

of $\exp(-\epsilon/2K_B T)S(|\kappa|, \hbar\omega)$ agree at low ϵ but as ϵ increases, the experimental values rise above the calculated ones. The discrepancy is rather small in the region where the $S^{(1)}$ and $S^{(2)}$ contributions are negligible. But where these contributions dominate, the calculated values are only about $\frac{2}{3}$ the measured ones.

This discrepancy between the experimental and calculated values suggests that either an appreciable correction to the data has been overlooked or that the computations fail to deal adequately with the vibrational excitations. The contributions from excitation of the higher energy modes near 0.36 eV, and from multiple excitations of the low-energy modes, have been examined and found to be negligible. Therefore, the computational errors must be sought in the procedures used in calculating $S^{(1)}$ and $S^{(2)}$. When rotation-vibration coupling and anharmonic effects are neglected, the vibrational intensities are related to the expectations $\langle \Delta r_{\nu\tau}^2 \rangle$. Here $\Delta r_{\nu\tau}$ is the displacement of the scattering atom ν during the τ normal vibration. These expectations depend on the force field used in the normal

coordinate analysis. Since more than one force field may give the correct vibrational frequencies but different normal modes, there is some possibility for altering $S^{(1)}$ and $S^{(2)}$ by changing the force field. Rotation-vibration coupling and anharmonic effects will cause perturbations which will produce some modification in the $\langle \Delta r_{\nu\tau}^2 \rangle$. The possibility that the proper treatment of one or more of these factors will resolve the discrepancy between calculated and observed results is being studied, but the work has not progressed to where definite conclusions can be drawn.

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Characteristic X-Ray Production in the M_V Shell in Ytterbium by 30–100-keV Protons*

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Characteristic M -shell x rays produced when protons of 30–100-keV energy are stopped in a thick target of ytterbium were observed by proportional-counter detection. By use of an aluminum absorber, radiation originating from the filling of M_V -subshell vacancies can be isolated. Thick-target yields of the M_V -shell and ($M_I + M_{II} + M_{III} + M_{IV}$)-shell x rays were measured separately. With extrapolated values of the fluorescence yield (0.06), the mass absorption coefficient (1500 cm²/g) and the stopping power, estimates of the ionization cross section for the M_V shell have been made (neglecting contributions from other subshells by Coster-Kronig transitions). These vary from 6×10^{-26} cm² at 30 keV to 2×10^{-22} cm² at 100 keV.

INTRODUCTION

THE investigation of ionization of atoms by proton bombardment has long been in the domain of nuclear physics. It has been mainly concerned with the evaluation of stopping powers and background subtraction in Coulomb excitation and other nuclear reaction experiments.¹ As time has passed and more detailed data have become available, many questions of a purely atomic nature have arisen.² The answers to these involve knowledge of the transition probabilities for the radiative and nonradiative reorganization

processes taking place in the atom following an ionizing event.³ Description of the total event from the ionization event to the observation of x rays in a detector places a severe test upon our understanding of atomic processes.

The phenomena can be separated into two parts; the production of "initial" vacancies in the inelastic scattering process and the reorganization of the atom filling all vacancies. During this reorganization the "initial" vacancies may be redistributed among the subshells of any given shell (Coster-Kronig transitions), e.g., $M_I \cdots M_V$ subshells.³ In cases where the quantum energy of the radiative process is low (< 5 keV), few (< 0.1) of the total number of vacancies are filled by photon emission. Given an accurate description of either the ionization event or the reorganization

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¹ J. Lindhard and M. Scharff, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.* 27, No. 15 (1953); and W. Whaling, *Nuclear Spectroscopy* (Academic Press, Inc., New York, 1960), Part A, Chap. I.

² J. M. Khan, D. L. Potter, and R. D. Worley, *Phys. Rev.* 134, A316 (1964).

³ E. H. S. Burhop, *The Auger Effect and other Radiationless Transitions* (Cambridge University Press, Cambridge, 1952).

process, it is possible to make accurate statements regarding the other.

In early measurements of x-ray production, accelerators were employed to provide proton beams of 100-keV to 4-MeV energy.⁴⁻⁹ The detectors employed were scintillation counters and were used to observe photons of energy greater than several keV. The fluorescence yields in the K shell for higher quantum energies (>10 keV) are of the order of magnitude of 50% and are well known.^{3,8} These experiments were able to test the theory of ionization to a high degree of precision (for K and L shells). The conclusions were that there exists a lower limit in bombarding energy where the Born approximation description of the proton trajectory is accurate. Below this limit a deflected trajectory description must be employed. Bang and Hansteen have performed this calculation for the K shell which has represented a significant improvement in the theory.¹⁰ The calculations and experiments evaluated average processes (i.e., over all subshells).

More recently experiments have been performed to measure the effective ionization cross section in a specific subshell.² With these data available it may be possible to employ the general conclusions of the previous experiments to gain some insight into the atomic processes. The present experiment falls into this category, with the measurement of the thick-target yield, x-ray production, and effective ionization cross section for the M_V shell of ytterbium.

In the present work, a thick target of ytterbium metal was bombarded by protons of 30-100-keV energy. The proportional counter detector was designed to observe radiations originating from vacancies in the M shell (quantum energy spread from 1.5-2.3 keV). Employing an aluminum absorber placed between the target and detector, radiations greater in energy than 1.559 keV were selectively removed, leaving M_V shell radiation as the predominant component. The experimentally determined quantity is the thick-target yield. From this and from estimates of the stopping power of the material for the protons and the absorption of the x rays, the x-ray production cross section can be obtained. By employing a suitable value for the fluorescence yield for the M_V shell an ionization cross section can be obtained. The cross sections presented here neglect the redistribution of initial vacancies. The relative

⁴ M. S. Livingston, F. Genevese, and E. J. Konopinski, *Phys. Rev.* **51**, 835 (1937).

⁵ H. W. Lewis, B. E. Simmons, and E. Merzbacher, *Phys. Rev.* **91**, 943 (1953).

⁶ P. R. Bevington and E. M. Bernstein, *Bull. Am. Phys. Soc.* **1**, 198 (1956).

⁷ E. M. Bernstein and H. W. Lewis, *Phys. Rev.* **95**, 83 (1954).

⁸ R. C. Jopson, Hans Mark, and C. D. Swift, *Phys. Rev.* **127**, 1612 (1962).

⁹ E. Merzbacher and H. W. Lewis, in *Handbook of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 34, p. 166.

¹⁰ J. Bang and J. M. Hansteen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.* **31**, No. 13 (1959).

TABLE I. Characteristic wavelengths.^a

λ (Å)	
8.138	M_{α_1} emission line Yb
8.122	M_{α_2} emission line Yb
7.9511	K absorption edge Al
7.893	M_{β_1} emission line Yb
7.009	M_{γ} emission line Yb

^a *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1963), 44th ed.

intensities of the lines suggest that this may be a poor assumption.

At the present time there are no calculated values of the ionization cross section for the M shell. By inference from the K - and L -shell calculations it is possible to conclude that the cross section for production of initial vacancies does not greatly differ across the subshells.⁹ The observed yields however indicate that well over half ($\approx 70\%$) of the final vacancies appear in the M_V shell. As no detailed knowledge is available of the Coster-Kronig and Auger processes in the higher atomic shells (M and above) much work remains to be done.

As a final consideration, the cross sections for the M_V shell of Yb and the K shell of Al are compared. The quantum energies of the photons are within 10%, yet the dependence upon bombarding energy is considerably different. This tends to confirm the Bang and Hansteen deflected trajectory approach which predicts a higher dependence upon energy for the larger Z atom (Yb).¹⁰

APPARATUS AND METHOD

The experimental equipment consisted of a proton ion source (electrodeless discharge), 120 kV (dc) accelerating column, analyzing magnet, target chamber, proportional counter, and associated amplifiers and scaling circuitry. The apparatus has been described in previous publications^{2,11} and will not be presented here in detail.

The target was mounted at 45° to the proton beam on the end of a 1-in.-diam aluminum rod. The x rays produced at the target were observed, after passage through various absorber foils, by a flow-mode (P-10 gas) proportional counter (2 in. i.d. \times 12 in. length, with a 0.003-in. stainless-steel center wire). The counter window was a 5 mg/cm² beryllium foil held in place by the O-ring seals. The window transmission for the M_α lines was 0.40, with a counter efficiency of 100%. An absorber foil changer allowed introduction of various aluminum and beryllium absorbers. The choice of these foils allowed correction for window absorption and separation of the spectrum lines.

The accuracy of the measurements were limited by knowledge of the charge collection ($\pm 5\%$), energy of the protons ($\pm 1\%$), and freedom of contamination of

¹¹ J. M. Khan and D. L. Potter, *Phys. Rev.* **133**, A890 (1964).

TABLE II. Thick-target yield and ionization cross section—Yb.^a

E_p (keV)	30	40	50	60	70	80	90	100
$I_\alpha^0(\pm 15\%)$	8.90×10^{-10}	2.20×10^{-8}	1.42×10^{-7}	4.70×10^{-7}	1.19×10^{-6}	2.37×10^{-6}	4.15×10^{-6}	6.51×10^{-6}
$\frac{dI_\alpha^0}{dE}$	1.88×10^{-10}	4.60×10^{-9}	1.87×10^{-8}	4.92×10^{-8}	9.43×10^{-8}	1.44×10^{-7}	2.03×10^{-7}	2.53×10^{-7}
$S(E)^b$	66	88	110	110	110	110	110	110
$\sigma_1 = \frac{1}{n} \frac{dI_\alpha^0}{dE} S(E)$	3.46×10^{-27}	1.16×10^{-25}	5.91×10^{-25}	1.55×10^{-24}	2.98×10^{-24}	4.53×10^{-24}	6.40×10^{-24}	7.98×10^{-24}
$\sigma_2 = \frac{\mu}{\rho n} I_\alpha^0$ ^c	4.26×10^{-28}	1.06×10^{-26}	6.80×10^{-26}	2.26×10^{-25}	5.57×10^{-25}	1.14×10^{-24}	1.99×10^{-24}	3.12×10^{-24}
$(\sigma_I)_\alpha = \sigma_1 + \sigma_2$	3.88×10^{-27}	1.27×10^{-25}	6.59×10^{-25}	1.78×10^{-24}	3.54×10^{-24}	5.67×10^{-24}	8.39×10^{-24}	1.12×10^{-23}
$(\sigma_I)_\alpha^0 = \frac{(\sigma_x)_\alpha^0}{0.06}$ ^d	6.44×10^{-26}	2.13×10^{-24}	1.10×10^{-23}	2.96×10^{-23}	5.90×10^{-23}	9.45×10^{-23}	1.40×10^{-22}	1.87×10^{-22}
$I_\beta^0(\pm 25\%)$	3.70×10^{-10}	6.09×10^{-9}	4.67×10^{-8}	1.48×10^{-7}	3.81×10^{-7}	7.44×10^{-7}	1.25×10^{-6}	1.82×10^{-6}

^a Units; I_α^0 —x rays per proton at surface; dI_α^0/dE —x rays per proton per keV; $S(E)$ —keV-cm² per mg; $\sigma_I = (1/\omega)\sigma_x = (1/\omega)(\sigma_1 + \sigma_2)$ —cm².

^b S. D. Warsaw and S. K. Allison, *Rev. Mod. Phys.*, **25**, 779 (1953); $S(E) = dE/dR$.

^c $\mu/\rho = 1500$ cm²/g (extrapolated); *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1963), 44th ed.

^d $\omega = 0.06$ extrapolated; Ref. 3.

the target. The latter represented the most serious error source, although a maximum error of $\pm 5\%$ has been attached to this source on the basis of contamination vs time and beam current.¹¹

MEASUREMENTS

The quantity desired is the ionization cross section. In the simple case of ionization in a single subshell with subsequently emitted radiation having a well-defined energy, the ionization cross section can be obtained from the thick-target yield I_μ by the formula⁹:

$$\sigma_I = \frac{\sigma_x}{\omega} = \frac{1}{\omega} \left[\frac{1}{n} \left(\frac{dI_\mu}{dE} \right) \frac{dE}{dR} + \frac{1}{\rho} I_\mu \right].$$

In this equation ω is the fluorescence (or radiative) yield of the shell, n the atoms per mass unit, dE/dR the stopping power of the target material for the protons, and μ/ρ the mass-absorption coefficient corresponding to the self-absorption of the target for its own characteristic x ray.

The simplifying assumptions embodied in the above equation do not hold for the M shell as a whole because of the broad spread in binding energies of the M subshells, ranging from 2398 eV (M_I shell) to 1529 eV (M_V shell). Not only does one expect a relative variation in production of initial ionization but one must know relative intensities and specific μ/ρ values for the characteristic lines in order to obtain a meaningful average value. Under the present experimental conditions, this is not possible. It is possible, however, to employ a suitable absorber for the emitted radiation which will remove all lines except the $M_{\alpha_1\alpha_2}$ lines, which originate from the M_V subshell. For Yb, this absorber is aluminum. This is demonstrated in Table I. Thus, only radiation predominantly from the M_V shell is transmitted.

There is another process taking place which serves to complicate the analysis. This involves the existence of Coster-Kronig transitions which transfer vacancies from the M_I , M_{II} , M_{III} , and M_{IV} subshells into the M_V subshell.³ At the present time there are no reliable measurements of the relative probabilities of these transitions. This, then, represents the most serious uncertainty in interpreting the data in terms of an ionization cross section. It is also true that no fluorescence yield value is available for the M_V shell. This can, however, be estimated and is given a value of 0.06, which may be good to a factor of 2.³

This experimental procedure was to obtain values of the thick-target yield (measured in x rays per proton) for both the α component [$(I_\mu)_\alpha^0$ which includes M_{α_1} and M_{α_2}] and the components highly absorbed in the aluminum [$(I_\mu)_\beta^0$, which includes M_β , M_γ , and other higher energy lines]. The equations employed in this analysis and the respective transmissions of the aluminum absorbers and the counter window are given in the Appendix.

The results obtained for the thick-target yields, x-ray production, and ionization cross sections are presented in Table II.

DISCUSSION

Three quantities are obtained at each energy. These are I_α^0 , I_β^0 , and $(\sigma_I)_\alpha$. The thick-target yields are measured and from these, with knowledge of the stopping power, self-absorption, and fluorescence yield, an estimate of an ionization cross section is obtained. The numerical manipulation is quite straightforward.

The process discussed here occurs in the following steps: Energy is supplied to the M shell of the atom in the case considered here by the proton. Associated with each M subshell there is a probability of ionization, which depends, among other things, upon the proton

energy, the binding energy of the electron, and the wave functions describing the electron and proton. We now have a distribution of what might be called initial vacancies. Next, processes must be considered that alter this distribution. These are the Coster-Kronig transitions, which when energetically possible will move the vacancy to another less tightly bound subshell. Finally the Auger process must be considered, which has the effect of transferring vacancies out of the M shell without photon emission. This analysis is obviously oversimplified, but describes the main points to be considered.

In looking at the relative values of I_α^0 and I_β^0 it is obvious that one or more processes are active in enhancing the radiation observed from the M_V subshell, which has 6 of the total 18 M -shell electrons, but accounts for some 70% of the photons emitted. It seems reasonable to assume, then, that the ionization cross section calculated must reflect the cross sections of other subshells as well. At the present time there is little information available that will assist in sorting out the relative effectiveness of Coster-Kronig and Auger processes. In addition, the relative cross sections for initial vacancy production are not accurately known.

As it is impossible at the present time to compare the measured cross section with a calculated value for the M_V shell, it is useful to make a comparison with the cross section observed in the shell of another element but having the same quantum energy. Aluminum in the K shell is chosen.¹² The binding energies are within 10%. Figure 1 shows these two cross sections as a function of energy from 30–100 keV.

The Yb (M_V) cross section appears to decrease much more rapidly with decreasing proton energy than does the Al (K). [$\sigma_I(\text{Yb})/\sigma_I(\text{Al})$ varies from 20 at 100 keV to 2.7 at 30 keV.] From the analysis of Bang and Hansteen it seems clear that at these bombarding energies Coulomb deflection of the projectile dominates the energy dependence.¹⁰ The quantity that characterizes their calculation (and implies the classical nature of the trajectory) is the ratio of the distance of closest approach to the nucleus to the de Broglie wavelength of the proton. In the energy range considered here this ratio is much greater than unity. The slope of the cross section increases with increasing values of the distance of closest approach. (The effective radii of both the aluminum K electrons and the ytterbium M electrons are of comparable magnitude).¹³ However, the distance of closest approach is proportional to Z of the nucleus, which for ytterbium is over 5 times that for aluminum, for the same bombarding energy, implying a greater

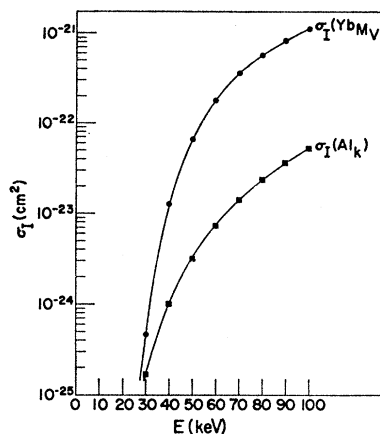


FIG. 1. Ionization cross sections for ytterbium and aluminum: 30–100 keV.

dropoff with decreasing energy. This seems to be added confirmation of a deflected trajectory description of the proton. It is hoped that in the near future this approach will be extended to the L and M shells.

APPENDIX

In the absorption analysis of the x-ray spectrum, three absolute measurements were made at each energy. These were:

$$N_1 = I_\alpha^0 \left(\frac{I}{I_0} \right)_\alpha^{\text{Be}} + I_\beta^0 \left(\frac{I}{I_0} \right)_\beta^{\text{Be}} \quad \text{—Be counter window only}$$

$$N_2 = I_\alpha^0 \left[\left(\frac{I}{I_0} \right)_\alpha^{\text{Be}} \right]^2 + I_\beta^0 \left[\left(\frac{I}{I_0} \right)_\beta^{\text{Be}} \right]^2 \quad \text{—Be absorber foil + window}$$

$$N_3 = I_\alpha^0 \left(\frac{I}{I_0} \right)_\alpha^{\text{Al}} \left(\frac{I}{I_0} \right)_\alpha^{\text{Be}} + I_\beta^0 \left(\frac{I}{I_0} \right)_\beta^{\text{Al}} \left(\frac{I}{I_0} \right)_\beta^{\text{Be}} \quad \text{—Al absorber foil + window.}$$

(See Ref. 2 for detailed discussion of method and notation).

Note: In N_2 it was assumed that the distribution of components in α and β did not change. This is valid for I_α^0 to a high approximation. For I_β^0 this assumption is much weaker.

In N_3 the β term is negligible due to the high selective absorption of the β components which lie above the aluminum K edge [aluminum K jump ratio ≈ 10].

At 50 and 100 keV, a number of relative measurements were made to obtain transmission factors for the foils employed. The results are:

$$(I/I_0)_\alpha^{\text{Be}} = 0.40 \text{ (0.001 in. Be),}$$

$$(I/I_0)_\alpha^{\text{Al}} = 0.49 \text{ (0.00023 in. Al).}$$

¹² R. D. Worley, D. L. Potter, and J. M. Khan, Lawrence Radiation Laboratory, Livermore, California (to be published).

¹³ J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 1.