$K\beta/K\alpha$ Radiative-Transition-Probability Ratios for Elements of Low Atomic Numbers in Amorphous and Crystal Forms

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(Received 14 August 1972)

The $K\beta/K\alpha$ radiative-transition probabilities have been measured for 26 elements ranging in atomic numbers from $_{11}$Na to $_{45}$Rh. The samples were in an amorphous state except $_{17}$Cl and $_{35}$Br, which were in crystal form. The elements $_{11}$Na, $_{12}$Mg, $_{19}$K, and $_{20}$Ca were studied in both amorphous and crystal forms. The K vacancies were produced by radiation from commercial $_{74}$W and $_{24}$Cr x-ray tubes. The corrected measured ratios are compared with the most recent calculations based on a relativistic Hartree–Fock–Slater (RHFS) potential and relativistic screened Coulomb potential. Although the form of the dependence of this ratio on atomic number predicted on the basis of a RHFS potential seems to be correct, the experimental values are consistently higher than the calculated results. Comparison with other recent experimental results is also made.

INTRODUCTION

Several recent measurements of the $K\beta/K\alpha$ transition-probability ratios were reported.[1–4] Basically these were performed on elements with atomic numbers $Z \geq 30$. Two most recent experiments[5,6] pushed these measurements down to $_{18}$Ar.

Relativistic calculations of the $K\beta/K\alpha$ transition probabilities were recently carried out by Scofield,[7] Babushkin,[8] Rosner and Bhalla,[9] and Lu *et al.*[10] The calculations in Refs. 7, 9, and 10 use a relativistic Hartree–Fock–Slater (RHFS) potential for the atom, and their results are in good agreement over the region covered in this experiment. Babushkin based his calculations on a relativistic screened Coulomb (RSC) potential; he took into account the electron screening effect as prescribed by Slater[11] and Burns.[12] His results based on a potential screened by Burns's prescription show better agreement with experimental values.[13] These are later compared with the results of this experiment. Two reviews of this subject have recently been made.[14,15]

This work was initiated primarily to measure systematically the $K\beta/K\alpha$ radiative-transition-probability ratio near the limit of low atomic numbers and to investigate the effect of embedding the atom in an ionic crystal on its radiative-transition probability.

EXPERIMENTAL

The amorphous samples studied were thick blocks of the elements of varying purities but all were better than 99.5% pure. The crystals were also thick samples and were mounted with their clearly cleaved surface exposed to the exciting radiations. No attempt was made to rotate them about the direction of the exciting beam. K vacancies in samples with $Z \geq 23$ were produced by an unfiltered x-ray beam from a $_{74}$W commercial x-ray tube; and low-Z elements were excited by radiation from a commercial $_{24}$Cr x-ray tube. The exciting tubes were activated by a constant potential provided by a commerical x-ray unit. The samples under investigation were locked in a single-crystal spectrometer which was partially evacuated (~0.2 mm of Hg). The detecting unit is a flow proportional counter using a mixture of argon and methane, some 90% Ar and 10% CH_4. While the spectrometer scans the region of interest, the data were plotted on a chart recorder. Several different diffraction crystals were used (see Table I). At least three complete runs were taken for each sample. Because of the interesting dip observed at $_{30}$Zn, ten complete runs were taken for each of the elements $_{30}$Zn and $_{29}$Cu. To reduce experimental uncertainties in the study of the elements $_{11}$Na and $_{12}$Mg, eight complete scans were taken for each of their amorphous and of their crystal samples.

The geometrical setup is such that the emerging beam makes an angle of about 30° with the surface of the sample under investigation. Under this geometry it was found that the measured $K\beta/K\alpha$ ratio varies slowly with the value of the potential on the exciting tube. As an example, the value of $K\beta/K\alpha$ for $_{39}$Y increased by about 5% when the voltage across the $_{74}$W tube increased from 19 to 22 kV, and also increased by about 5% when the voltage increased from 22 to 30 kV. Thus with such a value of the takeoff angle, the effect of self-absorption in the irradiated sample on the value of $K\beta/K\alpha$

TABLE I. $K\beta/K\alpha$ radiative-transition-probability ratios. The diffraction crystals have the following compositions: Lymr → $Pb(C_{14}H_{27}O_2)_2$, Gypsum → $CaSO_4 \cdot 2H_2O$, PET → $C_5H_{12}O_{14}$.

Z	Element	Form	Diffraction crystal	$K\beta/K\alpha$
11	Na	amorphous	Lymr	0.008
11	Na	Na(OH)	Lymr	0.009
12	Mg	amorphous	Lymr	0.011
12	Mg	MgO	Lymr	0.012
13	Al	amorphous	Gypsum	0.018
14	Si	amorphous	PET	0.030
15	P	amorphous	PET	0.038
16	S	amorphous	PET	0.059
17	Cl	NaCl	PET	0.095
19	K	amorphous	PET	0.123
19	K	KCl	PET	0.124
20	Ca	amorphous	PET	0.128
20	Ca	$CaCO_3$	PET	0.130
21	Sc	amorphous	LiF	0.133
22	Ti	amorphous	LiF	0.135
23	V	amorphous	LiF	0.137
24	Cr	amorphous	LiF	0.138
25	Mn	amorphous	LiF	0.138
26	Fe	amorphous	LiF	0.136
27	Co	amorphous	LiF	0.138
28	Ni	amorphous	LiF	0.136
29	Cu	amorphous	LiF	0.134
30	Zn	amorphous	LiF	0.132
31	Ga	amorphous	LiF	0.143
32	Ge	amorphous	LiF	0.150
35	Br	$MgBr_2$	LiF	0.168
39	Y	amorphous	LiF	0.190
40	Zr	amorphous	LiF	0.192
41	Nb	amorphous	LiF	0.193
45	Rh	amorphous	LiF	0.250

is not very sensitive to the magnitude of the voltage on the exciting tube, a fact that reduces the complexity of correcting for self-absorption. Under the present setup, the diffraction crystals may be exchanged by remote controls and locked in their proper position without disturbing the vacuum in the spectrometer.

Previous experiments of this type were limited at low-Z elements by the resolutions of the spectrometer detector used. This work was carried systematically for low-Z elements until it became difficult to detect the presence of the $K\beta$ lines. In 6 out of 32 runs taken for $_{11}$Na and $_{12}$Mg, the $K\beta$ lines were not distinctly apparent.

In all the observed spectra the $K\beta$ and the $K\alpha$ lines were well resolved and were all measured in the first order, except those of $_{11}$Na and $_{12}$Mg, for which the spectra were studied in the third and fourth order, respectively.

RESULTS AND DISCUSSION

The results of this work are presented numerically in Table I, and also graphed as a function of atomic number in Fig. 1. Also plotted are the theoretical results from Refs. 7 and 8, curves 1 and 2, respectively.

The transition probability $K\beta/K\alpha$ was assumed to be proportional to the ratio of the areas under the two characteristic lines. The area is taken as the product of the height of the peak and its full width at half-maximum. The raw data were corrected for differential self-absorption by assuming a mean depth of formation of characteristic lines in the irradiated samples. The values of the mass-absorption coefficients used were those tabulated by McMaster *et al.*[16] Corrections for the efficiency of the flow proportional counter as a function of the photon energy were also made.

The diffraction efficiency of a mosaic crystal is proportional to the value of the wavelength of the diffracted radiation,[17] and away from the crystal absorption edges, it is nearly proportional to the mass-absorption coefficient of the diffraction crystal,[18] which is inversely proportional to λ^3. Thus under the present geometry and for our choice of diffraction crystals, the crystal reflectivity is nearly independent of the reflected wavelength, and no correction was attempted for such an effect.

An error analysis was carried out for all the studied elements. The resulting experimental uncertainties were nearly equal to or smaller than 2% for all the elements with $13 \leq Z \leq 45$, except for

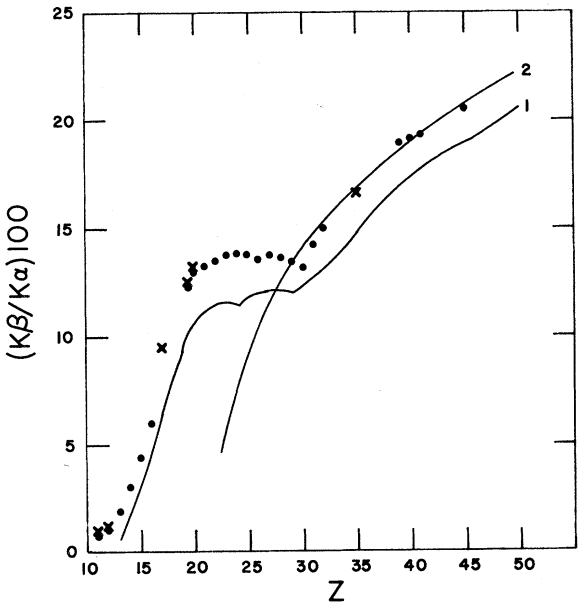

FIG. 1. $K\beta/K\alpha$ radiative-transition-probability ratio as a function of atomic number Z. Curve 1 is from Ref. 7 and curve 2 is from Ref. 8. The solid dots are from amorphous samples and the crosses are from crystalline samples.

$_{29}$Cu and $_{30}$Zn, where such uncertainties were found to be about 1.5%. Uncertainties of about 25% were calculated for both $_{11}$Na and $_{12}$Mg in both crystal and amorphous samples. Our corrections for the efficiency of the counter and for self-absorption and our lack of correction for the reflectivity of the diffraction crystals could have introduced additional errors.

The results of this experiment as well as those from previous works agree well with the theoretical results based on a RSC potential,[8] for elements with $Z \geq 31$. As a matter of fact, the values of the $K\beta/K\alpha$ radiative-transition probabilities for elements with $31 \leq Z \leq 92$ are well established, and our work on the elements $_{35}$Br, $_{39}$Y, $_{40}$Zr, $_{41}$Nb, and $_{45}$Rh was performed as a check on the accuracy of our correction calculations. Although the shape of the dependence of the $K\beta/K\alpha$ ratio on atomic number is well represented by the results obtained with calculations based on a RHFS potential,[7] these theoretical results are consistently 10–20% lower than the most trusted experimental values. Furthermore, the theory predicts the existence of two small "dips" in the value of $K\beta/K\alpha$: one at $_{29}$Cu and the other at $_{24}$Cr. Previously performed systematic measurements of this ratio[5,6] detected no dips in the "flat" region $20 \leq Z \leq 30$; McCrary *et al.*[5] did not measure the ratio $K\beta/K\alpha$ for the critical elements $_{30}$Zn and $_{31}$Ga. In this work, the $K\beta/K\alpha$ ratio for $_{30}$Zn was found to be consistently lower than those for $_{29}$Cu and $_{31}$Ga, and no dip was detected at $_{24}$Cr.

The existence of a dip in this region of atomic number is of some significance, as it is the result of the effect of the $4s$ and $3d$ electrons on transitions from the lower p states. The theoretical dips occur for elements with only one electron in the $4s$ state. The theory also predicts dips under similar conditions of electronic structure in the ratios $L\gamma_1/L\beta_1$ $[(L_{II}-N_{IV})/(L_{II}-M_{IV})]$ and $L\beta_{2,15}/L\alpha$ $[(L_{III}-N_{IV,V})/(L_{III}-M_{IV})]$ for the element $_{65}$Tb. Measurements of the two ratios[19] show a clear dip at $_{69}$Tm, which corresponds to the presently observed dip at $_{30}$Zn.

The $K\beta/K\alpha$ ratios for the four elements $_{11}$Na, $_{12}$Mg, $_{19}$K, $_{20}$Ca were measured in both amorphous and crystalline forms. Contrary to what one may expect, at least for the low-Z elements, for all four elements the ratio $K\beta/K\alpha$ was larger from crystalline samples. The difference is small and is within experimental error. Prior to corrections the $CaCO_3$ sample gave a value of $K\beta/K\alpha$ for $_{20}$Ca some 5% larger than that from the amorphous sample; most of that difference was found to be due to the differential self-absorption by the oxygen atoms of the crystalline sample. Both $_{35}$Br and $_{17}$Cl were only measured for crystalline sample; in the case of $_{35}$Br, one expects the same value of $K\beta/K\alpha$ from both amorphous and crystalline samples, as the studied transitions are deep within the atom. Although difficult to judge because of the large slope of the curve at $Z=17$ (see Fig. 1), the value of $K\beta/K\alpha$ for $_{17}$Cl from NaCl crystal seems to be larger than what one would expect for atomic chlorine.

CONCLUSION

The present results prove the existence of a dip in the value of the $K\beta/K\alpha$ radiative-transition probability at $_{30}$Zn. This dip has never been observed before. Except for that important point, our results and those reported in Refs. 5 and 6 are in good agreement in the region covered by these previous works.

Values of the $K\beta/K\alpha$ radiative-transition-probability ratios are reported here for the first time for elements $_{11}\text{Na} \leq Z \leq {}_{17}\text{Cl}$. The presence of low-$Z$ atoms in amorphous or crystalline samples seems to have very little effect if any on their values of $K\beta/K\alpha$.

ACKNOWLEDGMENTS

One of the authors (S. I. S.) wishes to thank the California State University (Long Beach) Administration for the granting of a special leave to work on this project.

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PHYSICAL REVIEW A VOLUME 6, NUMBER 6 DECEMBER 1972

Many-Body Calculation of the Photodetachment Cross Section of O^- †

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Many-body perturbation theory is used to calculate the total photodetachment cross section of O^- from threshold to 1.1 keV. This nonrelativistic calculation uses the velocity form of the dipole approximation. We include the effects of resonances owing to $2s \rightarrow 2p$ and $1s \rightarrow 2p$ excitations. Comparison is made with experiment and other theoretical treatments.

I. INTRODUCTION

The photodetachment cross section of O^- has been the subject of several theoretical and experimental studies, primarily because of its astrophysical applications. The first calculation was performed by Bates and Massey.[1] Since the accurate determination of the electron affinity of oxygen[2] and the accurate measurement of the absolute cross section by Smith,[3] good results in the range from threshold to about 3.2 eV were obtained by improving the Hartree–Fock calculation through the use of polarization potentials.[4–6] Utilizing Temkin's method of polarized orbitals,[7] the calculation of Henry[8] showed good agreement with experiment up to about 3.6 eV.

In order to take into account the effect of electron correlations on the photodetachment cross section of O^-, we present here a detailed calculation of that cross section using the many-body perturbation theory of Brueckner[9] and Goldstone[10] and our techniques for the application of this theory to atoms.[11–14] Recently, the Brueckner–Goldstone theory was used to calculate the photoionization cross section of Fe, both initial- and final-state correlations being included.[15,16]

In Sec. II we discuss the theory. Section III contains the details of the calculation and also the numerical results. We present results for the total photodetachment cross section, contributions to the cross section from the individual subshells, and also our lowest-order results, which are essentially Hartree–Fock results. The discussion and conclusions are presented in Sec. IV.

II. THEORY

In applying many-body perturbation theory to the photoionization problem, we use the perturbation expansion for the frequency-dependent polarizability[14] $\alpha(\omega)$ together with the relation[17]

$$\sigma(\omega) = (4\pi\omega/c)\,\mathrm{Im}\,\alpha(\omega). \tag{1}$$

Here $\sigma(\omega)$ is the photoionization cross section, ω is the photon energy, and c is the speed of light (137.037 in atomic units).

The lowest-order contribution to $\alpha(\omega)$ due to the electronic state $|p\rangle$ is given by[14]

$$-\sum_k |\langle k|z|p\rangle|^2 \left(\frac{1}{\epsilon_p - \epsilon_k + \omega} + \frac{1}{\epsilon_p - \epsilon_k - \omega}\right), \tag{2}$$

where z represents $\sum_{i=1}^N z_i$. Since $\epsilon_p - \epsilon_k + \omega$ may vanish, we add a small imaginary part $i\eta$. We then obtain

$$\lim_{\eta\to 0}(\epsilon_p - \epsilon_k + \omega + i\eta)^{-1} = P(\epsilon_p - \epsilon_k + \omega)^{-1} - i\pi\delta(\epsilon_p - \epsilon_k + \omega), \tag{3}$$

where P represents principal-value integration. Since our continuum states are normalized according to

$$P_{kl}(r) \rightarrow \cos[kr + \delta_l + (q/k)\ln 2kr - \tfrac{1}{2}(l+1)\pi], \tag{4}$$

where $V(r) \rightarrow q/r$ as $r \rightarrow \infty$, we may replace the summation over k in Eq. (2) by $(2/\pi)\int dk$.[11,12] Using Eq. (3) we obtain

$$\mathrm{Im}\,\alpha(\omega) = (2/k_0)\,|\langle k_0|z|p\rangle|^2, \tag{5}$$

where