Materials Science and Technology (MS&T) 2013
October 27-31, 2013, Montreal, Quebec, Canada

Optical and X-ray Imaging Techniques for Material Characterization

MEASUREMENT OF MAGNETIC QUADRUPOLE-ELECTRIC DIPOLE MIXING RATIOS AND ANGULAR DISTRIBUTION PARAMETERS IN ATOMIC INNER-SHELL TRANSITIONS

Ridvan Durak[1], M. Recep Kacal[2], Ferdi Akman[3], Fatma Akdemir[1], Oguz Aksakal[1], M. Fatih Turhan[4]

[1]Physics Department, Science Faculty, Ataturk University, 25240 Erzurum / Turkey
[2]Physics Department, Science and Art Faculty, Giresun University, 28200 Giresun / Turkey
[3]Physics Department, Science and Art Faculty, Bingol University, 12000 Bingol / Turkey
[4]Ataturk Voc. School of Health Serv., Afyon Kocatepe University, 03200 Afyon / Turkey

Keywords: X-rays, Mixing ratios, Angular distribution parameters, Atomic transitions

Abstract

In studies of the angular distribution of the magnetic L_3-subshell X-ray transitions it has been generally assumed that observed radiations consist of pure electric dipole transitions and contributions from higher-order multipole terms have been overlooked. However, this assumption is questionable, especially in the case of heavy elements and high energies. In this study, by analysis of the angular distribution of the 22.6 keV photon induced X-ray transitions of U, Tl, Ta and Er the subshell alignment , the anisotropy parameters have been measured and from the measured parameters α kinematic coefficients, M2/E1 mixing ratios and polarization degrees have been deduced by energy dispersive X-ray fluorescence (EDXRF) system. The obtained results were compared with a few experimental and theoretical predictions available in the literature.

Introduction

In atomic inner-shell photoionization studies, X-ray transitions give important indications about atomic structure. An accurate knowledge of the nature of the X-ray transitions is very important in the analysis of angular distribution of X-ray radiation and angular correlations of two consecutive X-ray transitions (K and L), measurements of X-ray fluorescence and ionization cross sections, radiative and non-radiative transition probabilities researches and developing more reliable theoretical models describing fundamental inner-shell ionization processes.

In studies of the angular distribution of the L_3 (j = 3/2) magnetic subshell X-ray transitions it has been generally assumed that observed radiations consist of pure electric dipole (E_1) transitions and contributions from magnetic quadrupole transitions (M_2) have been usually overlooked [1-2]. However the contribution of these transitions to the atomic X-ray transitions increases with increasing energy of the X-ray transition and atomic number. This can give rise to modify of the angular distributions, of the polarization and so of the anisotropy (β) and of the correlation parameters (A_{22}) and of the transition rates of electric dipole allowed K, L, M,... X-ray spectral lines in the region of heavy elements or cause produce of the some weaker lines in the spectra. This approximation is supported by theoretical results [3] whose results were obtained using relativistic single-particle Hartree-Slater wave functions for the X-ray transition matrix element of different multipoles. For instance, Bambynek *et al*. calculated that the $\delta 1$ $(M2/E1)$ mixing ratio for the Ll line is less than 1% for any elements [4]. This state causes significant discrepancies and deviations (several times larger deviation than the theoretical predictions) between experimental results and theoretical predictions of angular distributions and angular correlations of L and M X-ray lines. Therefore, there are needed new experimental studies taking into consideration influence of the higher-order multipole terms, in particular effect of the $M2$ magnetic quadrupole transitions [5-8].

In this study, angular distribution of U, Tl, Ta and Er elements induced by the excitation energy of 22.6 keV X-rays emitted from a ^{109}Cd radioactive point source were measured. Afterward the $\beta(Ll)$, $\beta(L\beta_6)$, $\beta(\alpha_{1,2})$ and $\beta(L\beta_{2,15})$ anisotropy and alignment parameters and effect of the mixing ratio $\delta 1$ $(M2/E1)$ on these anisotropy parameters were investigated from the angular dependence measurements.

Experimental Procedure

The experiments were carried out using a ^{109}Cd point source of strength 40 mCi. The exciting source and samples are placed on goniometry graduated turntable so that angles could be arranged accurately. The L X-rays emitted from the target were detected by a Si(Li) detector (FWHM = 160 eV at 5.9 keV, active area 12 mm^2, thickness 3 mm, Be window thickness 0.025 mm). The detector was also placed in a step-down shield made from Pb, Fe and Al to minimize the detection of any radiation coming directly from the source and scattered from the surroundings.

The spectra were measured at six different angles varied from 90° to 140° at intervals of 10°. The angle of incidence radiation with sample without changing the source- target solid angle was kept fixed at 60°. The spectra were accumulated in time intervals ranging from 4 to 12 h in order to sufficient statistical accuracy. A typical L X-ray spectrum of U at θ= 140° is shown in Fig. 1.

Theory

The angular distribution of X-ray lines from the decay of photoionization aligned L_3-sub-shell vacancies given by the

$$I(\theta) = (I_0/4\pi)[1 + \beta P_2(Cos\theta)] \quad (1)$$

if the ionization and detection system are axially symmetric and there is only a single vacancy in ionized atom. Where I_0 denotes the total intensity emitted into the 4π solid angle, P_2 is the second-order Legendre polynomial and β is the anisotropy parameter.

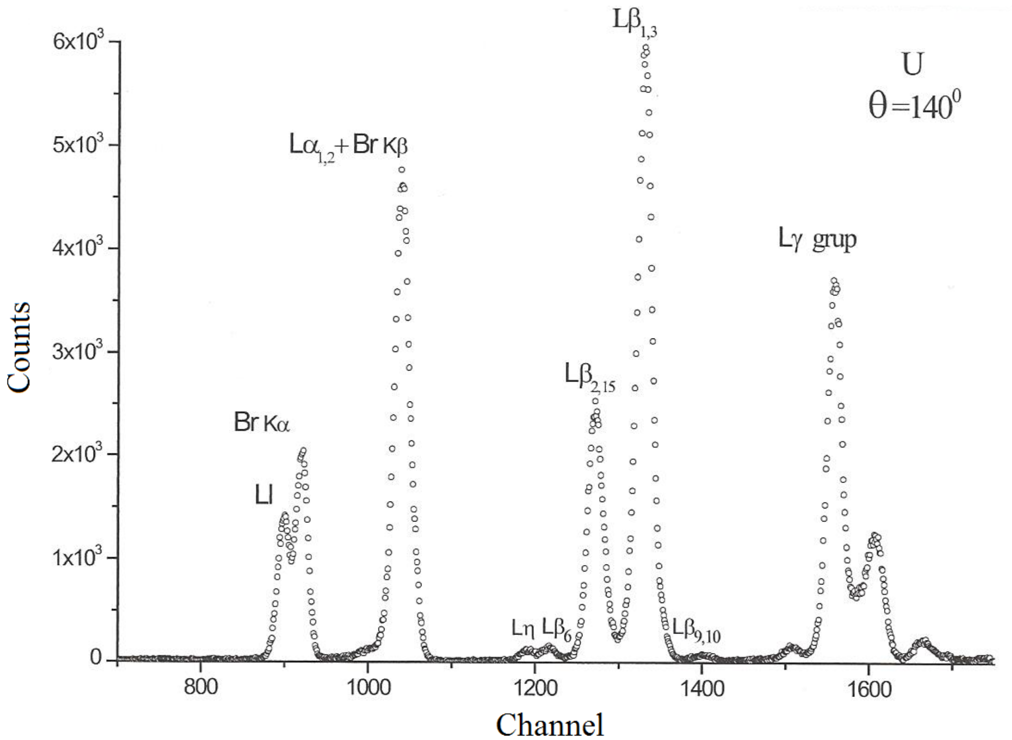

Figure 1. A typical *L* X-rays spectrum of *U* at θ = 140°.

For independent ionization and decay processes β can be expressed as

$$\beta = \kappa\alpha A_2 \tag{2}$$

where A_2 is the alignment parameter (the nonstatistical population of the various magnetic substates). The kinematic coefficient α depends on the total angular momentum of initial and final states and on the mixing ratios of the X-ray transition. The correction factor κ takes into account that L_3 holes can also be created by Coster-Kronig transitions. Among the L_3 sub-shell X-rays the $L\alpha_2(L_3 - M_4)$ and $L\beta_{15}(L_3 - N_4)$ transitions have a special character, namely that magnetic terms do not occur in their multipole expansions and they assume as pure electric dipole transitions. The energy-level diagram of L_3 x- rays transition and decay scheme of heavy elements are showed in Fig. 2.

For the El allowed *L* transitions practically only the M2 component can be mixed with the El, and the parameter can be expressed as function of δ1(M2/E1) for the different transitions

$$\begin{aligned}
&\alpha(L\ell) = 0.5 - \sqrt{3}\delta1(L\ell)\\
&\alpha L(\beta 6) = 0.5 - \sqrt{3}\delta(L\beta_6)\\
&\alpha(L\beta 2) = 0.1 + \sqrt{7/5}\,\delta1(L\beta_2)\\
&\alpha(L\alpha 1) = 0.1 + \sqrt{7/5}\,\delta1(L\alpha_1)\\
&\alpha(L\alpha 2) = -0.4\\
&\alpha(L\beta 15) = -0.4
\end{aligned} \tag{3}$$

where the quadratic terms in δ_1 were neglected.

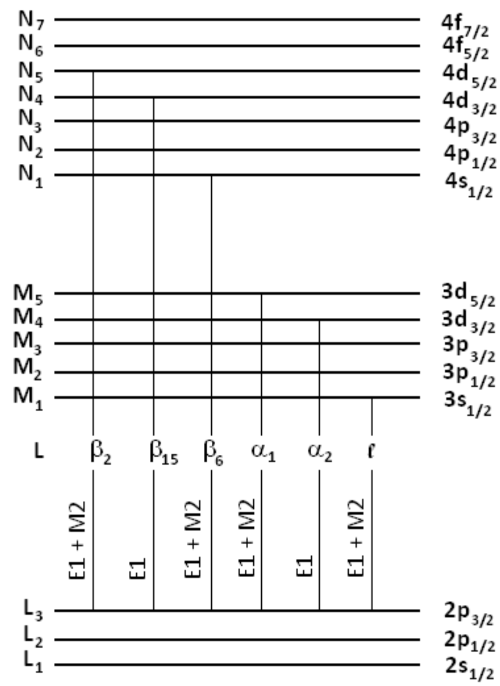

Figure 2. The energy level diagram of L_3 X-rays transition and decay scheme of heavy elements.

If $L\alpha_1$ and $L\alpha_2$(and similarly the $L\beta_2$ and $L\beta_{15}$) lines are not resolved by Si(Li) detector, the α parameter for the $L\alpha_{1,2}$and $L\beta_{2,15}$ lines are given by,

$$\alpha\left(L\alpha_{1,2}\right) = \left(\left(0.1 + \sqrt{7/5}\,\delta 1(L\alpha_1) - 0.4\mathrm{R}_\alpha\right)/(1 + \mathrm{R}_\alpha)\right) \tag{4}$$
$$\alpha(L\beta_{2,15}) = \left(\left(0.1 + \sqrt{7/5}\,\delta 1\left(L\beta_2\right) - 0.4\mathrm{R}_\beta\right)/\left(1 + \mathrm{R}_\beta\right)\right)$$

where $\mathrm{R}_\alpha$and R_β denote the intensity ratio of the $L\alpha_1$ and $L\alpha_2$lines and the $L\beta_2$ and $L\beta_{15}$ lines, respectively.

The $I_{Li}/I_{Lj}\ (\theta)$ intensity ratios determine by using the well-known equation;

$$\frac{I_{Li}}{I_{Lj}}(\theta) = \frac{N_{Li}}{N_{Lj}}(\theta)\frac{T_{Lj}}{T_{Li}}(\theta)\frac{\varepsilon_{Lj}}{\varepsilon_{Li}}(\theta) \tag{5}$$

where $N_{Lj}/N_{Li}(\theta)$ is the ratio of the counts under the L_j and L_i peaks at angle θ, $T_{Lj}/T_{Li}(\theta)$ is the ratio of the self-absorption correction factors of the target for the L_j and L_i at angle θ and $\varepsilon_{Lj}/\varepsilon_{Li}(\theta)$ is the ratio of the detector-efficiency values for the L_j and L_iX-rays at angle θ.

The ratio of β anisotropy parameters of different X-rays transitions, having the same final states, does not depend on the alignment parameters and is independent of the ionization process (as long as single ionization is the dominating ionization process). The ratio of the anisotropy parameters of these lines can be written as

$$\frac{\beta^i}{\beta^j} = \frac{\alpha^i \kappa A_2}{\alpha^j \kappa A_2} = \frac{\alpha^i}{\alpha^j} \tag{6}$$

where the superscripts (k = i,j) refer to two different transitions [7].

Results and Discussions

The intensities of L_3 X-rays lines were normalized to the total intensity of the X-rays lines of the isotropic $L\gamma$ group. For the elements, the normalized intensity of L_3 X-rays were calculated using the Eq.5. The normalized intensities were fitted to the function (1) and showed in Fig.3 as function of the second-order Legendre polynomial. The measured anisotropy parameters from the relative intensity of L X-rays and $\alpha(Ll)/\alpha(L\beta_6)$ and $\alpha(Ll)/\alpha(L \propto_{1,2})$ kinematic coefficients ratios obtained from their ratios are listed along with the standard deviation errors in Table 1.

Table.1. The experimental anisotropy parameters (β), $\alpha(Ll)/\alpha(L\beta_6)$ and alignment , the anisotropy parameters$\alpha(Ll)/\alpha(L\alpha_{1,2})$ kinematic coefficients ratios, .

	U	**Tl**	**Ta**	**Er**
$\beta(Ll/L\gamma)$	-0.209±0.009	-0.137±0.009	-0.132±0.007	-0.139±0.008
$\beta(L\beta_6/L\gamma)$	-0.177±0.010	-0.118±0.007	-	-
$\beta(L\alpha_{1,2}/L\gamma)$	-0.026±0.001	-0.019±0.001	-0.019±0.001	-0.020±0.001
$\beta(L\beta_{2,15}/L\gamma)$	-0.030±0.002	-	-0.021±0.001	-0.023±0.001
$\alpha(Ll)/\alpha(L\beta_6)$	1.18±0.08	1.16±0.09	-	-
	1.27±0.07*			
$\alpha(Ll)/\alpha(L\alpha_{1,2})$	8.04±0.51	7.21±0.50	6.95±0.47	6.95±0.47
	6.24±0.78*			6.87±1.53*
A_2	-0.592±0.023	-	-	-
$\delta_1(Ll/L\gamma)$	0.011±0.002	-	-	-
	0.036±0.014*			
	0.0001006**			
$\delta_1(L\beta_6/L\gamma)$	0.053±0.008	-	-	-
	0.086±0.016*			
	0.0001842**			

^{109}Cd radioactive source has a 3.6 % probability of emitting 88.04 keV γ rays and K shell of *Tl* can be ionized by these rays. The K shell vacancy can be transferred to the L_3 sub-shell and it produces a negative effect on the anisotropy parameters. Our approximate calculations display that such a transfer of vacancy is 0.1% compared to the produced vacancies by the direct ionization of the L_3 sub-shell of *Tl* with 22.6 keV X-rays. So, we did not correct for such an effect here. K shell binding energy of U is above 88.04 keV and such an effect for U does not occur.

To determine the alignment parameters (A_2) of the L_3 X-rays of elements obtained without neglecting mixing ratios ($\delta 1\,(M2/E1)$), the anisotropy parameter of $L\alpha_2$ or $L\beta_{15}$ line that multipole expansions do not consists of magnetic terms (pure $E1$ decay) has to be measured as experimental. But the $L\alpha_1$, $L\alpha_2$ and the $L\beta_2$, $L\beta_{15}$lines are not resolved by Si(Li) detector. Therefore, the total intensities of $L\alpha_{1,2}$and $L\beta_{2,15}$ lines were measured by the detector.

The theoretical $\alpha(Ll)/\alpha(L\beta_6)$ and $\alpha(Ll)/\alpha\left(L \propto_{1,2}\right)$ kinematic coefficients ratios were calculated with and without mixing ratio using theoretical estimates [9]. Scofield's calculations indicate that with increasing Z the contribution of the quadrupole mixing on kinematic coefficients is increasing. We observed for Ll line the largest value of anisotropy parameter. So, it is the most appropriate line to examine effect of mixing ratio on kinematic coefficients. For U, *Tl*, elements, the experimental $\alpha(Ll)/\alpha(L\beta_6)$ values were found to be 1.18±0.08 and 1.16±0.09, respectively and the results are about 19 and 16 % larger than the theoretical calculations [9]. This state shows that the mixing ratio is larger for the $L\beta_6$ line than for Ll the line. The result is compatible with the theoretical values.

To determine the alignment parameters (A_2) of the L_3 X-rays of elements obtained without neglecting mixing ratios ($\delta 1\,(M2/E1)$), the anisotropy parameter of $L\alpha_2$ or $L\beta_{15}$ line that multipole expansions do not consists of magnetic terms (pure $E1$ decay) has to be measured as experimental. But the $L\alpha_1$, $L\alpha_2$ and the $L\beta_2$, $L\beta_{15}$lines are not resolved by Si(Li) detector. Therefore, the total intensities of $L\alpha_{1,2}$and $L\beta_{2,15}$ lines were measured by the detector.

The theoretical $\alpha(Ll)/\alpha(L\beta_6)$ and $\alpha(Ll)/\alpha\left(L \propto_{1,2}\right)$ kinematic coefficients ratios were calculated with and without mixing ratio using theoretical estimates [9]. Scofield's calculations indicate that with increasing Z the contribution of the quadrupole mixing on kinematic coefficients is increasing. We observed for Ll line the largest value of anisotropy parameter. So, it is the most appropriate line to examine effect of mixing ratio on kinematic coefficients. For *Th* and *Tl* elements, the experimental $\alpha(Ll)/\alpha(L\beta_6)$ values were found to be 1.19±0.09 and 1.16±0.09, respectively and the results are about 19 and 16 % larger than the theoretical calculations [9]. This state shows that the mixing ratio is larger for the $L\beta_6$ line than for Ll the line. The result is compatible with the theoretical values.

For Ll lines of U and Au elements, the obtained experimental mixing ratio values $\delta 1\,(M2/E1)$ the by who used 0.5 and 1.5 MeV protons for excitations are larger about 400-900 times than Scofield's theoretical estimates and the results demonstrated that knowledge of the mixing ratio is necessary in inner-shell alignment studies. We have found the $\alpha(Ll)/\alpha(L\alpha_{1,2})$ ratios of Ll and $L\alpha$ transitions of *U, Tl, Ta and Er* elements to be 8.04±0.51, 7.21±0.51, 6.95±0.47 and 6.95±0.47 respectively. These ratios significantly deviate from theoretical value of 10.2 [9] and the deviations is quite beyond the error limit of the measurements.

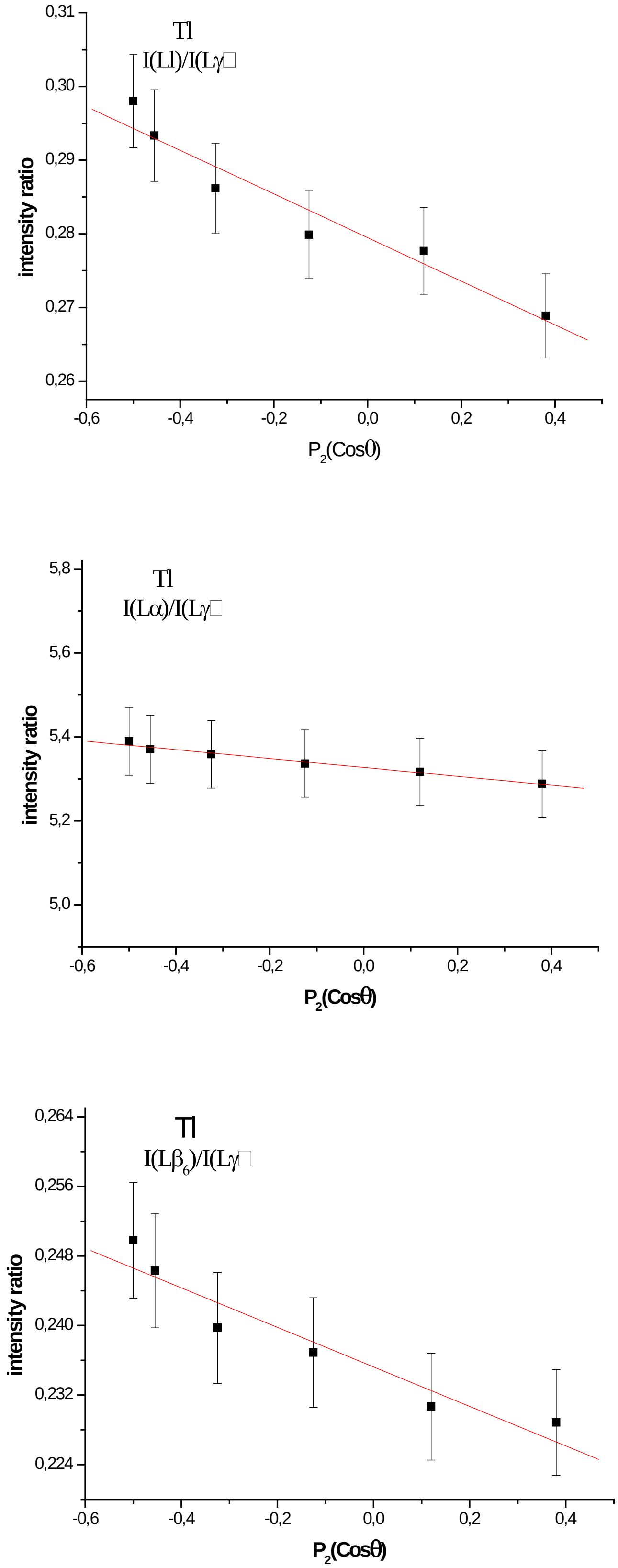

Figure 3. Measured relative intensities of $L\ell$, $L\beta_{2,15}$, $L\alpha_{1,2}$ and $L\beta_6$ lines of the *Tl* elements as a function of $P_2(Cos\theta)$.

Our the results clearly exhibit that knowledge of the $\delta 1\,(M2/E1)$ magnetic quadrupole mixing ratio becomes important in angular distribution studies and it cannot be neglected in these experimental studies.

To obtain a more definite conclusions on the contribution of the $\delta 1\,(M2/E1)$) mixing ratio to anisotropy parameters in angular distribution studies, more experimental investigations are clearly needed.

References

1. W. Jitschin, H. Kleinpoppen, R. Hippler, and H. O. Lutz,. L-shell alignment of heavy atoms induced by proton impact ionization. J. Phys. B: At. Mol. Opt. Phys. (12**)**, (1979) 4077–4084.
2. J. Palinkas, L. Sarkadi, and B. Schlenk, L3-Subshell Alignment In Gold Following Low-Velocity Proton And He^+ Impact Ionization, J. Phys. B. 13 (1980) 3829-3834.
3. J.H. Scofield, Relativistic Hartree-Slater Values for K and L X-ray Emission Rates. At. Data Nucl. Data Tab. (14) (1974) 121–137.
4. W. Bambynek, B. Crasemann, R.W. Fink, H. U. Freund, H. Mark, C. D. Swift, R. E. Price, P. Venugopal Rao, X-ray Fluorescence Yields, Auger, and Coster-Kronig Transition Probabilities. Rev. Mod. Phys. (44**)** (1972) 716.
5. H. Yamaoka, M. Oura, K. Takahiro, T. Morikawa, S. Ito, M. Mizumaki, S. Semenov, N. Cherepkov, N. Kabachnik, and T. Mukoyama, Alignment following Au L_3 photoionization by synchrotron radiation. J. Phys. B: At. Mol. Opt. Phys. (36**)** (2003) 3889–3897.
6. T. Papp, Y. Awaya, A. Hitachi, T. Kambara, Y. Kanai, T. Mizogawa, and I. Török, Angular distribution measurement of various L_3 X-ray transitions. J. Phys. B: At. Mol. Opt. Phys. (24**) (**1991) 3797.
7. T. Papp, J.L. Campbell, and J. A. Maxwell, Deviation from the single-particle model in the angular distribution of thorium L_3 x rays in proton-impact ionization Phys. Rev. A (48**)** (1993) 3062.
8. T. Papp, and J. L. Campbell, Non-statistical population of magnetic substates of the erbium L_3 sub-shell in photoionization. J. Phys. B: At. Mol. Opt. Phys. (25) (1992)3765.
9. J. H. Scofield, Theoretical Radiative Transiton Rates For K- and L-Shell X Rays. Lavrence Livemore Laboratory Report No. Ucrl 51231, (1972).