Magnetic-quadrupole–electric-dipole mixing in L_3 x-ray transitions of heavy elements

T. Papp, J. Pálinkás, and L. Sarkadi
Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, H-4001, P.O. Box 51, Hungary
(Received 16 March 1990)

The angular distribution of L_3 x rays of Th and U ionized by 1.5-MeV protons has been measured and the anisotropy parameters of these lines have been deduced. The ratios of the anisotropy parameters of the different L_3 lines were found to disagree with the theoretical predictions. For U, the alignment of the L_3 subshell has been determined from the angular distribution of the $L\alpha_2$ line, and from the measured anisotropy of the other L_3 x-ray lines the magnetic-quadrupole–electric-dipole mixing ratios were deduced. The experimental mixing ratios for the $ns_{1/2}$-$2p_{3/2}$ transitions are significantly larger than the theoretical values.

I. INTRODUCTION

Several experimental studies of the L_3-subshell alignment of heavy elements were performed in the last decade (see Refs. 1–4, and references therein). In these studies the experimental alignment parameters were deduced from the measured angular distribution or polarization of the emitted $Ll(L_3\text{-}M_1)$ x-ray line assuming pure electric dipole ($E1$) transition. This assumption[5] is supported by the results of a calculation by Scofield,[6] where the x-ray transition matrix elements of different multipoles were calculated using relativistic single-particle Hartree-Slater wave functions. This calculation gave small magnetic quadrupole ($M2$) mixing to the $E1$ amplitude for electric dipole allowed L_3 x-ray transitions. As an example it predicts that the $M2$-$E1$ mixing ratio (δ_1) for the Ll line is less than 1% for any element.[7]

These theoretical calculations were in accord with the results of K-L angular correlation measurements.[8] The experimental K-L angular correlation parameters (A_{22}) agreed with the theory of the $K\alpha_1$-$L\alpha$ cascade, and in tendency agreed with the theory for the $K\alpha_1$-Ll cascade. The K-L angular correlation parameters, however, depend on the mixing ratios of both transitions of the cascade and therefore do not give direct information on the $M2$-$E1$ mixing in the individual transitions of a K-L cascade.

The study of the angular distribution of L_3 x-ray lines of heavy elements ionized by low-velocity protons gives a very good possibility for the study of the $M2$-$E1$ mixing in L_3 x-ray transitions.[9] In these cases the ionizing collision produces large (-0.5) alignment on the L_3 subshell, and the influence of the $M2$ mixing in a single M-L_3 transition can be studied. In an earlier Rapid Communication[10] we reported experimental determination of the $M2$-$E1$ mixing ratios (δ_1) for the L_3 x-rays of gold, and found that the $M2$-$E1$ mixing ratio for the Ll transition was about 4%, i.e., 6 times larger than the theoretical value. Our observation showed that the $M2$-$E1$ mixing has to be taken into account in the determination of the alignment parameters. The results were in accord with the conclusion of an earlier K-L angular correlation study on lead.[8]

The existence of the $M2$ component in the transitions is a relativistic effect, and one can expect that the $M2$-$E1$ mixing is even larger for the L x-ray transitions of heavier elements. The above-mentioned calculation by Scofield[6] also showed this tendency. In the present study we have extended our measurements to thorium and uranium, which give the further advantages that the angular distribution of the $L\beta_6(L_3\text{-}N_1)$ and $L\beta_{2,15}(L_3\text{-}N_{5,4})$ transitions can also be studied with a semiconductor detector.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

The angular distribution of x-ray lines from the decay of collisionally aligned L_3-subshell vacancies is given by the

$$W = W_0[1+\beta P_2(\cos\theta)] \tag{1}$$

formula, if the ionization and detection systems are axially symmetric, and there is only a single vacancy in the ionized atom. Here P_2 is the second-order Legendre polynomial, β is the anisotropy parameter, which for independent ionization and decay processes can be expressed as

$$\beta = k\alpha A_2 , \tag{2}$$

where A_2 is the alignment parameter, and a depends on the total angular momentum of the initial and final states and on the mixing ratios of the x-ray transition.[9,10] The correction factor k takes into account that L_3 holes can also be created by Coster-Kronig transitions.[1]

Among the L_3-subshell x rays the $L\alpha_2(L_3\text{-}M_4)$ and $L\beta_{15}(L_3\text{-}N_4)$ transitions have a special character, namely that magnetic terms do not occur in their multipole expansions.[6] Since the reduced matrix element of the $E3$ is much smaller than that of the $E1$, and the $E2$ transition is parity forbidden, one can assume that these transitions have pure $E1$ character and their a parameter is the $E1$ value (-0.4). Therefore, the A_2 parameter of the L_3

subshell can be determined precisely from the measured anisotropy parameters of the $L\alpha_2$ and $L\beta_{15}$ x rays, and using this A_2 parameter the experimental α values for the other L_3 x rays can be determined from their measured anisotropy parameters.

For the $E1$ allowed L_3 transitions practically only the $M2$ component can be mixed to the $E1$,[6] and the a parameter can be expressed as function of δ_1 for the different transitions[9,10]

$$\begin{aligned} \alpha(Ll)&=0.5-\sqrt{3}\delta_1(Ll)\ ,\\ \alpha(L\alpha_1)&=0.1+\sqrt{7/5}\delta_1(L\alpha_1)\ ,\\ \alpha(L\beta_6)&=0.5-\sqrt{3}\delta_1(L\beta_6)\ ,\\ \alpha(L\beta_2)&=0.1+\sqrt{7/5}\delta_1(L\beta_2)\ , \end{aligned} \tag{3}$$

where the quadratic terms in δ_1-s were neglected.

If the $L\alpha_1$ and $L\alpha_2$ (and similarly the $L\beta_2$ and $L\beta_{15}$) lines cannot be separated by the detector only, the net anisotropy of the $L\alpha_{1,2}$ and $L\beta_{2,15}$ lines can be obtained from the angular distribution measurement. Using the branching ratios from Ref. 11, the deduced α parameters for Th and U are given by

$$\begin{aligned} \alpha(L\alpha_{1,2})&=0.048+1.06\delta_1(La_1)\ ,\\ \alpha(L\beta_{2,15})&=0.051+1.06\delta_1(L\beta_2)\ . \end{aligned} \tag{4}$$

Accurate experimental values for δ_1-s can be obtained for these systems, where the collisionally induced alignment is large, and the correction factors are small. Corrections have to be made for the multiple ionization,[12] and for the Coster-Kronig transitions. For uranium the minimum of these corrections occurs at 1–1.5-MeV proton impact, where the alignment is still large.

Another crucial point in this experiment is the separation of the $L\alpha_2$ transition from the $L\alpha_1$ (or the $L\beta_{15}$ from the other transitions). This separation can be achieved for certain elements using appropriate absorbers in front of a Si(Li) detector.[10,13] In the present study this separation of the $L\alpha_2$ and $L\alpha_1$ lines of U were performed using a bromine absorber, with its K-absorption edge falling between the $L\alpha_2$ and $L\alpha_1$ lines. Using appropriate (25 mg/cm^2) thickness the attenuation for the $L\alpha_1$ is much larger (200) than for the La_2 (2), and the $L\alpha$ line of the spectrum measured by a Si(Li) detector behind the absorber is mainly (90%) the $L\alpha_2$ line.

The experimental setup in this measurement was similar to that used in our previous angular distribution measurements,[14] and only the main points are summarized here. The 1.5-MeV proton beam, obtained from the 5-MV Van de Graaff generator of ATOMKI was collimated to 1 mm on the target, tilted at 45°. Th and U targets of 100 μg/cm^2 produced by a chemical method[15] on 10-μg/cm^2 carbon backing were used. The x rays were detected with a Si(Li) detector having a 190 eV full width at half maximum (FWHM) resolution at 5.9 keV. The detector was assembled on a turn table and could be rotated around a small scattering chamber. The detector target distance was 7 cm, and the x-ray exit slit on the scattering chamber was covered with 4 mg/cm^2 Al and 107 mg/cm^2 polyethylene terephthalate (PET) foils.

The angular distribution of the $L\alpha_2$ line of U was measured using a 25-mg/cm^2 Br absorber in front of the Si(Li) detector to absorb the $L\alpha_1$ line. The absorber was produced by pressing the 1:1 mixture of NaBr and a plastic matrix into a 10-mm-diam disk, which has been mounted on the beryllium window of the detector. The effect of the La escape peak on the Ll angular distribution has been studied in a separate measurement, where a 9-mg/cm^2 Se absorber was mounted on the Be window to reduce the $I(L\alpha)/I(Ll)$ ratio.

The angular distribution of the uranium L x rays was measured in three different runs: without an absorber, with a NaBr absorber, and with a Se absorber. The angular distribution of the thorium L x rays was measured without absorber. To avoid the pileup effects, a low counting rate was used (between 10^3 and 2×10^3 counts/sec). The spectra were measured at ten different angles in the range of 15°–105°. In each spectra the Ll line had more than 10^5 counts. A typical Th spectrum can be seen in Fig. 1.

The x-ray spectra, measured without an absorber, were analyzed with a Gaussian fitting program, which fitted a quadratic polynomial background and an appropriate number of Gaussian peaks simultaneously. A linear function plus a step function convolved with a Gaussian was used to fit the background in spectra measured with absorbers. The width of the Gaussian corresponded to the detector resolution.

The attenuation of the x-ray lines in the absorber does not affect the determination of the anisotropy parameter, since the absorption is in the same at each angle. It has to be taken into account, however, in the determination of the Coster-Kronig correction. This correction was calculated from the measured line intensities,[1] and we used the mass attenuation coefficient of Montenegro *et al.*[16] and McMaster *et al.*[17] to correct the measured line intensities for absorption by the window and absorbers.

In the analysis of x-ray spectra measured with absorbers two further problems have to be considered: (i)

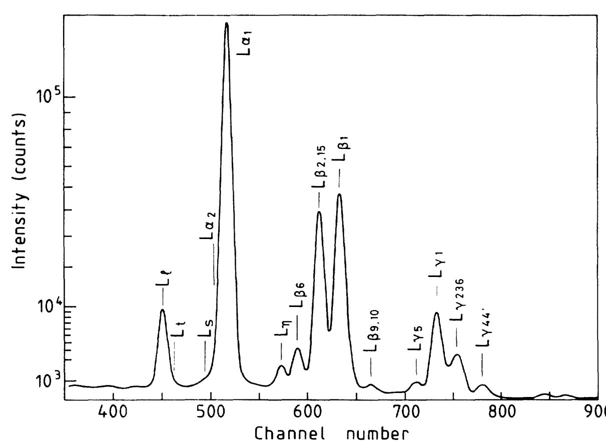

FIG. 1. L-shell spectrum of Th, ionized by 1.5-MeV-proton impact, and measured with a Si(Li) detector at 90°.

The spectrum contains the fluorescent $K\alpha$ and $K\beta$ peaks of the absorber. (ii) The absorber cuts out part of the $L\alpha_2$ satellites and the normally applied Coster-Kronig corrections have to be modified.

The $K\alpha$ line of the absorber can be seen in the spectra as a shoulder on the higher-energy part of the Ll line and can be fitted together with the Ll line. It can also be estimated from the applied geometry and the absorber thickness.[13] The intensity of the $K\beta$ can be determined from the $K\alpha$ intensity, using the known $I(K\alpha)/I(K\beta)$ ratio.[11]

Considering the effect of the $L\alpha_2$ satellites one has to take into account that there are different types of $L\alpha_2$ satellites depending on their origin. L_3M satellites are emitted when an M-shell hole has been created simultaneously with the ionization of the L_3 subshell by the projectile. This L_3M double ionization has very small probability relative to the single ionization (a few times 10^{-3}; according to semiclassical approximation (SCA) calculations made in the independent-electron approximation[12]) and can be neglected. We have also checked the effect of double ionization experimentally. To enhance the effect of the double ionization we used helium projectiles in the energy range of 6–18 MeV, accelerated by the compact cyclotron. For He projectiles the ratio of double to single ionization increases with increasing projectile energy in this region. Using a bromine absorber in front of the Si(Li) detector we have measured the intensity ratio of the La_2 and Ll transitions as a function of the energy of the bombarding particle. We observed only a 2% change of the intensity ration in the whole energy range.[18] From this experimental finding one can conclude that the double L_3M ionization has a negligible effect at 1.5-MeV proton projectiles.

L_3M hole vacancies can also be created when L_1 vacancies decay into L_3M_4 and L_3M_5 double-hole states by Coster-Kronig transitions.[19] These L_3M Coster-Kronig satellites are isotropic and the usually applied Coster-Kronig correction takes into account this effect. The absorber, however, cuts some of the satellites and therefore reduces this correction. To estimate this reduction, we have determined the L_1 and L_3 subshell ionization cross-section ratio σ_1/σ_3 from the measured intensity of the $L\alpha, L\gamma_1, L\gamma_{2,3,6}$ lines (as in Ref. 20), and obtained $\sigma_1/\sigma_3=0.122\pm0.002$ for U and Th. Our estimation based on the measured σ_1/σ_3 ratio, the known Coster-Kronig transition probabilities[19] and the transition energies of the satellites[21] yielded that 3.5% of the total La_2 intensity is cut out by the absorber. The corresponding reduction in the Coster-Kronig correction has been taken into account.

The effect of a spectator vacancy in the N (or higher) shell on the L_3-subshell alignment or L_3-subshell x-ray angular distribution can be neglected, since the energy splittings of these two hole states[21] are much smaller than their widths.[7,22]

The position of the escape peak of the La line coincides with the position of the Ll line in the U spectrum, and could add a nearly isotropic contribution to the anisotropic Ll line. This may cause a systematic error in the angular distribution measurement of the Ll line. To check this possible systematic error the angular distribution of the L x-rays of uranium was also measured using a Se absorber in front of the Si(Li) detector. This absorber reduced the $L\alpha$ to Ll intensity ratio from 16 to 3.4, and therefore reduced the escape peak intensity by a factor of 5 relative to the Ll intensity. The anisotropy parameter of the Ll line, measured with and without a Se absorber were the same within 3% statistical error, confirming that the effect of the escape peak can be neglected. The same conclusion can be drawn from the fact that the escape peak of the Ll line was not seen in the spectra after a long measurement with more than 5×10^5 counts in the Ll peak.

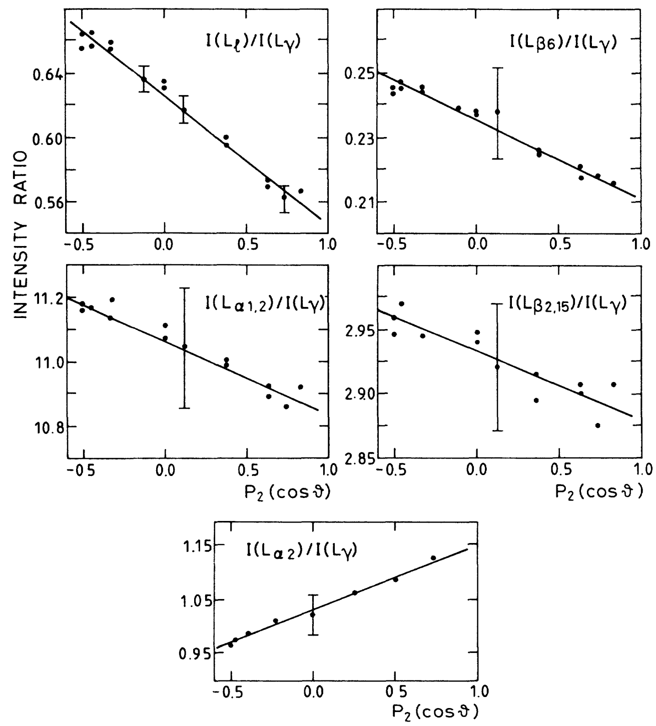

FIG. 2. The result of the angular distribution measurement of U ionized by 1.5-MeV protons as a function of the second-order Legendre polynomial.

The intensities of the L_3 x-ray lines were normalized to the total intensity of the x-ray lines of the $L\gamma$ group, which has isotropic angular distribution. These normalized intensities were fitted with function (1) and are shown for uranium in Fig. 2 as function of the second-order Legendre polynomial. Where two measured points appear at the same P_2 value, there the measurement was repeated to check the reproducibility. The $L\alpha_2$ transition clearly shows the opposite anisotropy, in accordance with the opposite sign of the α parameter.

III. RESULTS AND DISCUSSION

In an earlier study[9] it was found that the ratios of the anisotropy parameters of the Ll and $L\alpha$ lines sensitively depend on the $M2$-$E1$ mixing ratios (δ_1). The ratio of the anisotropy parameters of the Ll and $L\alpha$ lines are shown in Fig. 3. The results of Scofield's calculation (denoted by a dashed curve in Fig. 3) show that with increasing Z the effect of the quadrupole mixing is increasing. Our result, however, does not follow this tendency. The deviation of the measured ratio from the value of 10 (negligible mixing) is approximately the same or somewhat smaller for U and Th than for Au. From the tendency of the measured points one can expect that the mixing is important even at lower atomic numbers. This conclusion is further confirmed by the result of the $K\alpha_1$-Ll angular correlation studies,[8] where the deviation from the pure $E1$ assumption was found larger for the elements $Z=60-80$ than for the elements around $Z=90$.

The $L\beta_6$ and Ll lines should have the same angular distribution, assuming pure $E1$ decay in the independent electron picture. Our experimental $\beta(Ll)/\beta(L\beta_6)$ values for U and Th are about 20% larger than unity. This indicates [cf. Eq. (3)] that the mixing ratio is significantly larger for the $L\beta_6$ than for the Ll line.

From the experimentally determined anisotropy parameters (β) the α values for U were determined using Eq. (3) and the theoretical pure $E1$ α value for the $L\alpha_2$ transition. The results are summarized in Table I. The quoted errors of the anisotropy parameters are the standard deviation values obtained from the least-squares fitting of Eq. (1) to the measured angular distribution. The measured intensities were weighted with the inverse square of their one-standard-deviation errors obtained from the fitting of the spectra assuming Poisson counting statistics. The stated errors of a and δ_1 were calculated from the errors of the β parameters according to Eqs. (2)–(4) using standard error propagation rule.

Comparing the present results with our earlier data for Au (Ref. 10) one can conclude that the mixing ratios for the Ll and $L\alpha_1$ lines are somewhat smaller for uranium than for gold. This tendency contradicts the theoretical prediction[11] that the mixing as a relativistic effect increases with increasing atomic number. For the $L\alpha_1$ line the mixing ratio is in good agreement with the Scofield theory. We note here that a similarly good agreement with the Scofield theory was found in the study of angular correlation in the $K\alpha_1$-$L\alpha_{12}$ cascade for uranium.[23] For the Ll and especially the $L\beta_6$ transition, however, we observed large deviation from the Scofield theory. For the $L\beta_6$ line the measured mixing ratio (8%) is surprisingly large. It is interesting to note that the deviation between the experimental and theoretical values is large for the $ns_{1/2}$-$2p_{3/2}$ transitions and increases with increasing n. However, it should be emphasized that the mixing ratios were obtained assuming single ionization. This assumption is well established in the case of the M shell,[12,18] but may be questionable in the case of the N shell. Multiple N-shell ionization can decrease the anisotropy of the $L\beta_6$ transition, and in this way can play a disturbing role in the determination of the mixing ratio. Using the angular correlation method for the $K\alpha_1$-$L\beta_6$ cascade transition,[8] the effect of the multiple outer shell ionization can be excluded.

For U and A_2 alignment parameter can be determined from the β anisotropy parameter using the experimentally determined α values in Eq. (2). The k Coster-Kronig correction factor was calculated from the measured line intensities and $k=1.12\pm0.02$ was obtained for U (and also for Th). The error here does not contain the errors of the transition probabilities[11] and that of the Coster-Kronig coefficients.[22] The obtained $A_2=0.343\pm0.025$ is 16% larger than the value obtained from the Ll transition neglecting the $M2$ mixing. For Th, the mixing ratios could not be determined directly, therefore we assumed that α is the same as for U. For this case we obtained $A_2=0.367\pm0.025$ for Th. These alignment data are in

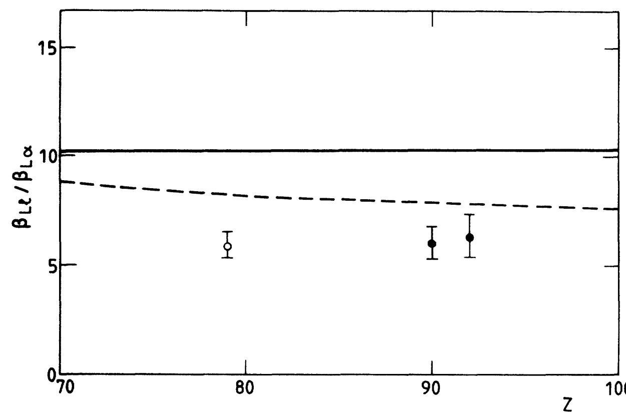

FIG. 3. Ratio of the anisotropy parameters of the Ll and La transitions for Th and U (solid circle) and for Au from Ref. 10 (open circle). The pure $E1$ assumption is represented by a solid curve, and the theoretical results of Ref. 4 by a dashed curve.

TABLE I. The anisotropy parameter (β) of the different L_3 x-ray lines of the Th and U ionized by 1.5-MeV protons. The α values and the mixing ratios (δ_1) for U were obtained assuming the theoretical α value (marked by an asterisk) for the $L\alpha_2$ transition.

	Th	U		
Transition	β	β	a	$10^2\delta_1$
Ll	-0.141 ± 0.006	-0.131 ± 0.004	0.43 ± 0.02	3.6 ± 1.4
La_{12}	-0.024 ± 0.003	-0.021 ± 0.003	0.069 ± 0.010	
$L\beta_6$	-0.118 ± 0.009	-0.105 ± 0.005	0.35 ± 0.03	8.6 ± 1.6
$L\beta_{2,15}$	-0.023 ± 0.004	-0.019 ± 0.003	0.062 ± 0.010	
La_2		0.131 ± 0.004	-0.4^*	
La_1			0.121 ± 0.010	1.8 ± 0.9

fairly good agreement with the present ionization theories.[24,25]

The presented results show that the angular distribution of the different x-ray transitions depend on the mixing ratios. The knowledge of the mixing ratios is important for the deduction of the parameters characterizing the ionization processes (e.g., subshell ionization cross sections, alignment tensor components). On the other hand, they can give an accurate test of the existing relativistic x-ray transition probabilities. From this point of view, the experimental study of the angular distribution of the $E1$ forbidden transitions gives a possibility to get information about the strength of the higher-order transition matrix element. Using a Si(Li) detector having better resolution than the one used in this work, the angular distribution of the L_t (L_3-M_2) transition can also be studied. The study of the effect of $M2$ mixing in $E1$ on the angular distribution of the x-ray transitions of rare earth elements is in progress.

ACKNOWLEDGMENTS

Financial support was provided by the National Scientific Research Foundation (OTKA), Grant No. 1184-1185, and by National Foundation for Junior Researchers (FKP), Grant No. 313371.

[1]W. Jitschin, H. Kleinpoppen, R. Hippler, and H. O. Lutz, J. Phys. B **12**, 4077 (1979).

[2]W. Jitschin, R. Hippler, R. Shanker, H. Kleinpoppen, R. Schuch, and H. O. Lutz, J. Phys. B **16**, 1417 (1983).

[3]J. Pálinkás, L. Sarkadi, and B. Schlenk, J. Phys. B **13**, 3829 (1980).

[4]U. Wille and R. Hippler, Phys. Rep. **132**, 129 (1986).

[5]E. G. Berezhko and N. M. Kabachnik, J. Phys. B **10**, 2467 (1977).

[6]J. H. Scofield, Phys. Rev. **179**, 9 (1969); Phys. Rev. A **10**, 1507 (1974).

[7]W. Bambynek, B. Crasemann, R. W. Fink, H. U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. Venugopal Rao, Rev. Mod. Phys. **44**, 716 (1972).

[8]A. L. Catz, Phys. Rev. A **2**, 634 (1970); E. S. Macias and M. R. Zalutsky, *ibid.* **9**, 2356 (1974).

[9]T. Papp, in *Proceedings of the 3rd International Seminar on High Energy Ion-Atom Collisions,* Debrecen, August 2–5, 1987, Vol. 294 of *Lecture Notes in Physics,* edited by D. Berényi and G. Hock (Springer-Verlag, Berlin, 1988), p. 204.

[10]T. Papp and J. Pálinkás, Phys. Rev. A **38**, 2686 (1988).

[11]J. H. Scofield, At. Data Nucl. Data Tables **14**, 121 (1974).

[12]T. Papp and L. Kocbach, J. Phys. (Paris) C **9**, 243 (1987).

[13]T. Papp and J. Pálinkás, Acta Phys. Hung. **65**, 209 (1989).

[14]J. Pálinkás, L. Sarkadi, B. Schlenk, I. Török, Gy. Kálmán, C. Bauer, K. Brankoff, D. Grambole, C. Heisler, W. Rudolph, and H. J. Thomas, J. Phys. B **17**, 131 (1984).

[15]L. F. Gáll, P. Mikecz, and T. Papp, Nucl. Instrum. Methods A **270**, 248 (1988).

[16]E. C. Montenegro, G. B. Baptista, and W. E. P. Duarte, At. Data Nucl. Data Tables **22**, 131 (1978).

[17]W. H. McMaster, N. Kerr Del Grande, J. H. Mallett, and J. H. Hubbel, University of California Radiation Laboratory, Livermore, Report No. UCRL-50174 (1972).

[18]T. Papp and J. Pálinkás (unpublished).

[19]M. H. Chen, B. Crasemann, and H. Mark, At. Data Nucl. Data Tables **24**, 13 (1979).

[20]S. Datz, J. L. Duggan, L. C. Feldman, E. Laegsgaard, and J. U. Andersen, Phys. Rev. A **9**, 192 (1974).

[21]F. Parente, M. H. Chen, B. Crasemann, and H. Mark, At. Data Nucl. Data Tables **26**, 383 (1981).

[22]M. O. Krause, J. Phys. Chem. Ref. Data **8**, 307 (1979).

[23]A. L. Catz and L. Finkel (unpublished).

[24]F. Rösel, D. Trautmann, and G. Baur, Z. Phys. A **304**, 75 (1982).

[25]L. Sarkadi, J. Phys. B **19**, 2519 (1986).