

The Absorption of Selenium in the Soft X-Ray Region*

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The absorption of selenium (from 180A to 240A) has been investigated experimentally. The absorption edge near 225A has been resolved into a double edge due to M_{IV} and M_V absorption. The separation of these edges is 0.7 ev. A minimum in the absorption is observed at 208A.

I. INTRODUCTION

IN the process of x-ray absorption by solids the energy of the light quantum $h\nu$ is used to raise an electron from its initial energy state into another state which is both permitted and empty. The probability that an electron will absorb the energy of an incoming quantum and be raised to a vacant state of energy E is proportional to the density of permitted states with energy near E . This quantity is usually called $N(E)$. The ultimate goal of most absorption measurements is to furnish information which may aid in the eventual determination of $N(E)$ for the substance under study.

The soft x-ray region (or the extreme vacuum ultraviolet) is suitable for this work because the electrons involved are lifted into the outer bands from initial levels which are sufficiently narrow that their width may be ignored. At the same time the total energy involved in the transition is considerably less than 100 times the width of the upper energy band. For this reason the spectrometer need not have unusually high resolving power.

II. EXPERIMENTAL PROCEDURE

Figure 1 is a simplified diagram of the equipment. The Rowland circle is one meter in radius. The plate holder follows the circle and the circle passes through the slit. The grating of 30,000 lines per inch is tangent to the Rowland circle. The angle of incidence is 85° . The source used for this work was a vacuum spark between copper electrodes operated from a 50-kv power supply. The equipment is essentially the same as that used by Skinner and Johnston¹ and Sanner.² Wavelengths were determined from known lines³ in the copper spectrum.

The absorber was mounted on a small metal plate with a hole in it, and this plate was located just behind the slit.

The absorber consisted of a thin foil of selenium evaporated onto a thin film of celluloid. In order to obtain the absorption due to selenium it is sufficient to compare the transmission through two absorbers for which the thickness of the selenium is different, but which are otherwise identical. Neither is it wise to use

a zero thickness of selenium on one of the absorbers, since this would alter the reflection of the radiation from the boundaries. Also, Pell and Tomboulian⁴ have observed that for aluminum there is an extra absorption band associated with the interface between the metal and the backing material. The use of a comparison absorber with no selenium would result in attributing such a band (if it exists for a collodion-selenium interface) to the selenium. On the other hand, if both absorbers have a sufficient thickness of selenium any effect associated with the interface will not show up in the comparison. For these reasons no measurements were made from absorbers having less than 470A of selenium.

The two absorbers used in any given comparison were made with celluloid from the same floating so that the celluloid films would be as identical as possible. These two were placed in the evaporator together and selenium deposited on one to a thickness t_1 , with the other covered over by means of a plate which could be moved from outside the vacuum. The plate was then turned aside and the evaporation continued until the selenium on the second absorber reached a thickness t_2 . The thicknesses t_1 and t_2 were determined by the interference of visible light reflected from the two surfaces of the selenium. The conversion to actual thickness requires the use of the index of refraction of selenium for the visible light used. Mercury green light was used and the index was found to be 2.9. The celluloid backing films were approximately 300A thick.

In a normal run four exposures were made on the

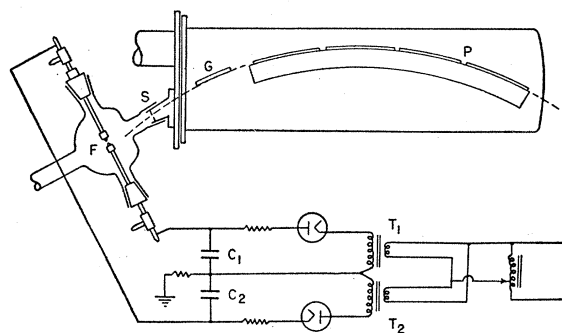


FIG. 1. The vacuum spectrograph showing the plateholder (P), the grating (G), the slit (S), and the vacuum spark (F). The essential features of the power supply are also shown.

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¹ H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **A161**, 420 (1937).

² H. Sanner, Z. Physik **94**, 523 (1935).

³ P. G. Kruger and F. S. Cooper, Phys. Rev. **44**, 826 (1933).

⁴ D. H. Tomboulian and E. M. Pell, Phys. Rev. **83**, 1196 (1951).

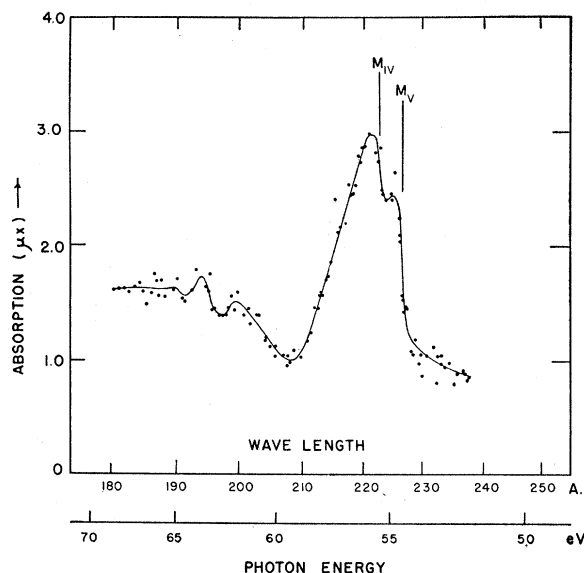


FIG. 2. The absorption due 1900Å of selenium. Notice the double edge near 225Å and the spectral window at 208Å.

same photographic plate. Three of these were made through the thinner absorber with varying exposures of K_1 , K_2 , and K_3 . The fourth exposure was then made through the thicker absorber with an exposure of K_4 . The exposure was determined by counting the number of sparks produced by the source. The plate was then developed with good agitation so that all four exposures received identical processing. Densitometer traces were then made from these spectra and measured in the usual manner.

The first three exposures are used to determine the response curve of the photographic emulsion. At each wavelength we have three points on the curve except that the exposures are relative not absolute. Using a number of different wavelengths many sets of points can be obtained, and these are then fitted into a smooth response curve by matching exposures at overlapping densities. The response curve obtained in this way is based on the assumptions that the response is constant over the wavelength range employed and that the reciprocity law is valid. The final comparison of the fourth exposure with one or more of the other three was made using this response curve. This method is reminiscent of the method used by Cady and Tomboulia⁵ in their emission studies.

⁵ W. M. Cady and D. H. Tomboulia, Phys. Rev. **59**, 381 (1941).

III. RESULTS AND CONCLUSIONS

The results of these investigations are shown in Fig. 2 which shows the absorption of selenium against wavelength and photon energy. The data for this curve were taken from two absorbers for which t_1 (the difference in thickness of selenium) was 1900Å and t_2 was 480Å. The measurements were repeated using another (but similar) pair of absorbers. The new curve and the original were practically identical in shape and location in the spectrum, whereas the values of μx agreed within about 5 percent. For the curve shown $K_1=4000$; $K_2=2000$; $K_3=1000$; and $K_4=4000$.

The absorption edge at 225Å is seen to be double representing the separation of the M_{IV} and M_V edges. This separation of 3Å or 0.7 eV is consistent with the value obtained by extrapolating from the M_{IV-V} separation of tungsten using the rule that this separation is proportional to $(Z-13)^4$.

The magnitudes of these two absorption jumps are predicted to be in the ratio of 2:3. The ratio is observed to be about 1:4, the M_V jump being relatively larger than predicted. Skinner has observed that in emission the L_{III}/L_{II} intensity ratio is the predicted value of 2 only for insulators. For semiconductors and metals the ratio is much larger. He attributes this to an Auger process. It is difficult to visualize how such a process could alter the strength of the absorption edges.

There is a minimum in the absorption about 4.6 eV above the absorption edge. Since this is essentially the same as 4.62 eV reported⁶ as the work function of selenium, this minimum corresponds to electrons which are nearly freed from the solid by the photon. Since the selection rule $\Delta L = \pm 1$ indicates that transitions $d \rightarrow s$ and $d \rightarrow d$ should be improbable, the absorption curve for the M_{IV-V} electrons represents the density of states $N_p(E) + N_f(E)$. Also, $N_f(E)$ for selenium is small so the absorption largely represents $N_p(E)$. The decline in absorption for wavelengths shorter than 218Å is probably due to a decrease in the density of these states. The fact that the conduction band arises from p electrons, whereas the next two bands above it arise from s and d electrons, gives support to this viewpoint.

The structure at shorter wavelengths is without explanation since the energies are too small to give Kronig structure, and the next absorption edge (M_{II-III}) is expected to lie near 100Å.

⁶ R. Hamer, J. Opt. Soc. Am. **9**, 256 (1924).