-ray or group of X-rays, Γ_i the total decay width to the Li subshell and σ_{Li}^{h} the Li subshell vacancy-production cross sections. The σ_{Li}^{h} terms are related to the L-subshell and K-shell ionization cross sections by

$$\sigma_{L1}^{h} = \sigma_{L1} + n_{K1} \sigma_K , \tag{5}$$

$$\sigma_{L2}^{h} = \sigma_{L2} + f_{12} \sigma_{L1} + (n_{K2} + f_{12} n_{K1}) \sigma_K , \tag{6}$$

$$\begin{aligned} \sigma_{L3}^{h} = {} & \sigma_{L3} + f_{23} \sigma_{L2} + (f_{13} + f_{12} f_{23}) \sigma_{L1} \\ & + (n_{K3} + f_{23} n_{K2} + f_{13} n_{K1} + f_{12} f_{23} n_{K1}) \sigma_K , \end{aligned} \tag{7}$$

where f_{ij} is the Coster–Kronig yield from the ith to the jth subshell, n_{Ki} is the average number of Li-subshell vacancies produced by transitions to the K shell, and σ_K and σ_{Li} are the ionization cross sections for the K shell and Li subshell respectively.

The fluorescence and Coster–Kronig yields are taken from Krause (1979) who quoted an uncertainty of 20%, the n_{Ki} are from Bambynek *et al.* (1972), whilst the decay widths are taken from Scofield (1974). The uncertainty present in some of the values will result in up to 25% uncertainty in the theoretical determination of the L_α/L_β and L_α/L_γ ratios; the form of the energy dependence of these results, however, will be unaffected. As can be seen from equations (1) and (2), the L_α/L_l ratio depends only on the emission rates and hence will not be affected by the uncertainties inherent in Krause's results.

Double Ionization

Since the discrepancy between the experimental and calculated intensity ratios has been attributed to multiple ionization, some discussion of the processes which could lead to multiply ionized atoms is necessary. Firstly, the perturbation caused by the sudden formation of a hole in a shell significantly dlstorts the radial wavefunctions of the electrons in the same shell or in an outer shell, but not in an inner shell. This change in the radial wavefunctions may well give rise to a second ionization which results from the rearrangement of the electron orbitals. This process is known as electron shake-off and has been treated by Aberg (1967) and Carlson *et al.* (1968). It should be noted that the shake-off probability depends wholly on the initial and final states of the atom and not on the incident electron energy.

A completely different mechanism was proposed by Gryzinski (1965). He calculated the probability of successive collisions of the incident electron with different electrons of the atomic system and also collisions between the ejected and remaining electrons (which, in Gryzinski's classical picture, would be outer shell electrons).

Cue and Scholz (1974) measured the Z dependence of the X-ray yields corresponding to KL and K ionized atoms at two electron energies, 20 keV and 2 MeV. The targets consisted of all elements between vanadium and nickel. These authors concluded that 'the observed energy dependence of the relative K_α-satellite yield seems to indicate contributions from both double-binary collision and shake-off processes in multiple-vacancy production by electron impact'. It would therefore appear that there is no simple model for multiple-vacancy production. However, the shake-off process occurs for photo-ionization as well as for particle impact and so cannot lead to the variations between the different vacancy production mechanisms postulated by Johnston *et al.* (1981) for the L_α/L_l ratio. In addition, since this process is energy independent it will be of no concern when considering the energy dependence of the L_α/L_β intensity ratio. For these reasons no calculation of double ionization due to electron shake-off was attempted and the process described by Gryzinski alone was considered.

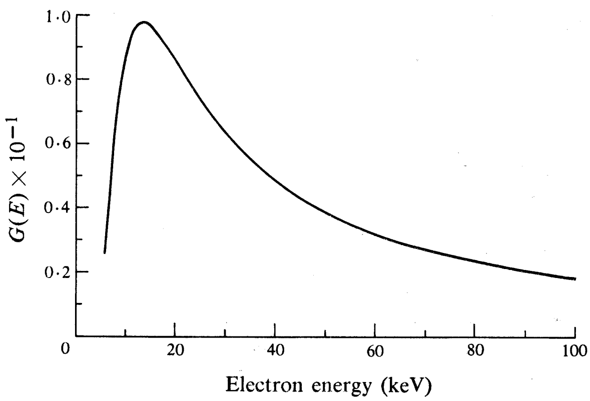

Fig. 2. The energy-dependent term $G(E, U_i, U_{ii})$ in the double-ionization cross-section formula, shown for ejection of an L 3 and an M 5 electron from tin.

Gryzinski's double-ionization cross-section formula, when applied to the production of double vacancies where one occurs in each of the L and M subshells, may be written as

$$\sigma^{\mathrm{d}}(E) = \sigma_0^2 n_{\mathrm{L}i} n_{\mathrm{M}ii} G(E, U_i, U_{ii})/4\pi\bar{r}^2 U_i^2 U_{ii}^2, \tag{8}$$

where $\sigma_0 = 6 \cdot 56 \times 10^{-14}\ \mathrm{eV}^2\ \mathrm{cm}^2$ for incident electrons, U_i and U_{ii} are the ionization energies of the first and second ionized electrons, E is the energy of the incident electron, $n_{\mathrm{L}i}$ and $n_{\mathrm{M}ii}$ are the number of electrons within the subshells being ionized, $\bar{r}$ is the average separation of the two electrons being ionized before ionization occurs (taken to be $n^2 r_0/Z$, where n is the principal quantum number and r_0 the Bohr radius), and G is a dimensionless factor which gives the electron energy dependence. This factor, as shown in Fig. 2, obtains its maximum value for an electron energy $E \sim 3(U_i + U_{ii})$, thereafter decreasing approximately as E^{-1} so that at high electron energies the double-ionization cross section becomes insignificant.

To calculate the hole-production cross section with a hole in one of each of the L and M subshells, Coster–Kronig transitions within these shells need to be considered. Coster–Kronig M-shell yields have been calculated by McGuire (1972) and his notation will be followed here. The cross section for producing a hole in each of the L 2 and M 2 subshells is

$$\sigma^{\mathrm{h}}_{\mathrm{L2,M2}} = \sigma_{\mathrm{L2,M2}} + S_{12}\,\sigma_{\mathrm{L2,M1}} + f_{12}\,\sigma_{\mathrm{L1,M2}} + S_{12}\,f_{12}\,\sigma_{\mathrm{L1,M1}}\,, \tag{9}$$

where $\sigma_{A,B}$ is the double-ionization cross section of the A and B subshells, S_{ij} the Coster–Kronig yield for the M-shell transition $j \rightarrow i$ and f_{ij} that for the L shell (Krause 1979). The expressions for the double-hole production cross section for higher L and M subshells, although not difficult to calculate, are tedious and so are not reproduced here. Contributions from Auger processes producing double vacancies in L and M subshells are relatively small for the targets considered here and so are ignored.

Gryzinski's calculation of the single-ionization cross section considers the scattering cross section for an electron incident on a bound electron in a Coulomb potential and is performed by considering the energy transferred to the ejected electron. The double ionization is treated as a special case of the single-ionization event where either the ionizing or ejected electron is involved in a subsequent collision, removing a second electron from the atom. Therefore, for a double-vacancy atomic state where the second vacancy is in the subshell from which electrons will de-excite to produce a particular X-ray, the X-ray production cross-section contribution from that X-ray will be

$$\sigma_{\nu} = \frac{\omega_{\mathrm{L}i}\,\Gamma_{i\nu}(\sigma^{\mathrm{h}}_{\mathrm{L}i} - \sigma^{\mathrm{h}}_{\mathrm{L}i,\mathrm{M}ii})}{\Gamma_i} + \frac{n-1}{n}\,\frac{\omega_{\mathrm{L}i}\,\Gamma_{i\nu}\,\sigma^{\mathrm{h}}_{\mathrm{L}i,\mathrm{M}ii}}{\Gamma_i}, \tag{10}$$

where the first term is the contribution to the L_ν X-ray intensity from atoms with a vacancy in the L i subshell and a full M ii subshell. The second term is the special case where there is one less electron available in the M ii subshell to de-excite and produce an L_ν X-ray and, as such, will be less than the full subshell X-ray intensity by a factor of $(n-1)/n$ where n is the number of electrons in the full subshell. Since the effect of double-vacancy states for weak transitions is negligible, the X-ray production cross sections, hereafter referred to as DBEA, are essentially

$$\sigma_{l} = \omega_{\mathrm{L3}}\,\Gamma_{3l}(\sigma^{\mathrm{h}}_{\mathrm{L3}} - \tfrac{1}{2}\sigma^{\mathrm{h}}_{\mathrm{L3,M1}})/\Gamma_3\,, \tag{11}$$

$$\sigma_{\alpha} = \omega_{\mathrm{L3}}\{\Gamma_{\alpha_1}(\sigma^{\mathrm{h}}_{\mathrm{L3}} - \tfrac{1}{6}\sigma^{\mathrm{h}}_{\mathrm{L3,M5}}) + \Gamma_{\alpha_2}(\sigma^{\mathrm{h}}_{\mathrm{L3}} - \tfrac{1}{4}\sigma^{\mathrm{h}}_{\mathrm{L3,M4}})\}/\Gamma_3\,, \tag{12}$$

$$\begin{aligned}\sigma_{\beta} = {} & \omega_{\mathrm{L3}}\,\Gamma_{3\beta}\,\sigma^{\mathrm{h}}_{\mathrm{L3}}/\Gamma_3 + \omega_{\mathrm{L2}}\,\Gamma_{2\beta_1}(\sigma^{\mathrm{h}}_{\mathrm{L2}} - \tfrac{1}{4}\sigma^{\mathrm{h}}_{\mathrm{L2,M4}})/\Gamma_2 \\ & + \omega_{\mathrm{L1}}\{(\Gamma_{1\beta_9} + \Gamma_{1\beta_{10}})\sigma^{\mathrm{h}}_{\mathrm{L1}} + \Gamma_{1\beta_4}(\sigma^{\mathrm{h}}_{\mathrm{L1}} - \tfrac{1}{2}\sigma^{\mathrm{h}}_{\mathrm{L1,M2}}) \\ & + \Gamma_{1\beta_3}(\sigma^{\mathrm{h}}_{\mathrm{L1}} - \tfrac{1}{4}\sigma^{\mathrm{h}}_{\mathrm{L1,M3}})\}/\Gamma_1\,. \end{aligned} \tag{13}$$

Larkins (1971) showed that multiple ionization of the valence shell of argon can give rise to large variations in the fluorescence yield for the subshell involved. However, as this work deals with deeply bound shells of much heavier atoms, we consider only the statistical argument given above in attempting to understand any variation of radiative widths or fluorescence yields due to multiply ionized states.

Table 1. Experimental X-ray intensity ratios for electron energies *E*

E (keV)	Intensity ratios for Sn L_α/L_γ	L_α/L_β	L_α/L_l	Intensity ratios for Gd L_α/L_β	L_α/L_l
20	$10\cdot39\pm0\cdot47$	$1\cdot337\pm0\cdot015$	$23\cdot83\pm0\cdot40$	$1\cdot371\pm0\cdot011$	$24\cdot63\pm0\cdot52$
40	$9\cdot71\pm0\cdot44$	$1\cdot343\pm0\cdot014$	$23\cdot47\pm0\cdot35$	$1\cdot312\pm0\cdot007$	$24\cdot39\pm0\cdot33$
60	$11\cdot08\pm0\cdot39$	$1\cdot396\pm0\cdot015$	$23\cdot46\pm0\cdot34$	$1\cdot299\pm0\cdot006$	$24\cdot48\pm0\cdot31$
80	$10\cdot04\pm0\cdot38$	$1\cdot376\pm0\cdot015$	$23\cdot24\pm0\cdot35$	$1\cdot275\pm0\cdot006$	$24\cdot66\pm0\cdot30$
100	$10\cdot23\pm0\cdot38$	$1\cdot351\pm0\cdot014$	$22\cdot91\pm0\cdot33$	$1\cdot277\pm0\cdot006$	$23\cdot97\pm0\cdot29$

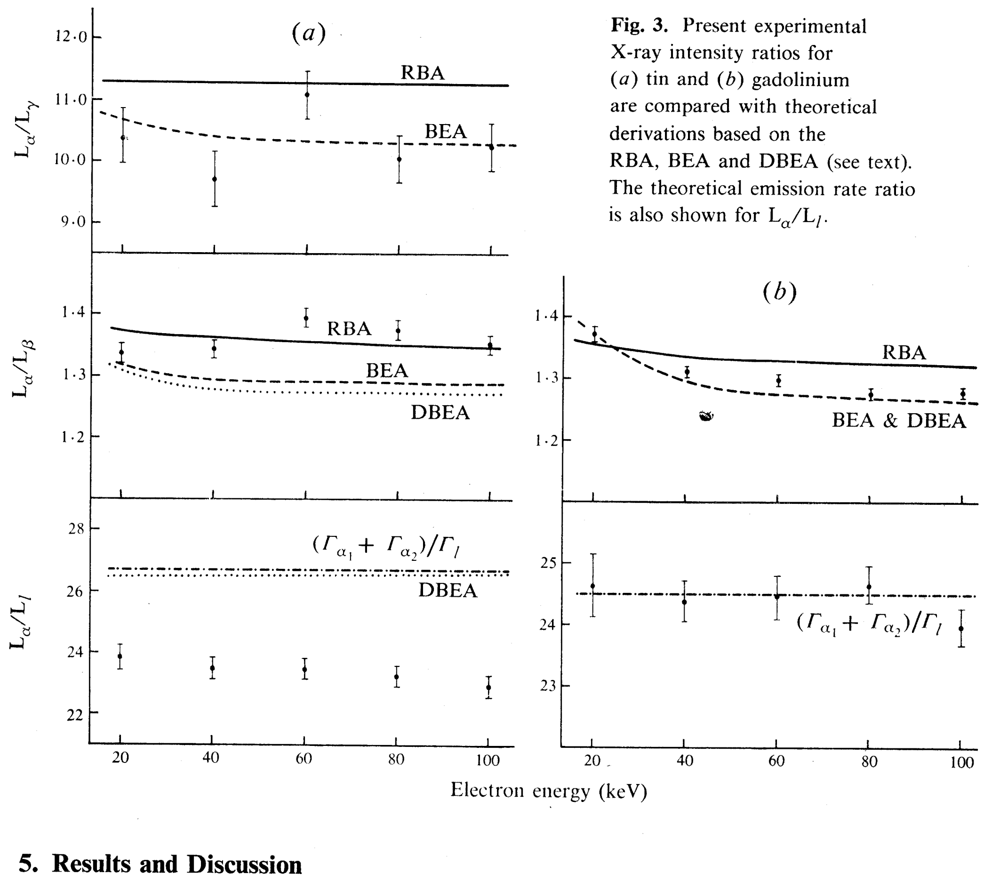

Fig. 3. Present experimental X-ray intensity ratios for (*a*) tin and (*b*) gadolinium are compared with theoretical derivations based on the RBA, BEA and DBEA (see text). The theoretical emission rate ratio is also shown for L_α/L_l.

5. Results and Discussion

The results for the relative X-ray production cross-section ratios L_α/L_γ, L_α/L_β and L_α/L_l are tabulated in Table 1 and compared with the theoretical data in Fig. 3. Unfortunately the L_γ data for Gd could not be analysed due to the presence of characteristic copper K X-rays superimposed on the Gd L_γ X-ray peaks. In general the L_α/L_γ results for Sn show reasonable agreement with the derivation using Gryzinski's (1965) binary encounter approximation (BEA) but lie about 10% below that of Scofield's (1978) relativistic Born approximation (RBA).

The L_α/L_β intensity ratio data for both Sn and Gd are within 6% of all three theoretical derivations. For Gd, the derivation which includes the effect of double vacancies (DBEA) does not vary significantly from the BEA from which it originated, and differs only slightly for Sn. No one theory fits the data well for both elements—the RBA fits better for Sn and the BEA for Gd. The L_α/L_β intensity ratio data for Gd decrease with electron energy more rapidly than the predictions of the RBA. This is in agreement with the observations of Genz *et al.* (1979) for higher Z elements. As has already been stated, the effect of double vacancies on the L_α/L_β ratio for Gd at these low energies is negligible. As the ratio of double to single ionization decreases with increasing energy and is a function of Z^{-2}, it therefore appears unlikely that the variation from theory reported by Genz for higher Z and higher energy data can be attributed to multiple-vacancy atomic states.

The L_α/L_l intensity ratio data for Gd show remarkable agreement with the theoretical ratios from Scofield's emission rates, whilst the Sn data lie consistently 14% below theory. At the electron energies used, the contribution from double vacancy states is expected to be at a maximum as the ratio of double to single ionization is largest at low energies but, as can be seen for Sn, the effect of double vacancies is insufficient to explain the experimental values. Also no explanation can be offered via a double-vacancy mechanism to account for the data by Johnston *et al.* (1981) for Gd, which at higher energies is below theory and the present data.

6. Conclusions

The X-ray intensity ratios L_α/L_γ, L_α/L_β and L_α/L_l have been determined for thin targets of Sn and Gd at electron impact energies between 20 and 100 keV. For the L_α/L_β ratio all theoretical calculations showed reasonable agreement with data. For Gd the L_α/L_l data agreed remarkably with theory, but the results for Sn were below the theoretical value. The effect of doubly ionized atomic states on these X-ray intensity ratios has been calculated in the semiclassical DBEA approximation. It is concluded that this effect, on its own, is not able to account for the discrepancies between theoretical and experimental values. Further work, both theoretical and experimental, is required before a satisfactory explanation of these intensity ratios, and their variation with the atomic number of the target and the incident electron energy, can be given.

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