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Relative strengths of the competing multipoles in the K and L series x-ray spectra in the NR limit

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Abstract. For most of the transitions of the K and L series x-ray spectra the ratio of the contributions of the competing multipoles, δ^2, is independent of the radial matrix element in the non-relativistic limit. In the present paper calculations of δ^2 are made in the non-relativistic limit which give the relative strengths of the two closely competing electric and magnetic multipoles. The dominant mode in the emission processes of the transitions in the K and L series x-ray spectra has been assigned on the basis of these calculations.

Keywords. X-ray spectral lines; forbidden lines; multipole emission; classification of spectral lines; radial matrix element; relativistic and non-relativistic limits.

1. Introduction

X-ray emission spectral lines are generally classified (Rubinowicz 1949) into two groups, namely allowed lines and the so-called forbidden lines. Allowed lines are those which obey electric dipole selection rules, whereas the forbidden lines correspond to higher order selection rules. The selection rules corresponding to the x-ray transitions are given in table 1 for ready reference. When a transition is allowed by more than one kind of multipole selection rule, it is usually classified in terms of all such allowed modes, *e.g.* we speak of magnetic dipole and electric quadrupole transition, etc. Based essentially on the selection rules, Padalia and Rao 1969; Padalia (1969, a, b) has classified the x-ray emission spectral lines. However, the contributions due to the different multipole fields (Jackson 1962) differ widely, and as such this classification fails to reflect the relative magnitudes of the contributions from the different multipole fields. Bhalla (1970) however, has used the individual contributions due to various multipole fields as the basis of classification but his work is limited to M series spectra only. In view of the numerous experimental studies on the forbidden lines carried out specially in India (Deodhar *et al*, Gokhale *et al*, Nigam *et al*, Mande and Takwale, etc. as in Ref. 5) in the past two decades, a large amount of data on x-ray spectral lines, specially in the K and L series, are now available (Bearden and Burr 1967; Salem *et al* 1974; Cauchois and Senemaud 1978). No classification of these lines based on the contributions from the different multipole radiations appears to have been made for the spectral lines of these series. In this paper, we estimate the ratios of the contributions of different electric and magnetic multipole radiations in the non-relativistic limit, in an attempt to extend the classification to the K and L series on the same lines as of Bhalla.

Table 1. Selection rules for significant multipoles in x-ray emission spectra.

Multipole	Δl	Δj	Remarks
Electric dipole (E1)	± 1	$0, \pm 1$	
Magnetic dipole (M1)	$0, \pm 2$	$0, \pm 1$	
Electric quadrupole (E2)	$0, \pm 2$	$0, \pm 1, \pm 2$	$j = \frac{1}{2} \leftarrow\vert\rightarrow j = \frac{1}{2}$
Magnetic quadrupole (M2)	$\pm 1, \pm 3$	$0, \pm 1, \pm 2$	$j = \frac{1}{2} \leftarrow\vert\rightarrow j = \frac{1}{2}$
Electric octupole (E3)	$\pm 1, \pm 3$	$0, \pm 1,$ $\pm 2, \pm 3$	$j = \frac{1}{2} \leftarrow\vert\rightarrow j = \frac{1}{2}$ $j = \frac{1}{2} \leftarrow\vert\rightarrow j = 3/2$
Magnetic octupole (M3)	$0, \pm 2,$ ± 4	$0, \pm 1,$ $\pm 2, \pm 3$	$j = \frac{1}{2} \leftarrow\vert\rightarrow j = \frac{1}{2}$ $j = \frac{1}{2} \leftarrow\vert\rightarrow j = 3/2$

(Besides the exceptions given in the remarks column, $j = 0$ to $j = 0$ is absolutely forbidden for all radiative transitions.)
Apart from these rules, magnetic transitions are allowed if $\kappa + \kappa' \neq 0$.

The calculation of the transition rate by a given multipole radiation between two atomic states involves, apart from the photon energy, a numerical factor and a radial matrix element (Edlabadkar *et al* 1980) which depend on the order of the multipole. In the non-relativistic (NR) limit the electric 2^L-pole and the magnetic 2^{L+1}-pole transition rates depend on the same radial matrix element (Scofield 1975). Even when the magnetic dipole (M1) is the lowest mode and the electric quadrupole (E2) is the next possible mode, the transition rates for the two multipole radiations depend on the same radial matrix element in the NR limit as will be shown in the next section. In all the above cases, the ratio of the contributions of the magnetic to the electric multipole rates is, therefore independent of the radial matrix element. In order to arrive at a better classification of the x-ray diagram lines, we have calculated the ratios for all those x-ray transitions of the K and L series, which are independent of the radial matrix elements.

2. Procedure for the calculations

Let the quantum numbers κ', μ' denote the initial electron state and κ, μ indicate the final electron state in an atom. After summing over the initial substates and averaging over the final substates, the electric multipole (EL) and magnetic multipole (ML) rates in atomic units ($e=\hbar=m=1$) are given by (Bhalla 1970)

$$\omega_{\kappa\kappa'}(\mathrm{EL}) = 2k\left[\frac{(2l'+1)(2l+1)(2j'+1)}{(2L+1)^2}\right] C^2(ll'L;00)\, W^2(jlj'l';\tfrac{1}{2}L)$$

$$\times \left\{\left(\frac{L+1}{L}\right)^{1/2}\left[(\kappa'-\kappa)\, I^{L-1\,(+)}_{\kappa\kappa'} + L\, I^{L-1\,(-)}_{\kappa\kappa'}\right]\right.$$

$$\left. -\left(\frac{L}{L+1}\right)^{1/2}\left[(\kappa'-\kappa)\, I^{L+1\,(+)}_{\kappa\kappa'} - (L+1)\, I^{L+1\,(-)}_{\kappa\kappa'}\right]\right\}^2, \qquad (1)$$

and

$$\omega_{\kappa\kappa'}(\mathrm{ML}) = 2k\,(\kappa+\kappa')^2\left[\frac{(2\bar{l}'+1)\,(2l+1)\,(2j'+1)}{L(L+1)}\right]$$

$$\times\, C^2(l\,\bar{l}'L;\,00)\,W^2(jlj'\bar{l}';\,\tfrac{1}{2}L)\left\{I^{L\,(+)}_{\kappa\kappa'}\right\}^2 \qquad (2)$$

with

$$I^{\lambda\,(\pm)}_{\kappa\kappa'} = \int_0^\infty (G_\kappa F_{\kappa'} \pm F_\kappa G_{\kappa'})\, j_\lambda\,(kr)\,\mathrm{d}r. \qquad (3)$$

Here the radial functions G and F are the large and small components respectively of the Dirac's wave function and the integral is over the radial distance r. Also $k=\alpha\,(E_f - E_i)$ and the other symbols have their usual meaning. In the NR limit, we take

$$F = \frac{1}{2c}\left(\frac{\mathrm{d}G}{\mathrm{d}r} + \kappa\frac{G}{r}\right). \qquad (4)$$

Equations (1) and (2) can then be simplified for two different cases.

Case I: When electric multipole is the lowest multipole of emission.

Assuming the potential to be localised about the nucleus, *i.e.* $kr \ll 1$, we may take

$$j_L(kr) = \frac{(kr)^L}{(2L+1)!!} \qquad (5)$$

The rates in the NR limit are then given by

$$\omega_{\kappa\kappa'}\,(\mathrm{EL}) = 2k\left[\frac{(2l'+1)\,(2l+1)\,(2j'+1)}{(2L+1)^2}\right] C^2\,(ll'\,L;\,00)\,W^2\,(jlj'l';\,\tfrac{1}{2}L)$$

$$\times\left[\left(\frac{L}{L+1}\right)^{1/2}\frac{(\kappa'-\kappa)\,(\kappa'+\kappa-L-1)}{(2L+3)!!}\left(\frac{k}{2c}\right)\right.$$

$$\left.+\left(\frac{L+1}{L}\right)^{1/2}\frac{1}{(2L-1)!!}\right]^2\left\{\int_0^\infty G_\kappa\,G_{\kappa'}\,(kr)^L\,\mathrm{d}r\right\}^2 \qquad (6)$$

and

$$\omega_{\kappa\kappa'}\,(\mathrm{ML}) = 2k\,(\kappa+\kappa')^2\left[\frac{(2\bar{l}'+1)\,(2l+1)\,(2j'+1)}{L(L+1)}\right]$$

$$\times\, C^2\,(l\bar{l}'L;\,00)\,W^2\,(jlj'\bar{l}';\,\tfrac{1}{2}L)$$

$$\times \left\{\left(\frac{k}{2c}\right)\frac{(\kappa+\kappa'-L)}{(2L+1)}\int_0^\infty G_\kappa G_{\kappa'}\frac{(kr)^{L-1}}{(2L-1)!!}\,\mathrm{dr}\right\}^2. \tag{7}$$

The amplitude mixing ratio, δ, of a transition is defined as the ratio of the reduced matrix elements of the magnetic multipole to the electric multipole contributions. Then δ^2 is the ratio of the corresponding multipole transition rates. We then have

$$\delta^2 = \frac{(M, L+1)\text{ rate}}{(E, L)\text{ rate}} = \left[\frac{(2\bar{l}'+1)(2L+1)^2}{(2l'+1)(L+1)(L+2)}\right](\kappa+\kappa')^2$$

$$\times \frac{C^2(\bar{l}l', L+1; 00)\, W^2(jlj'\bar{l}'; \tfrac{1}{2}, L+1)}{C^2(ll'\,L; 00)\, W^2(jlj'l'; \tfrac{1}{2}L)}$$

$$\times \left[\left(\frac{L}{L+1}\right)^{1/2}(\kappa'-\kappa) + \left(\frac{L+1}{L}\right)^{1/2}\frac{(2L+3)(2L+1)}{(\kappa+\kappa'-L-1)}\right.$$

$$\left.\times \left\{\frac{2}{\alpha^2(E_f-E_i)}\right\}\right]^{-2}. \tag{8}$$

Case II: When magnetic dipole is the lowest multipole of emission.

For $kr \ll 1$, the approximations in (4) and (5) give a vanishing matrix element for the M1 transition when $\Delta n \neq 0$. However, if the higher order terms neglected in (5) in the expression of $j_L(kr)$ are retained, we get a non-zero transition probability for the M1 decay mode, even in the NR limit given by (4). We, therefore, write

$$I^{1(+)}_{\kappa\kappa'} = \int_0^\infty j_1(kr)\,(G_\kappa F_{\kappa'} + F_\kappa G_{\kappa'})\,\mathrm{d}r$$

$$= \left(\frac{k}{2c}\right)\frac{(\kappa+\kappa'-1)}{3}\int_0^\infty G_\kappa G_{\kappa'} j_0(kr)\,\mathrm{d}r$$

$$+ \left(\frac{k}{2c}\right)\frac{(\kappa+\kappa'+2)}{3}\int_0^\infty G_\kappa G_{\kappa'} j_2(kr)\,\mathrm{d}r, \tag{9}$$

Retaining the $(kr)^2$ terms,

$$I^{1(+)}_{\kappa\kappa'} = \left(\frac{k}{2c}\right)\left[\frac{2-3(\kappa+\kappa')}{30}\right]\int_0^\infty G_\kappa G_\kappa\,(kr)^2\,\mathrm{d}r. \tag{10}$$

Thus,

$$\delta^2 = \frac{(M1)\text{ rate}}{(E2)\text{ rate}}$$

$$= \frac{(2\bar{l}' + 1)\,[2 - 3\,(\kappa + \kappa')]^2\,(\kappa + \kappa')^2}{48\,(2l' + 1)}$$

$$\times \frac{C^2\,(l\bar{l}'\,1;00)\,W^2\,(jlj'\,\bar{l}';\tfrac{1}{2}\,1)}{C^2\,(ll'\,2;00)\,W^2\,(jlj'\,l';\tfrac{1}{2}\,2)}$$

$$\times \left\{\frac{(\kappa + \kappa' - 3)\,(\kappa' - \kappa)}{105} + \frac{1}{\alpha^2\,(E_f - E_i)}\right\}^{-2} \qquad (11)$$

Since we have considered higher order terms in the expansion of $j_1(kr)$ one should ideally approximate F to higher orders in α in (4). The calculations then remain no more simple. However, the error introduced by not including the higher order terms is not too serious as will be evident from table 2.

3. Results and discussions

The values of δ^2 are calculated for the K and L series transitions which fall in the categories I or II. Our study shows that when more than two multipole transitions are possible, the contribution due to higher order multipoles is extremely small. Hence, in such cases, only the lowest two orders are considered. Table 2 shows the values of δ^2 for the KN transitions for uranium (Z=92) calculated using equations (8) and (11) and those calculated by Scofield (1969) using ralativistic Hartree-Fock-Slater wavefunctions. The fairly good agreement of our values with those obtained by Scofield justifies the validity of our approximations. Table 3 gives the δ^2 values calculated by us and the suggested classification for uranium. The energy values are taken from Bearden and Burr (1967).

All the transitions of the K and L series have been classified in these calculations except for $f_{5/2} \rightarrow s_{1/2}$ and $d_{5/2} \rightarrow p_{1/2}$, where M2 and E3 are the competing processes and $f_{7/2} \rightarrow p_{1/2}$, where M3 and E4 are the competing processes. Besides this our calcu-

Table 2. δ^2 values for KN transitions for $Z = 92$.

Transition	Possible multipoles	δ^2 (M rate/E rate)	
		Present	Scofield
KN_{III}	E1 M2	$9{\cdot}09 \times 10^{-3}$	$8{\cdot}5 \times 10^{-3}$
KN_{IV}	M1 E2	$1{\cdot}08 \times 10^{-3}$	$1{\cdot}04 \times 10^{-3}$
KN_{V}	E2 M3	$1{\cdot}06 \times 10^{-2}$	$1{\cdot}2 \times 10^{-2}$
KN_{VI}	M2 E3	—	$4{\cdot}07 \times 10^{-4}$
KN_{VII}	E3 M4	$1{\cdot}1 \times 10^{-2}$	$1{\cdot}33 \times 10^{-2}$

Table 3. δ^2 values for x-ray transitions for $Z = 92$.

Transition	Multipoles allowed	δ^2 (M rate/E rate)	Predominant mode
KL_I^+	M1	—	pure M1
KL_{II}^{++}	E1	—	pure E1
KL_{III}^{++}	E1, M2	$6{\cdot}75 \times 10^{-3}$	predominantly E1
KM_I	M1	—	pure M1
KM_{II}^{++}	E1	—	pure E1
KM_{III}^{++}	E1, M2	$8{\cdot}59 \times 10^{-3}$	predominantly E1
KM_{IV}	M1, E2	$1{\cdot}03 \times 10^{-3}$	,, E2
KM_V	E2, M3	$1{\cdot}01 \times 10^{-2}$	,, E2
KN_I	M1	—	pure M1
KN_{II}^{++}	E1	—	pure E1
KN_{III}^{++}	E1, M2	$9{\cdot}09 \times 10^{-3}$	predominantly E1
KN_{IV}	M1, E2	$1{\cdot}08 \times 10^{-3}$	,, E2
KN_V	E2, M3	$1{\cdot}06 \times 10^{-2}$	,, E2
KN_{VI}	M2, E3	**	—
KN_{VII}	E3, M4	$1{\cdot}1 \times 10^{-2}$	predominantly E3
KO_I	M1	—	pure M1
KO_{II}	E1	—	pure E1
KO_{III}	E1, M2	$9{\cdot}23 \times 10^{-3}$	predominantly E1
KO_{IV}	M1, E2	$1{\cdot}09 \times 10^{-3}$	,, E2
KO_V	E2, M3	$1{\cdot}07 \times 10^{-2}$	,, E2
L_IM_I	M1	—	pure M1
$L_IM_{II}^{++}$	M1	—	pure E1
$L_IM_{III}^{++}$	E1, M2	$2{\cdot}18 \times 10^{-4}$	predominantly E1
$L_IM_{IV}^{++}$	M1, E2	$2{\cdot}61 \times 10^{-5}$	,, E2
$L_IM_V^{++}$	E2, M3	$2{\cdot}8 \times 10^{-4}$	,, E2
L_IN_I	M1	—	pure M1
$L_IN_{II}^{++}$	E1	—	pure E1
$L_IN_{III}^{++}$	E1, M2	$3{\cdot}06 \times 10^{-4}$	predominantly E1
$L_IN_{IV}^{++}$	M1, E2	$3{\cdot}53 \times 10^{-5}$	,, E2
$L_IN_V^{++}$	E2, M3	$3{\cdot}72 \times 10^{-4}$	,, E2
L_IN_{VI}	M2, E3	**	—
L_IN_{VII}	E3, M4	$3{\cdot}04 \times 10^{-4}$	predominantly E3
L_IO_I	M1	—	pure M1
$L_IO_{II}^{++}$	E1	—	pure E1
$L_IO_{III}^{++}$	E1, M2	$3{\cdot}32 \times 10^{-4}$	predominantly E1
$L_IO_{IV}^{++}$	M1, E2	$3{\cdot}76 \times 10^{-5}$	,, E2
$L_IO_V^{++}$	E2, M3	$3{\cdot}95 \times 10^{-4}$	,, E2
$L_{II}M_I^{++}$	E1	—	pure E1
$L_{II}M_{II}$	M1	—	pure M1
$L_{II}M_{III}^{++}$	M1, E2	$5{\cdot}49 \times 10^{-4}$	predominantly E2
$L_{II}M_{IV}^{++}$	E1, M2	$8{\cdot}52 \times 10^{-6}$	,, E1
$L_{II}M_V$	M2, E3	**	—
$L_{II}N_I^{++}$	E1	—	pure E1
$L_{II}N_{II}$	M1	—	pure M1
$L_{II}N_{III}^{++}$	M1, E2	$7{\cdot}84 \times 10^{-4}$	predominantly E2
$L_{II}N_{IV}^{++}$	E1, M2	$1{\cdot}17 \times 10^{-6}$	,, E1

Table 3. (*Contd.*)

(1)	(2)	(3)	(4)
$L_{II}N_V$	M2, E3	**	—
$L_{II}N_{VI}^{++}$	E2, M3	5.24×10^{-6}	predominantly E2
$L_{II}N_{VII}$	M3, E4	**	—
$L_{II}O_I^{++}$	E1	—	pure E1
$L_{II}O_{II}$	M1	—	pure M1
$L_{II}O_{III}^{++}$	M1, E2	$8{\cdot}52 \times 10^{-4}$	predominantly E2
$L_{II}O_{IV}^{++}$	E1, M2	$1{\cdot}25 \times 10^{-5}$	,, E1
$L_{II}O_V$	M2, E3	**	—
$L_{III}M_I^{++}$	E1, M2	$9{\cdot}74 \times 10^{-5}$	predominantly E1
$L_{III}M_{II}^{++}$	M1, E2	$2{\cdot}88 \times 10^{-4}$	,, E2
$L_{III}M_{III}^{++}$	M1, E2, M3	8.29×10^{-3}*	,, E2
$L_{III}M_{IV}^{++}$	E1, E3	***	,, E1
$L_{III}M_V^{++}$	E1, M2, E3, M4	$4{\cdot}33 \times 10^{-4}$*	,, E1
$L_{III}N_I^{++}$	E1, M2	$1{\cdot}77 \times 10^{-4}$	,, E1
$L_{III}N_{II}^{++}$	M1, E2	$5{\cdot}08 \times 10^{-4}$	,, E2
$L_{III}N_{III}^{++}$	M1, E2, M3	$1{\cdot}3 \times 10^{-3}$*	,, E2
$L_{III}N_{IV}^{++}$	E1, E3	***	,, E1
$L_{III}N_V^{++}$	E1, M2, E3, M4	$6{\cdot}29 \times 10^{-4}$*	,, E1
$L_{III}N_{VI}^{++}$	M1, E2, M3, M4	$2{\cdot}37 \times 10^{-5}$*	,, E2
$L_{III}N_{VII}^{++}$	E2, M3, E4, M5	$2{\cdot}29 \times 10^{-4}$*	,, E2
$L_{III}O_I^{++}$	E1, M2	$2{\cdot}03 \times 10^{-4}$	,, E1
$L_{III}O_{II}^{++}$	M1, E2	$5{\cdot}75 \times 10^{-4}$	,, E2
$L_{III}O_{III}^{++}$	M1, E2, M3	$1{\cdot}44 \times 10^{-2}$*	,, E2
$L_{III}O_{IV}$	E1, E3	***	,, E1
$L_{III}O_V^{++}$	E1, M2, E3, M4	$6{\cdot}79 \times 10^{-4}$*	,, E1

*This value of δ^2 is for the two lowest multipoles.

**In these cases, δ^2 is not independent of the radial matrix elements and hence its value cannot be calculated with the present procedure.

***magnetic multipoles do not contribute for these transitions. E3 being two orders higher than E1 these transitions are classified as predominantly E1.

+Experimentally observed transitions, (Salem *et al* 1974).

++Experimentally observed transitions (Cauchois and Senemaud 1978).

lations are not extended to transitions from the P states as the assumption $kr \ll 1$ made in (5) would be a very far-fetched assumption for the P shell.

For the transitions under consideration, it is possible to draw the following conclusions from the present work:

(i) When one assumes a central force field and a localized potential, δ^2 can be obtained in the NR limit without the knowledge of the wavefunctions by using equations (8) and (11).

(ii) The value of δ^2 depends on the energy of the transition, $(E_f - E_i)$. Thus as the energy of the transition increases (or decreases) as one goes to higher (or lower) elements, the magnetic component increases (or decreases) for a given transition.

(iii) As seen from table 3, when the electric multipole is the lowest multipole, the transition is predominantly electric. When M1 is the lowest multipole then the emission is predominantly by the electric quadrupole mode.

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