PHYSICAL REVIEW VOLUME 100, NUMBER 4 NOVEMBER 15, 1955

Soft X-Ray Absorption of Tellurium and Vitreous and Metallic Selenium*

M. PARKER GIVENS, CHARLES J. KOESTER,† AND WILLIAM L. GOFFE
Institute of Optics, University of Rochester, Rochester, New York

(Received June 29, 1955)

The absorption of metallic selenium is compared with that of the vitreous form in the region from 200 A to 240 A. For these two forms of selenium and for tellurium, the absorption band is separated into two component bands. This has led to a revised estimate of 1.2 ev for the separation of the M_{IV} and M_{V} levels of selenium and 1.6 ev for the separation of the N_{IV} and N_{V} levels of tellurium.

INTRODUCTION

EXPERIMENTAL studies of the soft x-ray absorption of vitreous selenium[1] and of tellurium[2] have been reported previously. The purpose of this paper is to present the results of similar studies on metallic selenium and to give a brief discussion of the results.

The purpose of most soft x-ray absorption measurements is to provide information which may be of value in determining the density of states in the conduction band. In selenium and tellurium, this is complicated by the fact that the lower (or initial) state is double. Therefore, an effort has been made to correct for this doubling and so to reveal the shape which the absorption band should have had if the lower level had been single instead of double.

METHODS

The experimental procedures have been described in the earlier papers[1,2] and only points of special interest are mentioned here. The samples were prepared by vacuum evaporation. The thickness of the selenium films was determined by observing the color of the light reflected from them, a method which has been checked by interferometric measurements. These thickness observations were made with the film in the vitreous state, and it was then converted to the metallic form by heat treatment as described earlier.[3] No measurements were made of the thickness of the samples after their conversion to the metallic state. For this reason, the selenium deposit is here reported in terms of surface density rather than thickness. In bulk selenium, there is a 15% increase in density from the vitreous to the metallic form. Assuming bulk densities, a surface density of 100 μg/cm^2 corresponds to a thickness of about 2340 A of vitreous selenium or 2090 A of metallic selenium. This estimate, however, may be in some error because of imperfections in the evaporated films and the probability that these imperfections are largely removed by the heat treatment.

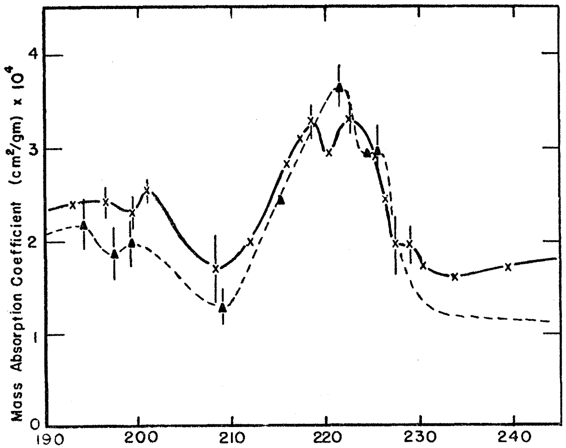

FIG. 1. The soft x-ray absorption band of selenium --▲---▲-- vitreous selenium; ——×———×—— metallic selenium.

The absorption curves for both forms of selenium are given in Fig. 1. In each case there is a strong absorption band in the region around 220 A and this band has a double peak. The detailed features of the two curves are not alike. Notice the apparent change in relative magnitude of the two peaks and the changes in their positions. Outside of the absorption band, the metallic form shows a somewhat higher absorption than the vitreous.

Since each of these curves represents the average of several different runs, vertical lines have been drawn at several points to indicate the standard deviation of the mean at each point. On this basis, it is possible to interpret the vertical separation of the two curves as experimental error. The structure at wavelengths shorter than the absorption band is different for the two forms. The shape of these curves is much better established than Fig. 1 would indicate. In the original work a great

TABLE I. Comparison of the absorption by two forms of selenium.

Feature	Location of feature (angstroms) Vitreous form	Location of feature (angstroms) Metallic form
Absorption edge	228.1	226.4
Peak at longer wavelength	225.5	222.8
Peak at shorter wavelength	221.6	218.7
Peak separation	3.9	4.1

---

* This work was supported initially by the Office of Naval Research and recently by the National Science Foundation.

† Now with the American Optical Company, Southbridge, Massachusetts.

[1] M. P. Givens and W. P. Siegmund, Phys. Rev. 85, 313 (1952).

[2] R. W. Woodruff and M. P. Givens, Phys. Rev. 97, 52 (1955).

[3] M. P. Givens, Rev. Sci. Instr. 25, 1130 (1954).

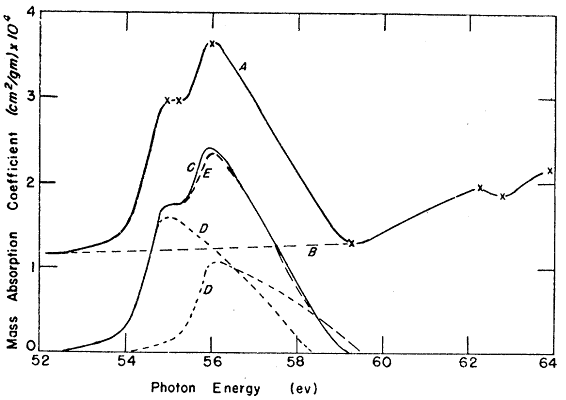

FIG. 2. Structure of the absorption band of vitreous selenium. *A*—Experimental curve. *B*—Background. *C*—Experimental curve minus background. *D*—Suggested individual peaks. *E*—Sum of the suggested peaks.

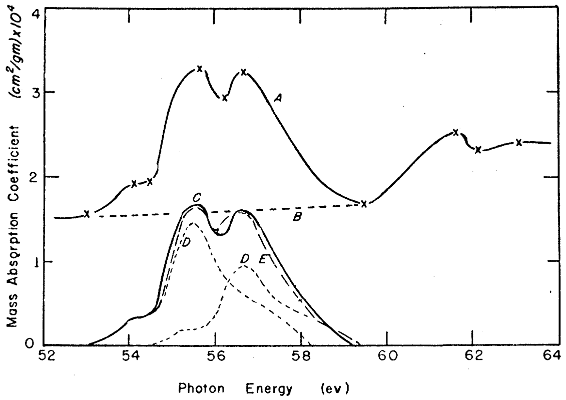

FIG. 3. Structure of the absorption band of metallic selenium. *A*—Experimental curve. *B*—Background. *C*—Experimental curve minus background. *D*—Suggested individual peaks. *E*—Sum of the suggested peaks.

many experimental points were observed, only a few of which are reproduced here. Upon repeating the experiment with a fresh sample a new curve was obtained, which duplicated the original in shape but differed from it in absolute magnitude. It is this uncertainty in absolute magnitude which is indicated by the vertical lines in the figure.

Table I shows some of the interesting features of these curves. The standard deviation of the mean for the location of the edges and peaks shown in the table is about 0.5 A. Since these edges and peaks differ in position between the two forms by considerably more than 0.5 A, the shift is probably real.

Since the doubling of the peaks is due to the separation of the M_{IV} and M_{V} levels, an effort has been made to resolve the absorption into two bands, each having a shape associated with the density of states within the conduction band. This has been done by using a method described by DuMond.[4]

The method requires that the following assumptions be made: (1) the two absorption bands must be identical in shape and differ only in intensity (i.e., vertical dimension), and (2) there is no other contribution to the absorption except from these two bands. This last assumption is equivalent to assuming there is no third band and that the background absorption can be subtracted out in some simple manner. The first assumption is reasonable because the M_{IV} and M_{V} levels are both *d* levels, which causes the shape of each absorption curve to be determined by the density of *p*- (and *f*-) type states in the conduction band. The relative intensity of the two bands and their horizontal (or energy) separation must be selected. These two quantities along with the background subtraction provide three parameters which may be adjusted to some extent in an effort to make the method work.

If the method is properly applied, and if the parameters are correctly selected, then the band will be resolved into its two components which may be added together to give the original band within experimental error. Some care must be exercised at this point. If the final recombined curve is required to fit the original more closely than the data justify, then additional structure (presumably extraneous) will appear in the component bands. For this reason, the reconstructed curves do not match exactly the original curves but are within the experimental uncertainty. It might be argued that these reconstructed curves are more meaningful than the original curves which were drawn by eye through the experimental points. In view of the possibilities, it is surprising that the results check as well as they appear to. The curves were plotted on a linear energy scale before beginning the resolution process.

RESULTS

The results of the resolution and recombination are shown in Figs. 2 and 3. The figures show the original curves, the assumed background, the absorption band after subtraction of background, the two separated bands, and finally the recombination of these bands.

For simplicity, the background was assumed to correspond to a straight line connecting the two minima beside the band. Slight variations from this line might have helped the situation somewhat, but any particular choice would have been hard to justify.

Several values of the parameters were tried. Intensity ratios of from 1.4 to 1.6 seemed to work very well. A value of 1.5 was selected, not only because it was near the middle of the satisfactory range but also because this is the relative probability of the transitions from the M_{IV} and M_{V} levels to the 4*p* levels in isolated selenium atoms.

The energy separation between the two bands represents the separation of the M_{IV} and M_{V} levels. A casual examination of the absorption curves indicates that this should be approximately one electron volt. A value

---

[4] J. W. M. DuMond, Revs. Modern Phys. **5**, 1 (1933).

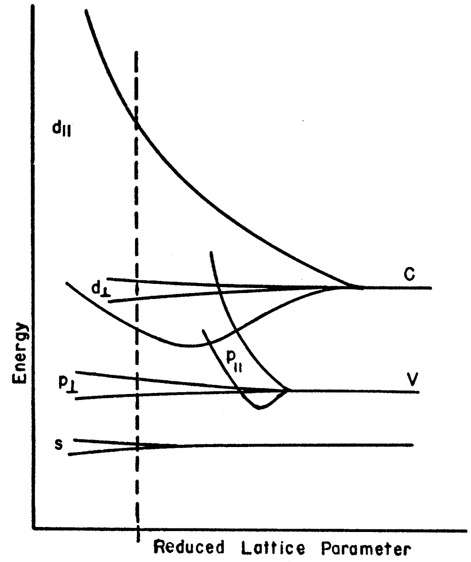

FIG. 4. Schematic diagram of the energy levels of tellurium (after Callen[5]), showing the broadening of the bands as the atoms are brought together. The subscripts indicate that the symmetry of the wave functions is perpendicular or parallel to the chain axis of the crystal. V is the valence band; C is the conduction band.

of 1.2 ev was selected because it could be used for both the metallic and vitreous curves; one should not expect the separation of the M_{IV} and M_{V} levels to be detectably different in these two cases. This value of 1.2 ev is somewhat larger than the value 0.8 ev predicted by the rule that this separation should be proportional to $(Z-13)^4$.

The separated curves of Figs. 2 and 3 should represent the function $N(E)$ or the density of states in the conduction band. For the two forms of selenium these curves are quite different. Certainly in the case of metallic selenium the curve indicates a narrow band superimposed on a broader weaker band. In view of the theoretical work of Nussbaum[4] and Callen[5] on tellurium, and since selenium and tellurium have similar electronic and crystalline structures, the following explanation is suggested for the shape of the density of states curve of metallic selenium (see Fig. 4).

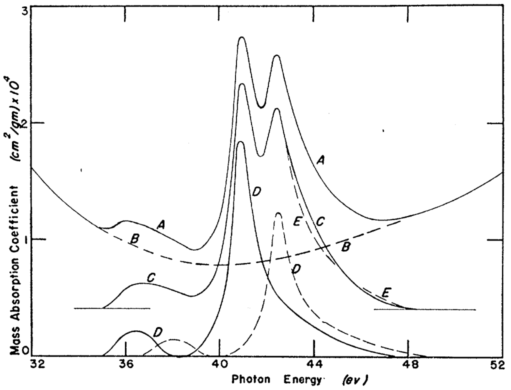

FIG. 5. Structure of the absorption band of tellurium. A—Experimental curve (minus 2×10^4 cm²/g). B—Background. C—Experimental curve minus background. D—Suggested individual peaks. E—Sum of the suggested peaks. Curves C and E have been displaced vertically.

The valence electrons are $4p$ electrons, of which there are four per atom. In the crystal, the $4p$ band is divided into two branches. In one branch the wave functions are symmetrical about lines parallel to the crystallographic chain axis; this branch can accommodate two electrons per atom. The other branch is due to electrons having their wave functions symmetrical about lines perpendicular to the crystallographic chain axis; this branch can accommodate four electrons per atom. At normal interatomic distances, the perpendicular branch is filled and the parallel branch is at a much higher energy, so that the latter is empty and takes no part in the absorption band which has been observed. The conduction band arises from states corresponding to $4d$ states of the isolated atom. This band also divides itself into two parts, a narrow band of perpendicular symmetry and a wider band of parallel symmetry. Unlike the p band, these two parts are superimposed rather than separated. The observed absorption is believed to be due to transitions from the $3d$ (i.e., $M_{\text{IV-V}}$) levels to this $4d$ band. The violation of the selection rule $\Delta l=\pm1$ may be ignored on the grounds that this rule is not valid in the solid, or one may recall that the states in the $4d$ band are of mixed character and have some p- or f-type symmetry. In any case, such violations of the selection rule are common in solids. On the basis of this interpretation, the experimental data indicate that the narrow $4d$ perpendicular band begins about 2 ev above the bottom of the broader $4d$ parallel band. This is possible since the work function of selenium[6] is 4.62 ev.

In the case of vitreous selenium, the density-of-states curve is not an obvious superposition of two bands. This is probably due to the fact that the crystal structure is not well formed in vitreous selenium and so it is less meaningful to distinguish between directions parallel and perpendicular to the chains.

The absorption by tellurium is reproduced from the earlier work (Fig. 5). To this has been added the resolution of the band into its two component parts as was done for selenium. The value of 3:2 for the intensity ratio of the two components again proved satisfactory and a separation of 1.6 ev for the N_{IV} and N_{V} levels gave the best fit. However, a variation of ±0.05 ev in this value was not significant in the analysis. In this case a straight line for the background was entirely unusable, so a "reasonable" background curve was sketched in and the data were reduced.

The density-of-states curve thus obtained showed a strong peak at 40.9 ev, with a secondary peak at 36.5.

---

[4] A. Nussbaum, Phys. Rev. **94**, 337 (1954).

[5] H. B. Callen, J. Chem. Phys. **22**, 518 (1954).

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

The depth of the minimum between these two peaks was sensitive to the choice of background curve. Shown in the figure is the particular background curve which resulted in a zero minimum between these two maxima.

The interpretation here cannot be as simple as that suggested for selenium. The absorption corresponds to transitions from $N_{\mathrm{IV-V}}$ to $5d$. According to Callen,[5] the $5d$ band is made up of a broad band and a narrow band as before. However, the infrared absorption studies of Loferski,[7] interpreted in the light of Callen's work, indicate that the d perpendicular band begins less than 0.1 ev above the bottom of the d parallel band. Such a small separation would not have been resolved in the present study, so that the main absorption band between 39 ev and 46 ev is probably due to the combined effect of these two bands.

It is conceivable that exciton levels on impurity levels appear because the electron is leaving an ion behind with one extra positive charge. If this were the case, these levels would lie just below the conduction band and transitions into them might account for the small band on the low-energy side of the main band. This explanation is not entirely satisfactory because the impurity band proposed is wider than is customarily observed.[8] Also, the energy separation between the main band and the impurity band is large, in particular much larger than the 0.324 ev indicated by the data of Loferski as the separation between the valence and conduction bands. In addition, the width of the band is larger than 4.76 ev which is the work function of tellurium.[9]

---

[7] Joseph J. Loferski, Phys. Rev. **93**, 707 (1954).

[8] E.g., L. G. Parratt and E. L. Jossem, Phys. Rev. **97**, 916 (1955).

[9] Apker, Taft, and Dickey, Phys. Rev. **74**, 1462 (1948).

PHYSICAL REVIEW VOLUME 100, NUMBER 4 NOVEMBER 15, 1955

Velocity Analysis of Thermionic Emission from Single-Crystal Tungsten

GEORGE F. SMITH
Electron Tube Laboratory, Hughes Research Laboratories, Culver City, California

(Received June 24, 1955)

Hutson has recently observed a non-Maxwellian distribution of thermionic emission from various crystallographic directions of a tungsten single crystal. It is suggested that the true distribution is Maxwellian, and that the observed distribution is due to an analyzer resolution of 0.24 volt. Factors which might affect resolution are discussed, and Hutson's numerical results are recalculated on the basis of this explanation.

HUTSON[1] has recently reported a careful experiment in which he observed a departure from Maxwell-Boltzmann distribution in the electron emission from single-crystal tungsten. This departure, a low-energy deficit, was the same in various crystallographic directions. As Hutson has pointed out, it is unlikely that the various crystal directions would be patchy in just such a way as to yield identical distributions. He also noted that the reflection coefficient which he uses to account for the distribution has, as yet, no satisfactory theoretical explanation.[2]

We suggest that some extraneous effect in the analyzer might affect analyzer resolution in such a way as to produce the observed distribution. Hutson's experimental points[3] for 2000°K are plotted in Fig. 1, along with a Maxwell-Boltzmann distribution modified by a 0.24-v rectangular resolution. It is seen that the match is very good. The 0.24-v figure was chosen to match the 2000°K data by interpolation from curves for resolutions of 0.2 v and 0.3 v. The same 0.24-v resolution figure was also applied to a Maxwell-Boltzmann distribution for 1700°K. The match to Hutson's experimental points[4] for 1700°K was equally good.

Hutson calculates a tenfold better resolution, 0.024 v, from the dimensions of the analyzer and its operating potential. He states[1,5] that the same distribution was obtained when the resolution was electrically changed to 0.06 v by varying the magnetic field. He concludes that the instrumental resolution was adequate for the detail in the distribution. One might reason instead that the resolution was already limited at 0.24 v by some other factor and that it was not actually being changed by the variation in magnetic field. There is no obvious cause for a spurious loss in resolution. Interconnection of radial and axial energy components, caused by slight misalignment of the analyzer and accelerating diode appears to be ruled out by precision assembly.[1] Stray time-varying magnetic fields were too small to affect the resolution.[1] The presence of patch fields is perhaps the most plausible hypothesis. The configuration of the analyzer is given in reference 1, Fig. 1. A patch field at the central baffle slit would deflect electrons from their normal line focus. A simple order-of-magnitude calculation can be made if patch crystals in the tantalum

---

[1] A. R. Hutson, Phys. Rev. **98**, 889 (1955).

[2] C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949), Sec. IV.4; D. W. Juenker *et al*, Phys. Rev. **90**, 772 (1953); S. C. Miller, Jr., and R. H. Good, Jr., Phys. Rev. **92**, 1367 (1953).

[3] From reference 1, Fig. 5.

[4] From reference 1, Fig. 11.

[5] A. R. Hutson (private communication).