X-RAY ANGULAR CORRELATION AND L_{III} FLUORESCENCE YIELDS (*) (**)

F. BRAGANÇA GIL and M. J. TEMES D'OLIVEIRA
Laboratory of Physics, University of Lisbon, Lisbon, Portugal

ABSTRACT — The presently available theoretical and experimental values for the A_{22} coefficients of the X-ray angular correlation function are compared in order to discuss the calculated values for M2/E1 mixing ratios. The experimental values were obtained from previous angular correlation experiments and calculated from previous fluorescence yields determinations.

1 — INTRODUCTION

In most experiments the L_{III} fluorescence yields are established through the determination of the coincidence rates between K and L X-rays. The ω_3 fluorescence yield is then related to the true coincidence rate, $N_v(K\alpha_1 - L)$, by the expression

$$N_v(K\alpha_1 - L) = N(K\alpha_1)\,\varepsilon\,\frac{\Omega}{4\pi}\,t\,\omega_3 \tag{1}$$

where $N(K\alpha_1)$ is the $K\alpha_1$ counting rate, ε the intrinsic detector efficiency, $\frac{\Omega}{4\pi}$ the solid angle and t the transmission coefficient.

(*) Received April 25, 1973.
(**) Work is part of a research project supported by Instituto de Alta Cultura (Portugal) (Project L. F. 1-II).

Expression (1) is valid only if the K-L X-ray angular correlation is isotropic. Otherwise, the right-hand side of eq. 1 must be multiplied by the value of the angular correlation function, $W(\theta)$ [1].

According to the atomic decay scheme such an angular correlation should exist, fig. 1.

In fact, the theory of X-ray angular correlation has been already outlined by Moellering and Jensen [2] and later by

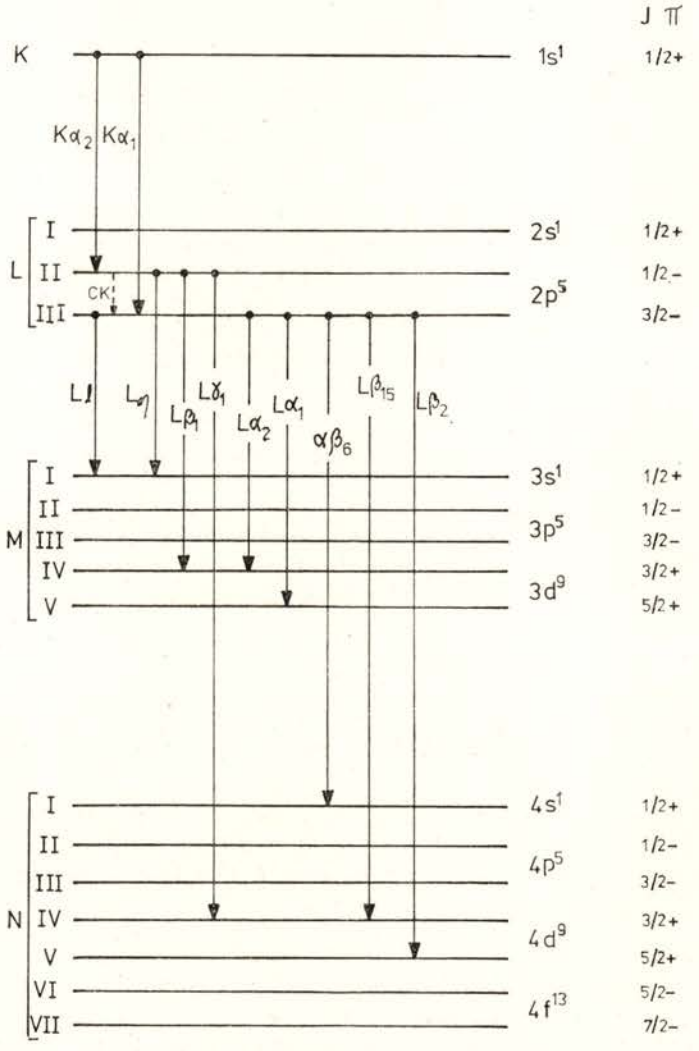

Fig. 1 — Atomic Decay Scheme

Babushkin [3]. Experimental evidence of such an angular correlation has been shown by Beste [4] and Konstantinov and Sazonova [5]. Also Price et al. [6] verified the influence of that correlation on the experimental determination of the ω_3 fluorescence yield.

This seems to prove that the effect of X-ray angular correlation must be considered when measurements of ω_3 fluorescence yields are performed.

2 — EXPERIMENTAL RESULTS AND THEORETICAL VALUES IN X-RAY ANGULAR CORRELATIONS.

The last survey about X-ray fluorescence yields and Auger and Coster-Krönig transition probabilities [7] included for the first time information about the effect of X-ray angular correlation in ω_3 coincidence measurements.

The atomic decay scheme shows that the X-ray transitions can have either E1 or E1 + M2 character.

The M2/E1 mixing ratio (δ^2) has been calculated by Scofield [8] in the case of $K\alpha_1$, $L\ell$, $L\alpha_1$, $L\beta_2$ and $L\beta_6$ transitions for the atomic numbers 50, 60, 70, 80, 90 and 100.

A plot of $\delta^2 vs.$ Z is presented in fig. 2, including the main transitions in K-L cascades.

The K-L angular correlation function is given by

$$W(\theta) = 1 + A_{22} P_2(\cos\theta) \tag{2}$$

where $P_2(\cos\theta)$ is the Legendre Polynomial of order 2.

In the present work the theoretical values for A_{22} have been compared to the experimental ones.

The first experimental determinations have been made by Wood et al. [9] and by Catz et al. [10] to [17] and are summarized in table I.

The results of Catz et al. show evidence for an E1 + M2 admixture in electromagnetic transitions between atomic shells. In the case of Tl and Pb these results seem to indicate that a better agreement between theory and experiment can be obtained assuming higher values for the M2/E1 mixing ratio for the transitions involved in the cascades. However this statement

becomes not so obvious if all the available exprerimental results are taken into account. Catz et al. have obtained the angular correlation functions between the unresolved $K\alpha$ radiation ($K\alpha_1 + K\alpha_2$) and three groups of L X-ray radiation, namely Ll, $L\alpha$ ($L\alpha_1 + L\alpha_2$) and $L\beta$ (mainly $L\beta_2 + L\beta_6 + L\beta_{15}$), respectively.

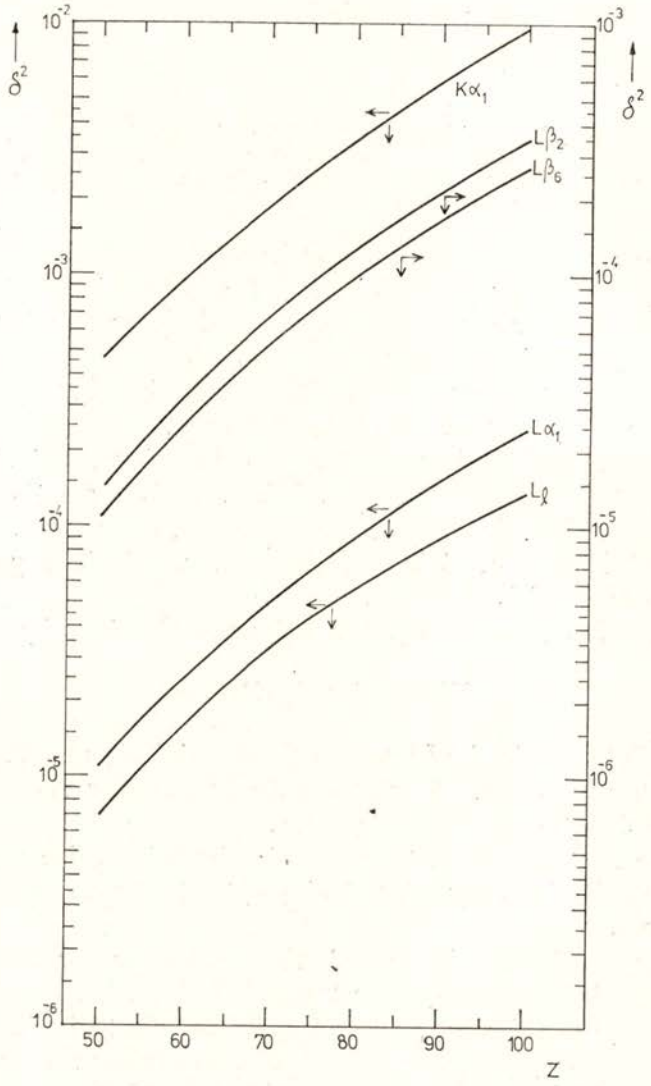

Fig. 2 — M2/E1 mixing ratios (δ^2) *vs.* the atomic number (Z).

TABLE I

Experimental values of A_{22} coefficients

Element	Cascade	A_{22} (multiples of 10^{-2})	Reference
$_{60}$Nd	$K\alpha - L\,l$	15 ± 4	[17]
	$K\alpha - L\,\alpha$	2.7 ± 0.3	
	$K\alpha - L\,\beta$	0.1 ± 0.5	
$_{65}$Tb	$K\alpha - L\,l$	14 ± 5	[17]
	$K\alpha - L\,\alpha$	2.6 ± 0.5	
	$K\alpha - L\,\beta$	-0.1 ± 0.5	
$_{65}$Tb	$K\alpha - L\,l$	15 ± 6	[13]
	$K\alpha - L\,\alpha$	1.4 ± 0.5	
	$K\alpha - L\,\beta$	0.9 ± 0.5	
$_{73}$Ta	$K\alpha - L\,\alpha$	2.48 ± 0.41	[12], [16]
	$K\alpha - L\,\beta$	-0.12 ± 0.46	
$_{81}$Tl	$K\alpha_1 - L\,l$	26 ± 5	[9]
	$K\alpha_1 - L\,\alpha$	5.0 ± 3.0	
$_{81}$Tl	$K\alpha - L\,l$	21.8 ± 2.0	[13], [16]
	$K\alpha - L\,\alpha$	3.63 ± 0.32	
	$K\alpha - L\,\beta$	1.31 ± 0.36	
$_{81}$Tl	$K\alpha - L\,l$	31 ± 6	[10]
	$K\alpha - L\,\alpha$	4.0 ± 1.3	
	$K\alpha - L\,\beta$	2 ± 1	
$_{82}$Pb	$K\alpha - L\,l$	23.32 ± 2.06	[14], [15]
	$K\alpha - L\,\alpha$	4.13 ± 0.36	
	$K\alpha - L\,\beta$	1.22 ± 0.42	

The angular correlation involving the $K\alpha_2$ radiation is isotropic since the final state has spin 1/2.

In the present work the calculated values of A_{22} are compared with the experimental results listed in table I. The calculation of those values must include the determination of the relative $K\alpha_2 - L$ and $K\alpha_1 - L$ coincidence rates since the angular correlation involves only the $K\alpha_1$ radiation but the measured coincidence rate is the sum of $K\alpha_1 - L$ and $K\alpha_2 - L$ coincidence rates.

For $K\alpha - L\alpha$ coincidences the relative intensity is given by

$$\frac{N_v(K\alpha_2 - L\alpha)}{N_v(K\alpha_1 - L\alpha)} = \frac{P(K\alpha_2)}{P(K\alpha_1)} \cdot f_{23} \tag{3}$$

where N_v are the true coincidence rates, $P(K\alpha_2)$ and $P(K\alpha_1)$ the emission rates for $K \rightarrow L_{II}$ and $K \rightarrow L_{III}$ transitions, respectively, and f_{23} is the Coster-Krönig $L_{II} \rightarrow L_{III}$ transition probability.

The same formula is valid for $N_v(K\alpha_2 - Ll)/N_v(K\alpha_1 - Ll)$ since the Ll radiation is due to the same Coster-Krönig transition between L_{II} and L_{III} atomic subshells.

For $K\alpha - L\beta$ coincidences the equivalent ratio is

$$\frac{N_v(K\alpha_2 - L\beta)}{N_v(K\alpha_1 - L\beta)} = \frac{P(K\alpha_2)}{P(K\alpha_1)} \cdot \left[\frac{\omega_2}{\omega_3} \cdot \frac{P(L\beta_1)/P(L_{II})}{P(L\beta)_{III}/P(L_{III})} + f_{23} \right] \tag{4}$$

where ω_2 and ω_3 are the fluorescence yields of the subshells L_{II} and L_{III} respectively, $P(L\beta_1)$ is the emission rate for the $L_{II} \rightarrow M_{IV}$ transition, $P(L\beta)_{III}$ is the sum of the emission rates for $L_{III} \rightarrow N_V$, $L_{III} \rightarrow N_I$ and $L_{III} \rightarrow N_{IV}$ transitions and $P(L_{II})$ and $P(L_{III})$ are the total emission rate of L_{II} and L_{III} X-ray, respectively.

In the present computation the values published by Scofield [18] for the emission rates have been used.

However the correlation $K\alpha_1 - L\alpha$ is an admixture of $K\alpha_1 - L\alpha_1$ and $K\alpha_1 - L\alpha_2$ correlations and this suggests that the value of A_{22} for $K\alpha_1 - L\alpha$ correlation must be an weighted average of the partial A_{22} coefficients for the above mentioned correlations.

The same situation occurs for $K\alpha_1 - L\beta$ correlations since the group $L\beta$ contains also several transitions from which only

the most important ones, $L\beta_2$, $L\beta_6$ and $L\beta_{15}$, have been considered, following the work of Catz et al..

The coefficient A_{22} has been computed for $K\alpha - Ll$, $K\alpha - L\alpha$ and $K\alpha - L\beta$ correlations for the atomic numbers where experimental results were available and also for all others where determinations of fluorescence yields and Coster-Krönig transition probabilities have been done with reasonable accuracy [7].

As already pointed out Catz et al. have suggested an increase in the M2 contribution to the Ll radiation in order to obtain better agreement between theory and experiment. This is valid for Tl and Pb but failed for other elements where experimental determinations are available.

In the present work the coefficient A_{22} has been computed starting from different values for the M2/E1 mixing ratios. The following sets of values have been considered:

1) Values of δ^2 given by Scofield;

2) $\delta^2 = 0$ for all the radiations of the cascade, corresponding to pure El transitions;

3) $\delta^2 = 0$ for $K\alpha_1$ transitions and the values of δ^2 given by Scofield for L transitions;

4) The values given by Scofield for $K\alpha_1$ transitions and $\delta^2 = 0$ for L transitions;

5) $\delta^2 = 0$ for $K\alpha_1$ transitions and δ^2 (Scofield) multiplied by 10 for L transitions.

For the $K\alpha_1 - Ll$ correlation the coefficient A_{22} has also been computed considering the value of δ^2 given by Scofield for the $K\alpha_1$ radiation and multiplying by ten the δ^2 values presented by the same author for Ll radiation.

All these calculations are summarized in table II and the results plotted in figs. 3, 4, 5 and 6.

In fig. 7 the values of A_{22} computed for the angular correlation with $K\alpha_1$ radiation only are plotted against the atomic number Z. In this calculation the values given by Scofield for the mixing ratios for the radiations involved in the cascades have been used.

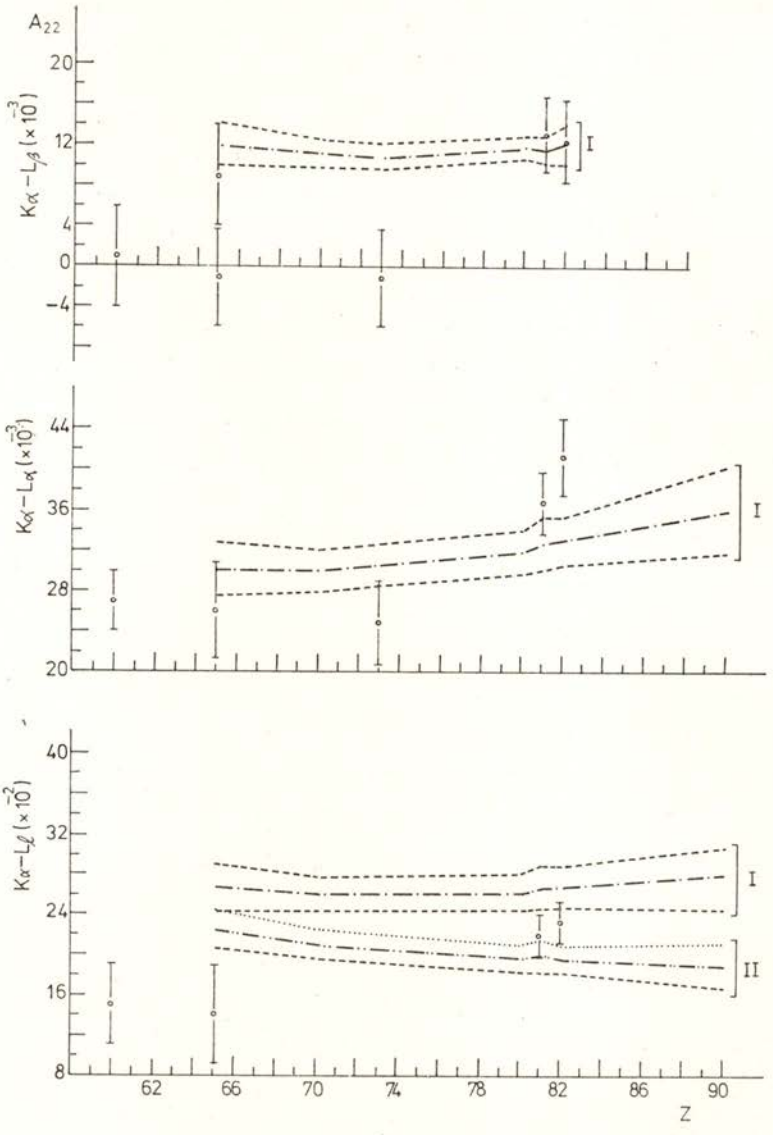

Fig. 3 — Values of the A_{22} angular correlation function's coefficient
I: see table II (*a*)
II: see table II (*f*)
Experimental values: see table I.

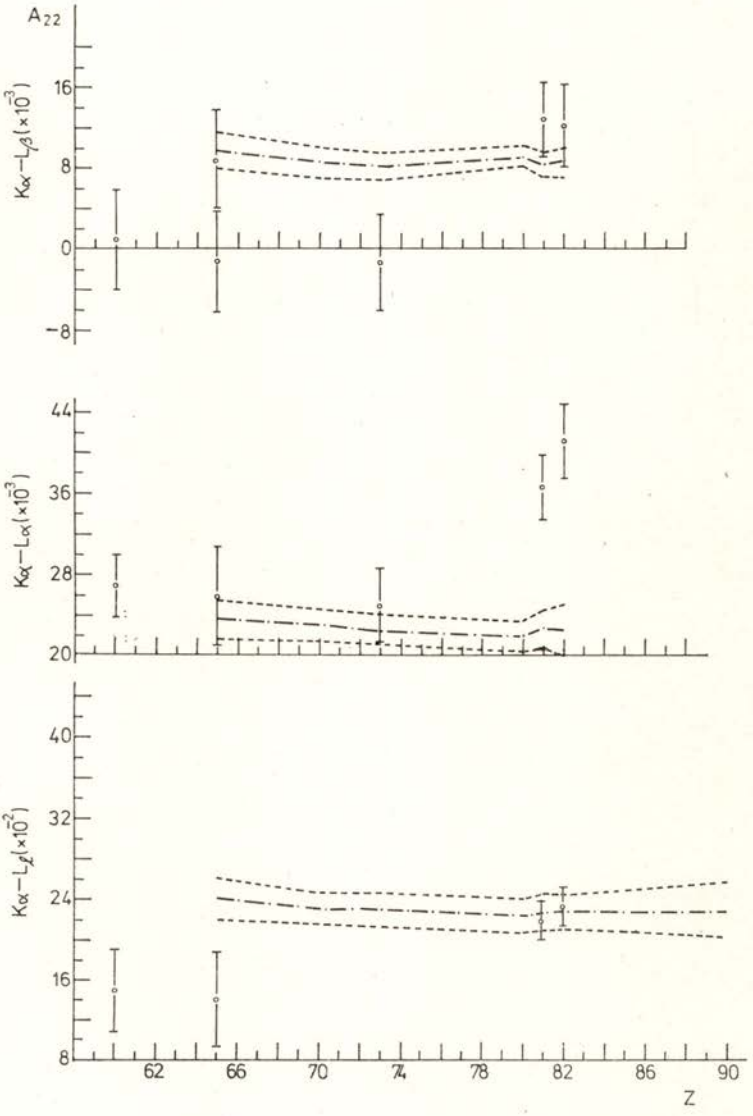

Fig. 4 — Values of the A_{22} angular correlation function's coefficient see table II (*b*)
Experimental values: see table I.

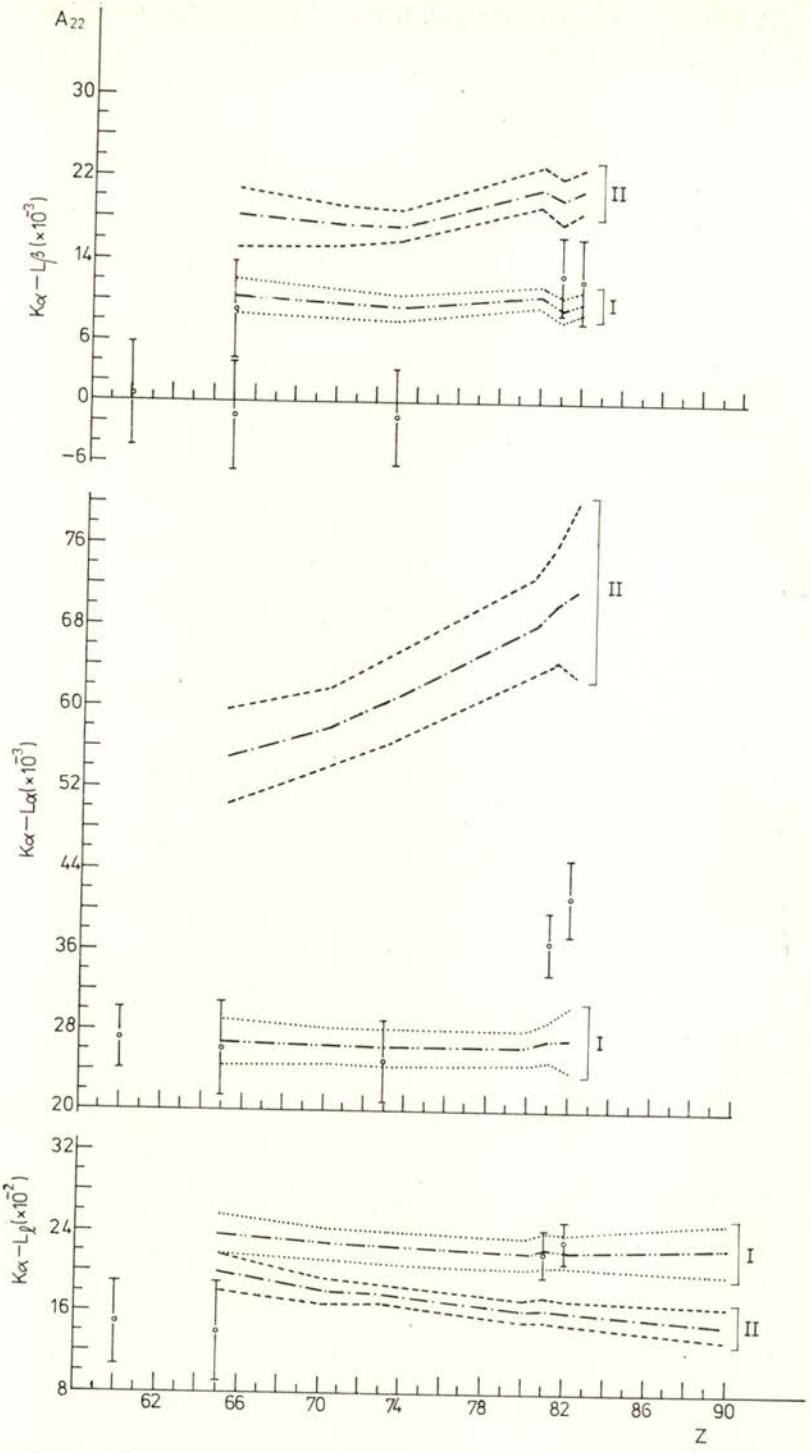

Fig. 5 — Values of the A_{22} angular correlation function's coefficient
I: see table II (*c*) — II: see table II (*e*). Experimental values: see table I.

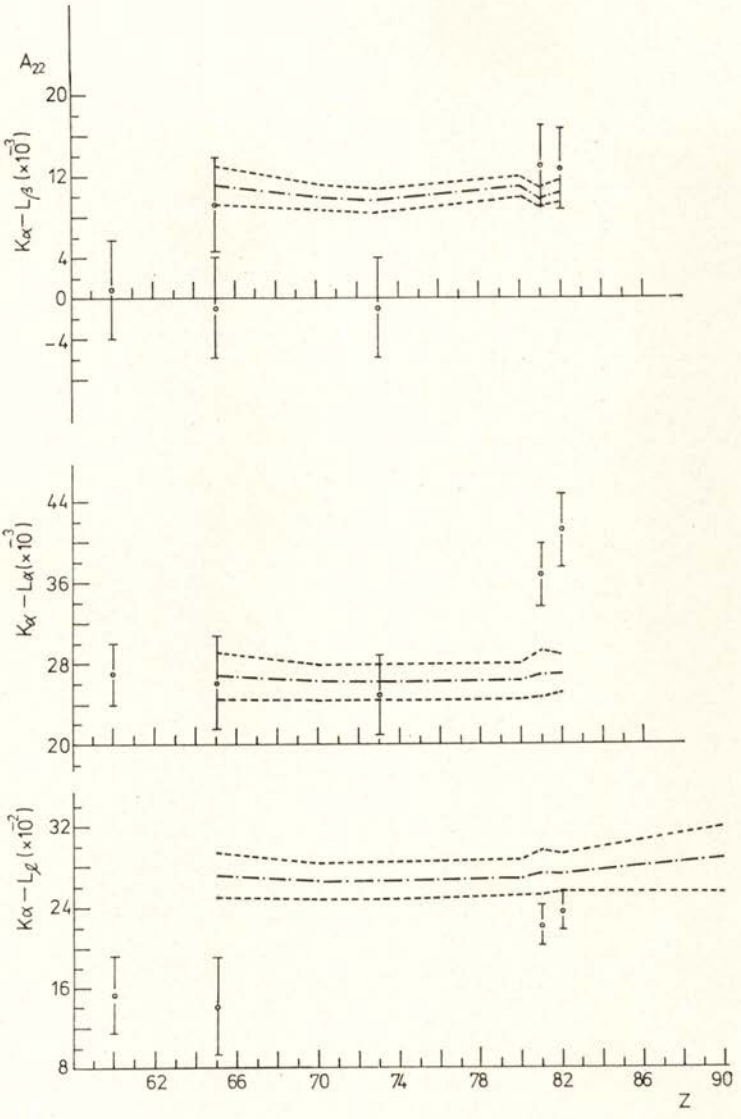

Fig. 6 — Values of the A_{22} angular correlation function's coefficient see table II (*d*)
Experimental values: see table I

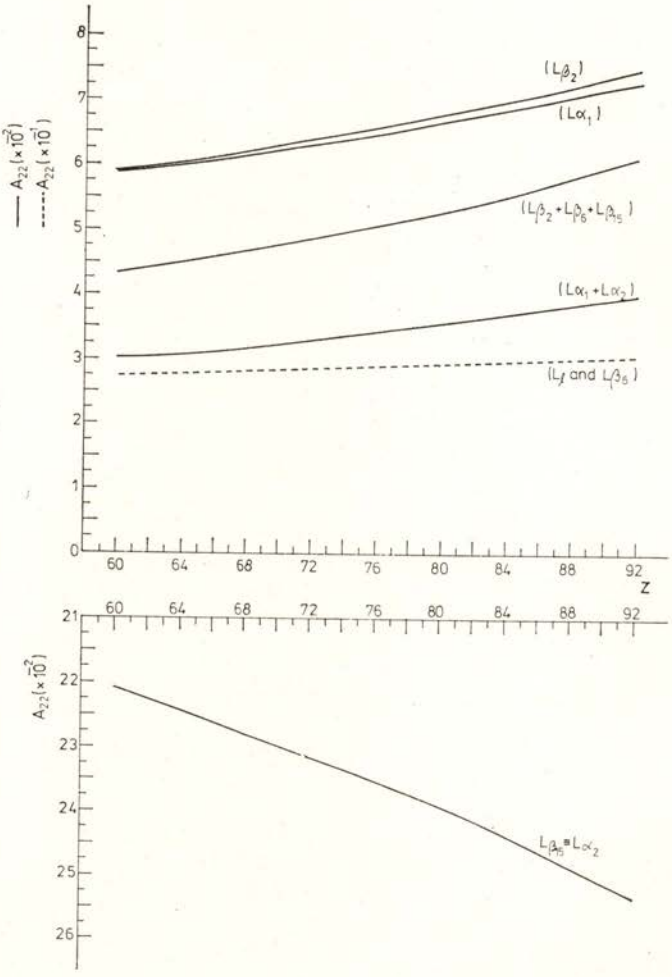

Fig. 7 — Values of the A_{22} coefficient for the $K\alpha_1 - L$ angular correlations with Scofield's values for the mixing ratios.

TABLE III

Theoretical values of A_{22} coeficients

Z	(a)			(b)			(c)			(d)			(e)			(f)
	Kα—Ll $\times 10^{-2}$	Kα—Lα $\times 10^{-3}$	Kα—Lβ $\times 10^{-3}$	Kα—Ll $\times 10^{-2}$	Kα—Lα $\times 10^{-3}$	Kα—Lβ $\times 10^{-3}$	Kα—Ll $\times 10^{-2}$	Kα—Lα $\times 10^{-3}$	Kα—Lβ $\times 10^{-3}$	Kα—Ll $\times 10^{-2}$	Kα—Lα $\times 10^{-3}$	Kα—Lβ $\times 10^{-3}$	Kα—Ll $\times 10^{-2}$	Kα—Lα $\times 10^{-2}$	Kα—Lβ $\times 10^{-3}$	Kα—Ll $\times 10^{-2}$
65	26.7± ±2.3	30.2± ±2.6	11.9± ±1.9	24.1± ±2.1	23.7± ±2.0	9.8± ±1.6	23.7± ±2.0	26.8± ±2.3	10.6± ±1.7	27.2± ±2.3	26.8± ±2.3	11.0± ±1.8	20.0± ±1.7	5.5± ±0.5	18.3± ±3.0	22.5± ±1.9
70	26.0± ±1.7	30.0± ±2.0	11.0± ±1.3	23.1± ±1.5	22.9± ±1.5	8.7± ±1.0	22.7± ±1.5	26.4± ±1.7	9.6± ±1.1	26.6± ±1.8	26.2± ±1.7	10.0± ±1.2	18.3± ±1.2	5.8± ±0.4	17.6± ±2.1	21.1± ±1.4
73	26.2± ±1.8	30.6± ±2.1	10.7± ±1.2	23.0± ±1.6	22.5± ±1.6	8.3± ±0.9	22.5± ±1.6	26.5± ±1.8	9.2± ±1.0	26.7± ±1.9	26.2± ±1.8	9.6± ±1.1	17.9± ±1.2	6.1± ±0.4	17.4± ±1.9	20.7± ±1.4
80	26.2± ±1.8	31.9± ±2.2	11.6± ±1.0	22.5± ±1.6	22.1± ±1.5	9.1± ±0.8	21.9± ±1.5	26.6± ±1.8	10.3± ±0.9	26.9± ±1.9	26.4± ±1.8	10.9± ±1.0	16.4± ±1.1	6.8± ±0.5	21.1± ±1.9	19.7± ±1.4
81	26.7± ±2.1	32.7± ±2.6	11.4± ±1.3	22.8± ±1.8	22.5± ±1.8	8.4± ±0.9	22.2± ±1.8	27.2± ±2.1	9.4± ±1.0	27.4± ±2.2	27.0± ±2.2	10.0± ±1.1	16.5± ±1.3	7.0± ±0.6	20.0± ±2.2	19.9± ±1.6
82	26.8± ±1.9	33.0± ±2.3	12.0± ±1.9	22.9± ±1.6	22.5± ±2.6	8.7± ±0.9	22.2± ±1.6	27.4± ±3.2	9.9± ±1.0	27.6± ±1.9	27.1± ±1.9	10.5± ±1.0	16.3± ±1.2	7.2± ±0.8	20.9± ±2.1	19.7± ±1.4
90	28.0± ±3 3	36.1± ±4.2	—	23.1± ±2.7	—	—	22.4± ±2.6	—	—	29.0± ±3.4	—	—	15.1± ±1.8	—	—	19.0± ±2.2

(*a*) Values of δ^2 given by Scofield [8]; (*b*) $\delta^2 = 0$ for all the radiations of the cascade; (*c*) $\delta^2 = 0$ for $K\alpha_1$ transitions and the values of δ^2 given by Scofield for the L*l* transition; (*d*) The values given by Scofield for $K\alpha_1$ transitions and $\delta^2 = 0$ for L transitions; (*e*) $\delta^2 = 0$ for $K\alpha_1$ transitions and δ^2 (Scofield) multiplied by 10 for L transitions; (*f*) δ^2 (Scofield) for $K\alpha_1$ transitions and δ^2 (Scofield) multiplied by 10 for L transitions.

3 — ω_3 FLUORESCENCE YIELDS AND K — L ANGULAR CORRELATIONS

Price et al. [6] measured the ω_2 and ω_3 values for several elements with atomic numbers between 71 and 92; the ω_3 determinations were made from $K\alpha_1 - L$ coincidence measurements with a geometric efficiency $(1/314) \pm 3\%$ corresponding to [7] a finite-solid-angle correction $f_\Omega = 0.980 \pm 0.030$. Some of these determinations were performed at $\theta = 180°$ and $\theta = 90°$ and the results obtained are listed in table III.

TABLE III

Experimental Fluorescence Yield's values for $\theta = 180°$ and $\theta = 90°$ between detector axis [6]

Element	$\omega_3\,(180°)$	$\omega_3\,(90°)$	Price et al.'s value	Error
$_{73}$Ta	0.254	0.236	0.254	$\pm 5\%$
$_{78}$Pt	0.317	0.290	0.317	$\pm 4.5\%$
$_{79}$Au	0.317	0.278	0.317	$\pm 4\%$
$_{90}$Th	0.517	0.476	0.517	$\pm 4\%$
$_{92}$U	0 500	0.398	0.500	$\pm 4\%$

In fact the A_{22} value can be deduced from the knowledge of $\omega_3(180°)$ and $\omega_3(90°)$ as shown below.

The anisotropy of the $K\alpha_1 - L$ angular correlation is given by

$$\mathfrak{A} = \frac{W(180°) - W(90°)}{W(90°)} \tag{5}$$

where $W(180°)$ and $W(90°)$ are the values of the angular correlation function $W(\theta)$ for $\theta = 180°$ and $\theta = 90°$ respectively.

On other hand, as already pointed out the expression for the determination of the ω_3 fluorescence yield from $K\alpha_1 - L$ coincidence measurements (eq. 1) must be replaced by

$$N_v(K\alpha_1 - L) = N(K\alpha_1)\,\varepsilon\,\frac{\Omega}{4\pi}\,t\,\omega_3\,W(\theta) \tag{6}$$

so that the experimental value for the anisotropy of the angular correlation between those radiations can be obtained from

$$\mathfrak{A} = \frac{\omega_3(180^0) - \omega_3(90^0)}{\omega_3(90^0)}. \tag{7}$$

The anisotropy $\mathfrak{A}$ is connected to the A_{22} coefficient of the angular correlation function by

$$\mathfrak{A} = \frac{3\,A_{22}\,f_\Omega}{2 - A_{22}\,f_\Omega} \tag{8}$$

where f_Ω is the finite-solid-angle correction.

By a straightfoward manipulation of eqs. (5), (7) and (8) the following expression is obtained

$$A_{22} = \frac{2\,[\omega_3(180^0) - \omega_3(90^0)]}{f_\Omega\,[2 \cdot \omega_3(90^0) + \omega_3(180^0)]} \tag{9}$$

which relates the coefficient A_{22} with the experimental quantities $\omega_3(180^0)$ and $\omega_3(90^0)$.

In table IV the theoretical values of A_{22}, calculated as previously mentioned, are compared with experimental values deduced from the results of Price et al. summarized in table III.

4 — DISCUSSION

The experimental results mentioned above show evidence for an angular correlation between the electromagnetic radiations disexciting the atomic levels. On the other hand the experiments

already performed show that the transitions are E1 + M2 mixtures.

From figs. 3 to 6 it is possible to see that, for the $K\alpha - L\alpha$ correlation, the best agreement between theory and available experimental results is obtained when both K and L transitions are considered as E1 + M2 admixtures, with the values of the mixing ratios given by Scofield [8]. This means that these mixing ratios must be almost exact for the $K\alpha$ radiation. However this

TABLE IV

Experimental and theoretical values for A_{22}

Element	A_{22} exp (a)	A_{22} theor.
$_{73}$Ta	0.050 ± 0.006	0.045
$_{78}$Pt	0.061 ± 0.007	0.047
$_{79}$Au	0.091 ± 0.010	0.048
$_{90}$Th	0.057 ± 0.006	0.055
$_{92}$U	0.160 ± 0.018	0.056

is not the case for the $K\alpha - Ll$ correlation. The suggestion of Catz et al. to use a value for the M2 contribution two times greater allows a better agreement to be reached for Tl and Pb but not for the lighter elements.

This is evident from fig. 3 where the A_{22} values, for the $K\alpha - Ll$ angular correlations, are plotted against Z, for two extreme situations: using the values given by Scofield for the mixing ratios and keeping those values for the $K\alpha$ transition but increasing them ten times for the Ll transition. According

(a) From Fluorescence Yields determinations [6].

to the available experimental results the A_{22} values should increase with Z; however the increase of the M2/E1 values for the Ll transitions goes in the opposite direction. Also, for the $K\alpha - L\beta$ correlation the values of Scofield agree with experimental results for Tl and Pb, but once again the discrepancy is evident for the lower atomic numbers.

However an earlier determination of the A_{22} value made by Catz [13] in Tb is in better agreement with the theoretical value than the later one [17].

On the other hand it is important to remark that the fluorescence yields and the Coster-Krönig values are needed for the theoretical calculations mentioned above and that the limits indicated in figs. 3 to 6 are due only to the experimental errors of those quantities.

So in order to compare theoretical and experimental values of mixing ratios it would be very useful to perform $K - L$ angular correlations experiments involving only $K\alpha_1$ radiation. In this case the $K\alpha_1 - Ll$ A_{22} value depends only on the mixing ratios of the transitions involved. For the $K\alpha_1 - L\alpha$ and $K\alpha_1 - L\beta$ angular correlations it will be necessary to consider also the emission rates of the L radiations but not the fluorescence yields and Coster-Krönig values.

On the other hand, measuring the L_{III} subshells fluorescence yields by $K\alpha_1 - L$ coincidences at two different angles one can calculate an A_{22} experimental value for the angular correlation between $K\alpha_1$ radiation and the L group.

The comparison between the results of Price [6] and those which can be obtained from the mixing ratios M2/E1 and the emission rates given by Scofield [8, 18] shows that:

i) Good agreement exists for $_{73}$Ta and $_{90}$Th

ii) A great discrepancy occurs in the case of $_{79}$Au and $_{92}$U

iii) For the $_{78}$Pt the two sets of values are not very far from agreement.

In an earlier paper of Gil et al. [19] an average value of A_{22} was calculated for the $K\alpha_1 - L$ angular correlation function in $_{92}$U and a good agreement was obtained between theory and experiment. However that calculation was performed under the assumption that all radiations involved in the cascade were

pure E1. The present analysis shows that this hypothesis is not admissible.

As already suggested it should be very useful to perform measurements of ω_3 fluorescence yields through $K\alpha_1 - L$ coincidences at different angles of the detector axis and for a wide range of atomic numbers.

Such experiments could give us further information supplementing the one obtained by angular correlations experiments.

ACKNOWLEDGMENT

We are very greatful to Mrs. M. C. Abreu Cunha and Mr. João Cunha who assited this work in preparing the manuscript.

REFERENCES

[1] H. FRAUENFELDER and R. STEFFAN, in α, β, γ ray Spectroscopy (Editor K. Siegbahn, Amsterdam 1965, p. 997).
[2] W. MOELLERING and J. JENSEN, *Z. Phys.* **144**, 252 (1956).
[3] F. BABUSHKIN, *Opt. Spectry.* (U.S.S.R.) **19**, 545 (1965).
[4] H. BESTE, *Z. Phys.* **213**, 333 (1968).
[5] A. KONSTANTINOV and T. SAZONOVA, *Bull. Acad. Sci. U.S.S.R. Phys. Sci.* **32**, 581 (1968).
[6] R. PRICE, H. MARK and C. SWIFT, *Phys. Rev.* **176**, 3 (1968).
[7] W. BAMBYNEK, B. CRASEMANN, R. FINK, H. U. FREUND, H. MARK, C. SWIFT, R. E. PRICE and P. VENUGOPALA RAO, *Rev. Mod. Phys.* **44**, 716 (1972).
[8] J. SCOFIELD, Private communication, (1971) in Ref. 7.
[9] R. WOOD, J. M. PALMS and P. VENUGOPALA RAO, *Phys. Rev.* **187**, 1497 (1969).
[10] A. CATZ and C. CORYELL, *Bull. Amer. Phys. Soc.* **14**, 85 (1969).
[11] A. CATZ, *Bull. Amer. Phys. Soc.* **15**, 72 (1970).
[12] E. MACIAS and A. CATZ, *Bull. Amer. Phys. Soc.* **15**, 72 (1970).
[13] A. CATZ and E. MACIAS, *Bull. Amer. Phys. Soc.* **15**, 880 (1970).
[14] A. CATZ, *Phys. Rev. Lett.* **24**, 127 (1970).
[15] A. CATZ, *Phys. Rev.* A **2**, 634 (1970).
[16] A. CATZ and E. MACIAS, *Phys. Rev.* A **3**, 849 (1971).
[17] A. CATZ and E. MACIAS, *Bull. Amer. Phys. Soc.* **16**, 126 (1971).
[18] J. SCOFIELD, *Phys. Rev.* **179**, 9 (1969).
[19] F. B. GIL, A. BARROSO, J. C. SOARES and J. G. FERREIRA, *Phys. Rev.* A **5**, 536 (1972).