the operators. The uncrossed diagram gives

$$(e^2/4m)\alpha_i\alpha_j A_i A_j = (e^2/4m)(A^2 + i\boldsymbol{\sigma}\cdot\mathbf{A}\times\mathbf{A}), \tag{7}$$

and the crossed one gives

$$(e^2/4m)\alpha_i\alpha_j A_j A_i = (e^2/4m)(A^2 - i\boldsymbol{\sigma}\cdot\mathbf{A}\times\mathbf{A}). \tag{8}$$

Thus, we see that the $\boldsymbol{\sigma}\cdot\mathbf{A}\times\mathbf{A}$ term in Eq. (5) is incorrect and should be omitted.

It is precisely this term which is responsible for the disagreement between various hfs calculations. A nonrelativistic calculation has been published[3] of the second-order perturbation-theory contributions to

$$R = (8\nu_2 - \nu_1)/\nu_1, \tag{9}$$

where ν_1 and ν_2 are the hfs of the $1s$ and $2s$ levels of a one-electron atom. The result is

$$\begin{aligned} R_s &= -[1-(2/3)\ln 2], \\ R_d &= -(1/8)[17/16-(5/3)\ln 2], \end{aligned} \tag{10}$$

in units of $g\alpha^2 m/M$ for s and d intermediate states, respectively, where g is the nuclear g factor and M is the proton mass. Reference 3 also quotes a result based upon the Dirac equation,[4]

$$R_s' = -[17/12-(4/3)\ln 2]. \tag{11a}$$

Another calculation[5] using the Dirac equation has yielded this value for R_s', and

$$R_d' = -[11/384-(1/24)\ln 2]. \tag{11b}$$

It is easy to show that $R_s'+R_d'$ goes over into R_s+R_d if one subtracts off the last term of Eq. (5).

We may remark that this cancellation is well known in other contexts, e.g., the Bethe-Salpeter equation[6] and the Breit interaction.[7]

It is a pleasure to acknowledge valuable discussions with Professor N. Kroll and Professor L. Foldy.

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[3] C. Schwartz, Ann. Phys. (New York) **6**, 156 (1959).

[4] L. L. Foldy has pointed out to me that Eq. (11a) is R_s', not $R_s'+R_d'$.

[5] D. A. Hockensmith, thesis, Case Institute of Technology, 1960 (unpublished).

[6] See Sec. 4 of W. A. Newcomb and E. E. Salpeter, Phys. Rev. **97**, 1146 (1955); M. M. Sternheim (to be published).

[7] See, for example, reference 2, p. 259.

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Photoelectric *K*-Absorption Cross Section of Lithium*

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The photoelectric absorption cross section of metallic lithium has been measured in the spectral region extending from 80 to 280 Å. The wavelength dependence deduced from the present experiment is in general agreement with that reported by previous investigators. A more refined technique has made it possible to determine the absolute value of the cross section. Theoretical calculations of the atomic cross section have also been carried out and the results compare favorably with observations. All the measurements were obtained with the use of a grazing incidence spectrometer which was provided with a specially designed auxiliary vacuum system in which the reactive samples were prepared and then transferred to the spectrometer chamber. Thus, the absorption measurements were carried out with a minimum of contamination risk. The surface densities of the thin absorbing films used were determined by observing the change in the resonant frequency of a quartz crystal as lithium vapor was condensed onto it. Spectrograms were obtained for different values of the surface density. The internal agreement of these results provided an indication of the consistency of the crystal monitor. The cross section reached a maximum of 2.60±0.3 mb at an incident photon wavelength of 193 Å. (The *K* edge of metallic lithium falls at 227 Å.)

I. INTRODUCTION

In this paper we present measurements of the previously unknown absolute photoelectric absorption cross section of metallic lithium in the neighborhood of the *K* edge (227 Å). The spectral region investigated extended from 80 to 280 Å. Although the wavelength dependence of the cross section was established by O'Bryan[1] and Skinner and Johnston[2] in 1937, techniques for determining, in a vacuum, the surface density of the absorbing layer of this highly reactive metal have become available only recently. In the present investigation it was possible to incorporate a device which did operate in a vacuum and which could monitor the small surface densities necessary for absorption work in the soft x-ray region. A grazing incidence spectrometer was used for comparing the incident and transmitted intensities and absorption spectra were recorded at a variety of surface densities, ranging from 11.2 to 22.6 μg/cm^2. The internal agreement of the observations provided an indication of the consistency of the monitoring by the crystal. The lithium films were pre-

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* Supported in part by the Office of Naval Research.

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[1] H. M. O'Bryan, Phys. Rev. **49**, 944 (1936).

[2] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **A161**, 420 (1937).

pared by thermal evaporation of the metal from a small furnace located in a specially designed auxiliary vacuum system attached to the spectrometer.

A theoretical evaluation of the atomic cross section has been carried out, and in a later section a comparison is made between the results of the measurements and the theoretical calculation.

II. EXPERIMENTAL

A. Spectrograph and Radiation Source

The cross section of a thin film of lithium is given by the formula[3]

$$\sigma = (11.5/s)\ \ln(I_0/I) \times 10^{-18}\ \text{cm}^2, \qquad (1)$$

where s is the surface density of the film in μg/cm^2 and where I_0 and I represent the incident and transmitted intensities. At each wavelength the measurement of I_0 and I was carried out photometrically by means of a grazing incidence spectrometer. The spectrometer and associated vacuum system are shown in Fig. 1. The dispersing element was a lightly ruled concave glass grating with 30 000 lines/in. and radius of curvature of 154 cm. The angle of grazing incidence was 4.64°. Ilford *Q*1 plates were used to detect the radiation. An occulter placed in front of a movable plate holder made it possible to make three contiguous exposures in the same plate. The source of radiation was similar to one used in a previous experiment,[3] and will not be described here. As in that experiment, argon was admitted into the capillary leak. In this instance, however, the purpose was not to obtain more spectral lines, but to prevent the contamination of the lithium films by the residual molecules of nitrogen and oxygen. The spectrum emitted from the capillary discharge was not as rich in lines as the spectrum from the vacuum hot spark used by the previous investigators; however, the density of lines from the capillary discharge was adequate for the purpose of establishing the absolute value of the cross section.

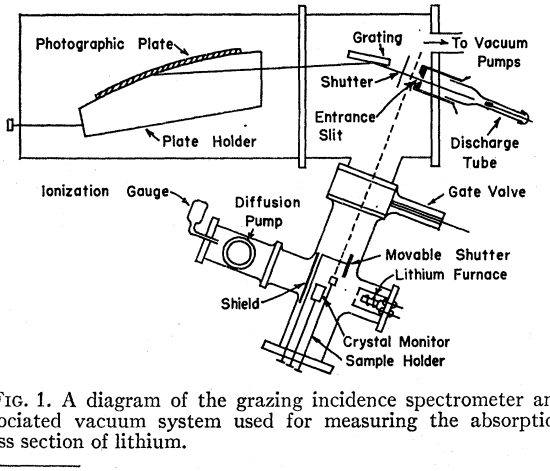

FIG. 1. A diagram of the grazing incidence spectrometer and associated vacuum system used for measuring the absorption cross section of lithium.

B. Preparation of Absorbers

The sample holder was initially located in the auxiliary evaporation chamber which was isolated from the main body of the spectrograph by means of a gate valve. The evaporation chamber was provided with its own diffusion pump, water-cooled baffle, and liquid-nitrogen trap. A freshly cut lump of the metal was washed in isopentane and then was inserted into the evaporation furnace consisting of a tantalum cylinder provided with heater coils and appropriate shields. A thin film of Zapon backed by a fine mesh screen served as the substrate on which the metal was condensed. Samples without the screen were found to be too fragile. During the initial stages of evaporation, the substrate was shielded from the furnace to avoid contamination of its surface. When the desired amount of lithium was deposited on the substrate, it was possible to transfer the absorber into the spectrometer through the gate valve and place it into the beam. The valve was kept closed during irradiation.

C. Measurement of Absorber Surface Density

Monitoring by a crystal oscillator provided the means for determining the surface density of the thin films of lithium. The decrease in the resonant frequency of a quartz crystal resulting from an increase of mass has been used previously for measurements of this type.[4–6] The method is well adapted for making measurements of the surface density in vacuum. In addition, the scheme is capable of detecting the very small surface densities involved. The resonant frequency of the crystal used in this experiment was 4.5 Mc/sec. Its sensitivity was such that a 1-cps change in its frequency corresponded to a lithium deposition of 1/50 μg/cm^2. The change in frequency resulting from an increase of mass was determined by beating the frequency of the monitoring crystal in the evaporation chamber against the frequency of a standard crystal external to the chamber. The crystal used for sampling the deposit was placed sufficiently close to the substrate to insure that both received the same mass per unit area. As a sort of check of the measuring equipment, the crystal was allowed to monitor a thin deposit of aluminum whose thickness was subsequently determined by an interferometric method.[7,8] The results were in reasonable agreement.

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[5] S. J. Lins and H. S. Kukuk, *Transactions of the Vacuum Symposium, 1960* (Pergamon Press, New York, 1960), p. 333.

[6] K. H. Behrndt and R. W. Love, *Transactions of the Vacuum Symposium, 1960* (Pergamon Press, New York, 1960), p. 87.

[7] S. Tolansky, *Multiple Beam Interferometry* (Oxford University Press, New York, 1948).

[8] G. D. Scott, T. A. Mclauchlan, and R. S. Sennett, J. Appl. Phys. **21**, 843 (1950).

It is estimated that the measurement of the total frequency change associated with a typical deposit has an uncertainty of about 50 cps. Such an uncertainty leads to an error of 10% in the measurements of the cross section. The sensitive response of the crystal afforded a way of observing the accumulation of contaminants upon the fresh lithium surface. It was noticed that there was a very slow steady change in the resonant frequency, presumably after the crystal had reached equilibrium subsequent to evaporation. This slow change was taken to mean that the fresh lithium surface was picking up nitrogen, oxygen, or organic molecules from the surroundings. As indicated by the drift of the crystal frequency during the time of the exposure, the accumulated mass due to such impurities was less than 5% of the mass of lithium evaporated. There was no change in this frequency drift when the evaporation chamber and the spectrometer were interconnected. This observation indicated that the pressure in that region, while high enough to allow the operation of the spark tube, was not such as to cause undue contamination of the absorber.

D. Operational Details and Sources of Error

The following steps were followed in measuring the absorption due to lithium. The plastic substrate was inserted into the spectrometer and an exposure was taken. Then the substrate was moved back into the evaporation chamber and lithium evaporated onto it. The lithium sample was returned to the spectrometer, and the photographic plate moved so that an unexposed portion of it could receive the dispersed radiation transmitted by the sample. The two successive runs will be labeled as I_0 and I exposures, respectively. For suitable photographic densities, 50 to 100 sparks were necessary for the I_0 exposure. On the other hand, up to 1200 sparks were required for the I exposure. The photographic records were reduced according to the scheme described in a previous paper,[3] and the absorption cross section was obtained by the use of Eq. (1).

The largest uncertainty in the experiment arises from the error in the measurement of the surface density of the thin films. Experience has shown that the relative intensities of the spectral lines produced by the spark tube are constant to within 5%, and the intensity ratios were chosen so that this error would not be magnified when the logarithm of their ratio was taken. As already mentioned, the absorbers could be regarded as essentially free of contamination so that the uncertainty in the cross section arises mostly from the determination of the surface densities. As already stated, this error is approximately 10%.

III. RESULTS AND DISCUSSION

Five runs were made, each at a different surface density. The results for several different wavelengths are shown in Fig. 2. In each case, the logarithms of the ratio of the transmitted to incident intensity has been plotted vs the surface density. These plots should result in straight lines whose slope multiplied by an appropriate factor yields the cross section for that particular wavelength. The cross sections attained in this manner are depicted in Figs. 3 and 4 as a function of the wavelength, as well as the energy of the incident photons. Figure 3 also includes the results of Skinner and Johnston[2]. The ordinate for their data is arbitrary, so that one may only compare the shapes of the curves. Figure 4 also includes the theoretical calculation of the cross section, discussed below. Table I lists the values of the absorption cross section for every spectral line used in the experiment.

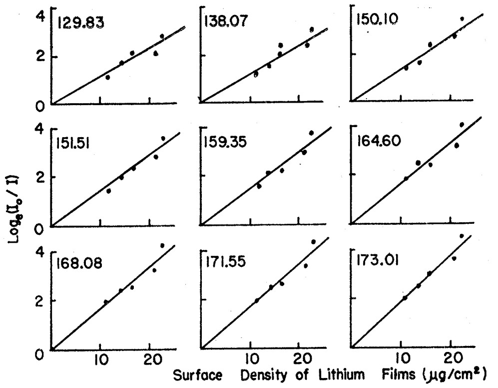

FIG. 2. Plots of $\ln(I_0/I)$ as a function of surface density of the lithium films. Each graph represents measurements at the particular wavelength indicated in the upper left-hand corner. The lines drawn through the points determine the absorption cross section for each wavelength.

Huang[9] has published detailed calculations of the absorption cross section of helium and we have modified his results to include the case of atomic lithium. For the ground state the wave function derived by

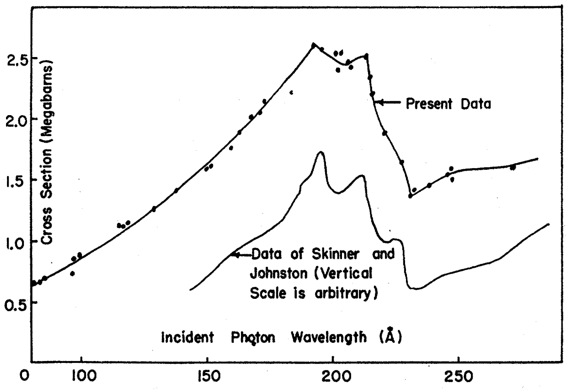

FIG. 3. The photoelectric K-absorption cross section of lithium vs the wavelength of the incident photons. Both the present data and the data of Skinner and Johnston are represented. The latter results are plotted on an arbitrary vertical scale because the thickness of the absorbing films was not known.

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[9] S. Huang, Astrophys. J. 108, 354 (1948).

TABLE I. The continuous photoelectric absorption cross section of lithium in the region of the K edge. The tabulation contains the wavelength, energy, and identification of the spectral lines used for the measurements. Also included are the number of observations at each wavelength.

Wavelength in Å	Energy in eV	Identification	No. of obs.	Cross section (mb)
80.57	153.87	Si VI	4	0.65
83.30	148.83	Si VI	4	0.67
85.32	145.31	Si VII, V	4	0.69
96.58	128.36	Si VI, V	5	0.74
97.29	127.43	Si V	4	0.86
99.6	124.47	Si VI	3	0.89
115.82	107.04	O VI	2	1.13
117.85	105.19	Si V	4	1.12
118.97	104.21	Si V	4	1.15
129.83	95.49	O VI, Mg IV	5	1.26
138.07	89.79	O V	5	1.42
150.10	82.59	O VI, Na IV	5	1.59
151.51	81.83	O V, Na V	5	1.61
159.35	77.79	O V	5	1.76
164.60	75.31	O V, Mg III, Na IV	5	1.89
168.08	73.76	O V, Na IV	5	2.01
171.55	72.27	Mg III, IV	5	2.05
173.01	71.66	O VI	5	2.14
184.04	67.36	O IV	5	2.21
192.82	64.30	O V	5	2.59
195.95	63.27	O IV	2	2.56
202.32	61.28	O V, Na III	2	2.54
203.00	61.07	O IV, C IV, Na III	4	2.40
203.86	60.81	O V, Na IV	2	2.54
207.24	59.82	O IV	2	2.46
214.25	57.86	O IV, Na III	2	2.51
215.20	57.61	Na III, O V	3	2.34
216.02	57.39	O V, Na III	2	2.20
220.35	56.26	O V	5	1.88
227.53	54.49	O V	4	1.64
231.20	53.62	O IV, V, Mg III	3	1.37
233.52	53.09	O IV	4	1.42
238.47	51.99	O IV	3	1.44
246.20	50.36	O III, Si VI	2	1.54
247.59	50.07	N V	2	1.59
248.60	49.87	O III	2	1.50
272.15	45.55	O IV	2	1.60

Eriksson[10]:

$$\psi=5.75e^{-2.83(r_1+r_2)}\times[1+0.332r_{12}+0.163(r_1-r_2)^2-0.0328r_{12}{}^2], \quad (2)$$

was used and the wave function for the final state was the product of two wave functions: (1) the wave function for an electron in the ground state and moving in the field of a nucleus having a charge of three units, and (2) the wave function of an electron with positive energy moving in the field of a nucleus with charge $+Z$. We have carried out the calculations for $Z=1$ and 2. The results are plotted in Fig. 4. The case $Z=2$ represents complete screening by the remaining $1s$ electron; while for $Z=1$, one has complete screening by both the $1s$ and the $2s$ electron. It is most probable that the correct value of Z lies somewhere between these two, or, in other words, we expect the observations to lie somewhere in the shaded region.

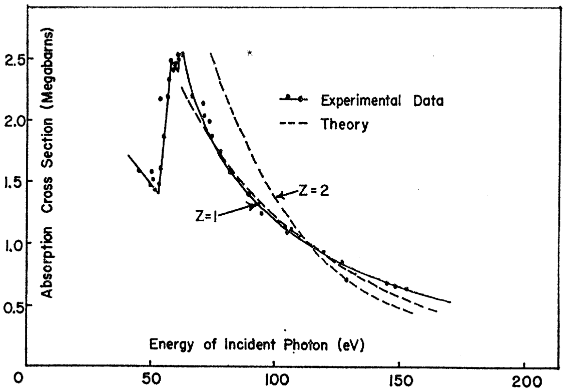

FIG. 4. The photoelectric K-absorption cross section of lithium as a function of the incident photon energy. The present experimental results are represented by dots and a solid line. The dashed lines represent the theoretical calculations. Agreement between experiment and theory is best for $Z=1$, where Z is the value of nuclear charge "seen" by the ejected electron.

We see that the shape of the curve and also the absolute value of the cross section agree best with the calculation corresponding to the case $Z=1$. The indications are that the screening of the nucleus by the $2s$ electron is more effective than might be expected at first sight. The absorption curve in the vicinity of the edge shows some secondary structure not predicted by the atomic theory. These peaks have been best explained by Hayasi,[11,12] who suggested that they might be absorption maxima superimposed on the background absorption curve. Hayasi assumed that the ejected electron goes into a so-called quasi-stationary state. This state is formed when the associated waves form a standing wave pattern in the vicinity of the ionized atom. This theory predicts a small number of intense absorption maxima, and for the case of lithium, Hayasi was able to predict with good accuracy the positions of the observed peaks. However, the main part of the absorption can be explained using a purely atomic theory. As in the heavier elements, the contribution of the bound-state wave function to the matrix element is small where the effects of the solid state on the final-state wave function are large.

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[11] T. Hayasi, Sci. Repts. Tohoku Univ. **34**, 185 (1951).

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