for example, to a combination band absorption with frequency near the fundamental optical absorption.

ACKNOWLEDGMENT

The authors wish to acknowledge the helpful suggestions and active interest and encouragement given to our work by Mr. Paul H. Egli.

Note added after completion of manuscript.—R. J.

Collins and H. Y. Fan[27] have recently reported measurements on the infrared lattice absorption of germanium, silicon, and diamond as a function of temperature. They conclude that the observed absorption in silicon and germanium and of Type II diamond is made possible by the thermal vibrations of the atoms. However, they do not suggest any mechanism for the absorption.

[27] R. J. Collins and H. Y. Fan, Phys. Rev. **93**, 674 (1954).

Soft X-Ray Absorption of Evaporated Thin Films of Tellurium*

Robert W. Woodruff† and M. Parker Givens
Institute of Optics, University of Rochester, Rochester, New York
(Received July 28, 1954)

The linear absorption coefficient of tellurium has been measured in the wavelength region 100A to 400A. A double peak was observed at about 300A; it is due to transitions from the $N_{\rm IV}$ and $N_{\rm V}$ levels to the conduction band. A large peak at shorter wavelengths was also observed.

I. INTRODUCTION

THE energy levels of materials in the solid state are broadened into bands by the interaction of the overlapping atomic wave functions. The bands may be considered to be composed of a very large number of levels so close together that they may be described by a continuous function $N(E)$, where $N(E)dE$ is the number of energy levels between E and $E+dE$.

The absorption of light associated with an electronic transition from some lower energy level to the levels in the range E to $E+dE$ is proportional to the function $N(E)$, and also to the transition probability, $f(E)$. Since $f(E)$ depends on the exact wave functions, its value is not known and, hence, measurement of the absorption can give only a qualitative picture of $N(E)$. Also to be considered is the fact that raising an electron out of an inner level alters the charge of one ion so that the observed energy level structure is that of a slightly perturbed lattice.

The lower or x-ray levels are broadened due to radiation damping and Auger transitions. These two effects have been studied by Prins.[1] He showed that on a linear energy scale the soft x-ray levels, which are about 100 volts below the valence band, are narrower than the deeper-lying levels such as the K and L levels. In studying the structure of the conduction band it is advantageous, therefore, to use the soft x-ray levels rather than the deeper-lying levels.

The experimental resolving power required to reveal a conduction band structure 0.1 volt wide is only about

1000 when using soft x-rays, but will be more than a hundred times that much when using transitions from the K levels. The soft x-ray region therefore offers experimental as well as theoretical advantage over the conventional x-ray region.

II. EXPERIMENT

The vacuum spectrograph used in this research was modeled after one used by Skinner and Johnston[2] and has been described by Siegmund[3] with certain modifications discussed by Carter.[4] In brief, the instrument is a grazing incidence mount of a two meter aluminum grating with 30 000 lines/inch. The source, the grating and the photographic plate holder are on the Rowland circle. The angle of incidence is 85°.

A vacuum of 5×10^{-5} mm Hg is maintained by means of two oil diffusion pumps, one on the main chamber and the other on the source chamber. The source is a spark between copper or silver electrodes from a 0.15-μf condenser charged to about 30 000 volts. This was effectively controlled by an air gap in series with the internal spark. The plate holder, situated behind an occulting diaphragm, was designed to be movable from outside through an "O" ring seal. Five exposures could be made on Eastman Kodak Spectroscopic Plates, type SWR Extra-thin, size 2 in.×10 in.

The wavelengths were determined from tables of the copper spark spectrum prepared by Kruger and

[1] J. A. Prins, Physica **2**, 231 (1935).

[2] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **A161**, 420 (1937).
[3] W. P. Siegmund, thesis, The University of Rochester Library, 1951 (unpublished); for a brief account of this work see Phys. Rev. **85**, 313–314 (1952).
[4] D. E. Carter, thesis, The University of Rochester Library, 1954 (unpublished).

Cooper.[5] They list the prominent lines found in a similar vacuum spark. Using this data and the calculated position, a fit can be made between existing lines and listed lines on a smooth curve of wavelength *versus* distance along the plate. Once this curve is firmly established, the wavelength may be read off for any plate so long as any one line is recognized.

Two films of tellurium, one thick and one thin to eliminate the effects of the interface, were deposited by vacuum evaporation onto two identical celluloid substrates. These were mounted close to the slit on the grating side in a device that allowed change from one absorber to the other from outside the spectrograph. Celluloid was chosen for a substrate because tellurium deposits on it in a continuous layer; because thin films of it are easily made by dropping cellulose nitrate dissolved in amyl acetate on water; and because the absorption in this region is known to be small from a measurement by O'Bryan.[6] The thicknesses of several tellurium films were measured with a Fizeau-type interferometer and a curve of thickness *versus* optical density established. It was then only necessary to measure optical density of later tellurium films to ascertain the physical thickness. The accuracy of these measurements was approximately 5 percent.

Recently it has been shown[7] that evaporated films of tellurium are not completely crystalline when deposited on substrates below 200°C. The resistivity of these films is, however, of the same order of magnitude as bulk tellurium. This indicates that there is probably a tendency for microcrystals to anneal into near-crystalline form. That the films are continuous layers is borne out by microscopic study of the evaporated films on celluloid. There is no evidence of grainy appearance. It has been concluded from the work of Keck[8] and Hendus[9] on selenium that the valence structure is the same in amorphous and crystalline forms. Since selenium and tellurium are isomorphous, the same argument is applicable here.

Five exposures were made with each set of absorbers, two through the thick film differing by a factor of two in number of sparks, two through the thin film with the same factor but different numbers of sparks, and a repeat exposure through the thin film to check the reproducibility. The plates were developed in *D*-19 in a tray with continuous agitation supplied by rocking while the temperature was maintained at 65°F. Care was taken to avoid contamination of the plates in any way.

A microdensitometer trace was made of each spectrum using a radiometer type device in which the deflection of the vane is proportional to the intensity transmitted by the plate. The instrument was run

[5] F. S. Kruger and P. G. Cooper, Phys. Rev. **44**, 826 (1933).
[6] H. M. O'Bryan, J. Opt. Soc. Am. **22**, 739 (1932).
[7] T. Sakurai and S. Munesue, Phys. Rev. **85**, 921 (1952).
[8] P. H. Keck, J. Opt. Soc. Am. **41**, 53 (1951).
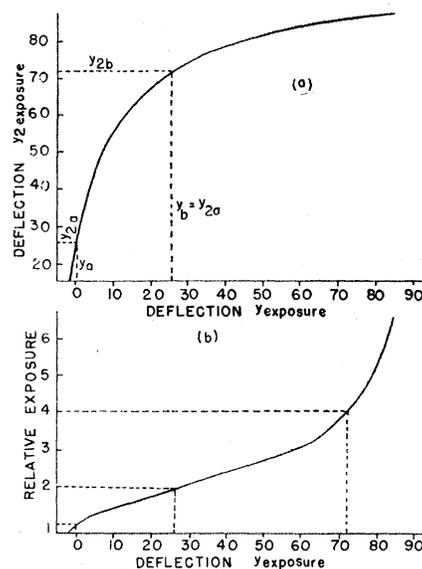[9] H. Hendus, Z. Physik **119**, 265 (1942).

FIG. 1. Calibration of the photographic emulsion. (a) Deflection for twice exposure *vs* deflection for single exposure. (b) Plate sensitivity, relative exposure *vs* densitometer deflection.

slowly enough to give accurate values for the narrow lines.

Mounting appropriate traces on a comparator, the deflections for one exposure and twice that exposure can be read and plotted as in Fig. 1(a). This was done for both thick and thin absorbers and the average taken. Data from this curve were then used to construct a plot of relative exposure *versus* deflection, Fig. 1(b). First there was arbitrarily taken some point, y_a, on the curve Fig. 1(a) in the region of small deflection. This was established as relative exposure 1 and plotted in Fig. 1(b). Now it can be seen that for twice that exposure the deflection was y_{2a}. This was relative exposure of 2. Now for deflection $y_b = y_{2a}$ there was found a corresponding y_{2b} for which exposure was 2×2 or 4. This process, continued to the largest values of y available, established a curve. More points were determined by taking as a starting value some other point on the relative exposure curve and repeating the process.
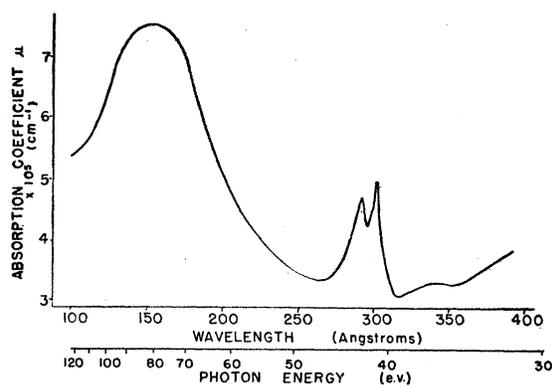

FIG. 2. The absorption of tellurium.

From this curve can be read an exposure to correspond to each measured deflection of every spectral line. The ratio of these exposures, thick to thin, multiplied by the inverse ratio of the actual number of sparks through each film gives the transmission at that line of the spectrum of a thickness of tellurium equal to the difference in thickness of the thick and thin samples. Using $T = e^{-\mu x}$, where x is the thickness, the value of μ, the absorption coefficient, can be computed for the wavelength of each spectral line.

If one compares curves from different samples, and allows for possible errors in thickness measurements, some discrepancies in the curves were still observed. For example, the slope of the curve (Fig. 2) at 200A was uncertain by about 10 percent. A short calculation showed that this could be accounted for by very large variations in the film thickness (i.e., pinholes) covering approximately 0.05 percent of the useful area of the sample. Microscopic examination of the samples indicated that this was quite possible. As a result of these calculations and observations the curves showing maximum slope were selected as being most typical of tellurium without pinholes.

III. RESULTS

Figure 2 shows the plot of absorption coefficient from 100A to 400A. The salient features are the double peak at about 300A and the large peak at about 155A. The
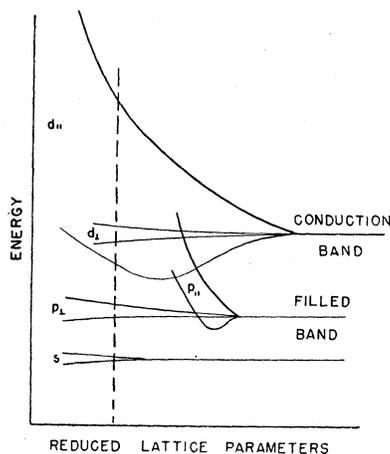

FIG. 3. Schematic diagram of the energy levels of tellurium (after Nussbaum and Callen) showing the broadening of the bands as the atoms are brought together. The subscripts indicate that the symmetry of the wave functions is perpendicular or parallel to the chain axis of the crystal.

double peak indicates that the transitions from the N_{IV} and N_V levels to the valence band are separated in this experiment. The peaks occur at 292A and 302A with width at half-maximum of 20A for the double peak. The edges as defined by Skinner[10] are estimated to be at 309A and 299A (40.0 ev and 41.3 ev). Bohr and Coster[11] predicted these edges from limiting frequencies of emission bands to be at 303A and 314A. More recently Chamberlain and Lindsay[12] proposed 289A and 291A.

The shape of the band can be interpreted to mean that there is a relatively narrow band with a high density of states superimposed on a broader band of low density. Figure 3 shows a diagram by Callen[13] and Nussbaum[14] indicating the band structure of tellurium as a function of the lattice parameter. The $\perp$ and $\parallel$ subscripts indicate that the symmetry of the wave functions is prependicular or parallel to the chain axis of the crystal, the parallel functions overlapping first. The l-selection rule requires that $\Delta l = \pm 1$ so the final state must be p or f since the N_{IV-V} levels are d states. It is possible that the peak arises from transitions from an N level to the middle part of d-perpendicular, which can be nearly pure p (of f) from mixing of d and p (or f) type states. The broadening at the base of the absorption curve can be attributed to the p (or f) states within the d-parallel band. Of course, the argument applies to both the N_{IV} and N_V levels separately.

The broad absorption band centered around 155A has an estimated width at half maximum of nearly 100A. The "edge" falls at 207A (59.6 ev). The expected transition is from N_{II-III} to the conduction band and should occur at about 105A (117.5 ev) according to Bohr and Coster[15] or 108A (114.5 ev) according to Nishina.[16] The discrepancy between these values and the experimental one is so large that there is serious doubt of the identification. The width of the band is very large, too large to be explained by the width of the N levels or valence band with any reasonable numbers. It may possibly be due to Kronig structure.

[10] H. W. B. Skinner, Trans. Roy. Soc. A239, 95–134 (1940).
[11] N. Bohr and D. Coster, Z. Physik 12, 342 (1923).
[12] K. Chamberlain and G. A. Lindsay, Phys. Rev. 30, 369 (1927). There is no mention in their paper of their recognition of the doublet nature of one of the initial levels. Disregard of this fact could produce error in the 291A value of the N_V level.
[13] H. B. Callen, J. Chem. Phys. 22, 518–522 (1954).
[14] A. Nussbaum, Phys. Rev. 94, 337–342 (1954).
[15] N. Bohr and D. Coster, Z. Physik 12, 342–374 (1923).
[16] V. Nishina, Phil. Mag. 49, 521 (1925).