Absorption and Emission Spectra of Silicon and Germanium in the Soft X-Ray Region*

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(Received July 16, 1956)

The absorption spectra of thin evaporated foils of Si and Ge have been investigated in the soft x-ray region extending from 70 A to 200 A. The thicknesses of the various absorbers ranged from several hundred to several thousand angstroms. The spectral region covers the $L_{2,3}$ and $M_{2,3}$ absorption discontinuities of Si and Ge, respectively. The $L_{2,3}$ edge of Si appears at 123 A, while the $M_{2,3}$ edge of Ge is centered at 101.5 A. The linear absorption coefficients on the high-energy side of the respective edges of Si and Ge are 1.4×10^5 cm^{-1} and 1.8×10^5 cm^{-1}. The emission spectrum of a Ge target was also studied in the 60 A to 600 A region. Two bands, whose peaks fall at 102.4 A and 104.3 A, have been identified as the M_2 and M_3 emission spectra, corresponding to transitions from the valence band into the M_2 and M_3 levels. With the aid of the present measurements and Skinner's data on the L emission bands of Si, it has been possible to arrive at an estimation of the magnitude of the energy gap in each semiconductor on the basis of the observed interval between emission and absorption edges. The range of forbidden energies as determined by the spectroscopic method is found to be 1.0 ev and 0.8 ev for Si and Ge, respectively.

INTRODUCTION

THE purpose of this paper is to present the results of experimental studies dealing with the soft x-ray emission and absorption spectra of the elemental semiconductors, silicon and germanium. Certain aspects of this investigation have already appeared in preliminary reports.[1] The spectral measurements fall in the neighborhood of 100 A and involve (1) the $L_{2,3}$ absorption edge of Si, (2) the $M_{2,3}$ absorption edge of Ge, and (3) the $M_{2,3}$ emission band of Ge. The spectra referred to have not been examined previously and their investigation was undertaken in the course of a sequential study of valence band spectra belonging to the light elemental solids.

Both silicon and germanium possess the diamond type of lattice structure. Each atom has four valence electrons ($3s^23p^2$ in the case of Si and $4s^24p^2$ in the case of Ge). Calculations of the electronic energy bands of Si were first carried out by Mullaney[2] who applied the Wigner-Seitz-Slater method to obtain a description of the energy bands using combinations of s, p, and d atomic wave functions. This initial calculation led to an energy spread of the filled levels amounting to about 16 ev, and a forbidden energy zone of 11 ev. More recently[3,4] Holmes, Yamaka and Sugitta, Bell and others have recalculated the band structure of Si and have obtained for the magnitude of the energy gap the values of 10, 1.08, and 1.3 ev, respectively. For germanium there exist[5,6] more involved analyses of the electronic structure of the valence and conduction bands. However, in both cases the theoretical studies have not as yet led to the determination of the level density function which is just what is needed for a more direct comparison with experimental results obtained from valence band spectroscopy.

EXPERIMENTAL

Descriptions of the experimental procedures followed in soft x-ray emission and absorption spectroscopy are to be found in several survey articles[7] and only details which are pertinent to the present work will be mentioned here. The silicon and germanium absorbers were prepared by vacuum evaporation of high purity crystals. The reasonably dense line spectrum emitted by a condensed spark discharge in a Pyrex capillary served as incident radiation in carrying out absorption measurements. The photometric procedures used in determining the wavelength dependence of the absorber transmission were those outlined in previous papers.[8,9] The instrumental arrangement and the reduction scheme employed in the study of the Ge emission spectrum resembled closely those described in an earlier paper.[10]

The absorbing silicon layer was supported by a thin zapon substrate. Rather than evaporate directly onto the substrate, it was found convenient to deposit the layer on a glass surface previously coated with "Victawet," a water soluble wetting agent. After removing the sample from the evaporation chamber, a dilute solution of Zapon was sprayed over the silicon layer to provide additional strength and to retard surface oxidation. By immersing the glass plate in water, the film was floated off and mounted on a suitable holder.

The particular mode of preparation makes it difficult

* The research was supported by the Office of Ordnance Research, U. S. Army.

1 D. E. Bedo and D. H. Tomboulian, Phys. Rev. **95**, 621 (1954); **100**, 1257(A) (1955); and Bull. Am. Phys. Soc. Ser. II, **1**, 225 (1956).

2 J. F. Mullaney, Phys. Rev. **66**, 326 (1944).

3 D. K. Holmes, Phys. Rev. **87**, 782 (1952).

4 E. Yamaka and T. Sugitta, Phys. Rev. **90**, 992 (1953). Bell, Hensman, Jenkins, and Pincherle, Proc. Phys. Soc. (London) **A67**, 562 (1954).

5 F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

6 F. Herman, Physica **20**, 801 (1954).

7 For a recent summary see H. Niehrs, Ergeb. exakt. Naturw. **23**, 359 (1950). This paper contains a good bibliography of the literature and includes references to earlier reviews of the field. See also the article by D. Tomboulian which is to appear shortly in *Handbuch der Physik* (Springer-Verlag, Berlin, to be published), Vol. 30.

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

9 R. W. Johnston and D. H. Tomboulian, Phys. Rev. **94**, 1585 (1954).

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

to measure the thickness of the silicon layer by weighing or by interferometry. Since molten silicon dissolves readily in tungsten, the material must be distributed within the evaporator so that only limited amounts of silicon come into contact with a given portion of the tungsten filament. As a result the spatial distribution of the vapor is anisotropic, and the calculation of the absorber thickness based on the geometry of the evaporator does not lead to reliable results. Hence the thicknesses of the silicon absorbers used in these experiments are to be regarded as estimates good to about 10%.

The germanium absorbers were prepared somewhat differently, since samples obtained by deposition onto a substrate at room temperature are likely to possess a granular structure. It is known[11] that if germanium vapor is condensed on a substrate which is heated to 400°C prior to and during evaporation, the resulting foils show crystalline properties. Consequently, the technique followed in this case consisted of coating a Pyrex plate first with the wetting agent and then with a film of plastic. The plate so treated was then heated to 400°C in the vacuum chamber and maintained at this temperature during evaporation. The matrix was subsequently removed from the plate following the scheme adopted in the case of silicon. The foils obtained by the above process appeared reddish-pink by transmitted light.

Electron diffraction studies[12] of the oxidation of single crystals of Ge at room temperature have indicated that no detectable oxide film is formed unless the surface is given special treatment. In the case of amorphous films of Ge and Si, Dash[13] has observed that the thickness of the oxide formed is a linear function of the thickness of the pure substance; and an hour's exposure to pure oxygen results in the formation of 60 A and 200 A oxide layers respectively on Ge and Si samples whose initial thickness was 1000 A. We have no knowledge concerning the crystalline structure of our silicon films. If granular in nature, an oxide layer amounting to about 10% of the absorber thickness may be formed during transfer of the specimen from the evaporation chamber to the vacuum spectrograph. The influence of possible surface contamination upon the absorption exhibited by Si samples will be discussed later. However, in view of the observations cited above, the corresponding contamination in the case of Ge may be regarded as entirely negligible in measurements involving crystalline specimens.

Since germanium evaporates readily, the foil thicknesses were calculated from the evaporator geometry by assuming that the distribution of the vapor was isotropic and that the foil had the density of the bulk material. The thickness determinations are expected to be reliable to within 5%. A check on the consistency of thicknesses of various absorbers will be presented. For the thicknesses used, exposure times of 2 to 3 hours yielded satisfactory spectrograms at a sparking rate of 16 sparks per minute.

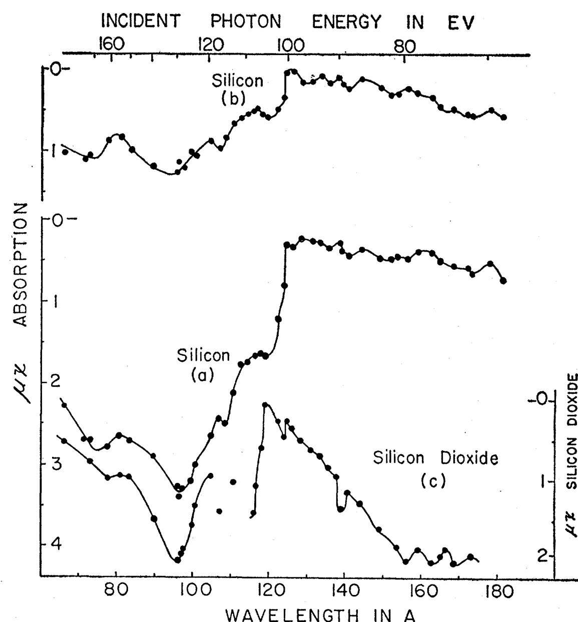

FIG. 1. Absorption curves for Si and SiO_2 in the neighborhood of the $L_{2,3}$ edge. The silicon absorbers used in obtaining the data for curves (*a*) and (*b*) had approximate thicknesses of 1200 A and 400 A, respectively. The SiO_2 specimen was about 2500 A thick.

The $M_{2,3}$ emission band of Ge is of low intensity. Reasonably good photographic densities were obtained in the course of 8 to 10 hour exposures using a target current of 200 ma with bombarding electron energies of 1200 ev. During the entire exposure, fresh germanium[14] layers were deposited on the target face at frequent intervals. Particular attention was paid to cleanliness of the x-ray tube which was operated at a pressure of 1×10^{-6} mm of Hg throughout the runs.

RESULTS

1. Absorption by Si in the Neighborhood of the $L_{2,3}$ Edge

Typical absorption curves are reproduced in Fig. 1. For the three curves shown, the ordinate (each with its appropriate zero) represents the experimentally determined quantity $\ln(I_0/I)$. In this expression I represents the beam intensity after passage through the absorbing layers of silicon and Zapon, while I_0 stands for the intensity of the radiation emergent from a second absorber having a much thinner layer of

[11] H. König, Reichsber. Physik 1, 4 (1944).

[12] W. H. Brattain and J. Bardeen, Bell System Tech. J. 32, 1 (1953).

[13] W. C. Dash, General Electric Research Laboratories, Report No. RL-857, April 1953 (unpublished).

[14] The high-purity Ge (impurities less than a few parts per billion) was provided by Dr. W. W. Tyler of the General Electric Research Laboratories and was made available to us by Professor E. L. Jossem.

silicon, but otherwise similar to the first. (See D. Tomboulian, reference 7 for a discussion of the scheme adopted in arriving at the absorption due only to the additional amount of semiconductor present in the first absorber.) The abscissa gives the wavelength of the incident radiation in angstroms. For the spectral range of interest, degradation of the beam due to scattering may be ignored. Since surface effects are compensated for by comparing two similar absorbers, the quantity $\ln(I_0/I)$ is equal to μx, where μ is the photoelectric linear absorption coefficient and x the absorber thickness.

Curve (*a*) shows the results for a Si absorber whose approximate thickness was 1200 A. The sudden increase in absorption which sets in at about 124 A is identified with the $L_{2,3}$ discontinuity. Owing to photometric errors, which can run as high as 10% in the case of weak lines, and the difficulty of obtaining a sufficiently dense incident spectrum, the curve can only be relied upon to portray the general behavior of the absorption in the neighborhood of the $L_{2,3}$ edge. The measurements for an absorber having a thickness of about 400 A are given by curve (*b*). The results displayed by the absorption curves of the two specimens are in reasonably good agreement as to the location of the edge and several other coarse structures. To test the influence of surface contamination by the oxide, the absorption spectrum of SiO_2 was also investigated. The absorbers were prepared in accordance with the previously described techniques, except that crystalline quartz was used in the evaporation. The measurements for a thick ($\approx$2500 A) quartz film are plotted in curve (*c*). The $L_{2,3}$ edge of Si in SiO_2 is clearly visible. Relative to the edge observed in the spectrum of the element, the $L_{2,3}$ discontinuity in the oxide is shifted toward shorter wavelengths by about 6 A (5.1 ev). A similar displacement in the wavelength position of the edge has been detected by Barton and Lindsay[15] in the K absorption spectrum of Si. (The K edge is located at 6715.2 x units and the corresponding shift is 12.5 x units or 3.45 ev.) The study of the shift in absorption edges arising from chemical combination has received considerable attention.[16] In the case of the oxides of the transition elements, the K absorption edge of the metallic component is shifted towards higher energies. The magnitude of the displacement is found to increase with increasing valence and decreasing atomic number. The oxides are semiconductors and the energy shift is associated with the energy gap between filled and unfilled states.

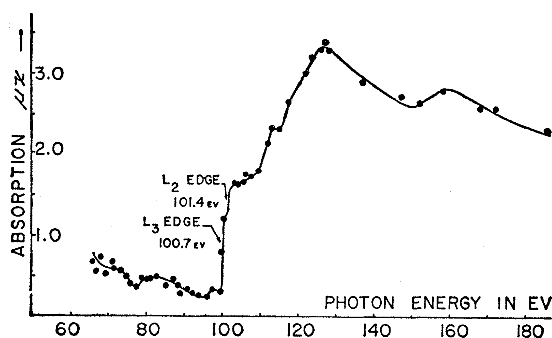

FIG. 2. The $L_{2,3}$ absorption spectrum of Si plotted as a function of the incident photon energy.

Though the measurements on the high-energy side of the edge in the absorption curve of the oxide are uncertain, a comparison of curves (*a*) and (*c*) shows that, except in the extreme short-wavelength region, there is little similarity between the absorption spectra of Si and SiO_2. Indeed, the transparency of the oxide diminishes rapidly for wavelengths higher than that of the edge. It may therefore be concluded that the particular Si absorber, whose spectrum is shown by curve (*a*), was free from significant contamination by the oxide.

We have also examined a large number of silicon absorbers which have been exposed to air from a few days to several weeks. In all instances it has been possible to observe the $L_{2,3}$ discontinuity characteristic of the element. In several runs, the oxide edge did appear somewhat more prominently than in the data presented in curve (*a*). The absorption curve (*b*) for the thinner Si absorber gives little evidence for the presence of oxidation. This observation seems entirely reasonable if one assumes that the distribution of grain sizes in the absorbing layer is independent of the layer thickness. The oxidation of the grain surfaces would be expected to proceed at the same rate for grains of a given size so that the actual amount of the oxide diminishes with decreasing thickness. It is expected that $\approx$90% of the initial Si deposit in the sample of curve (*b*) is unoxidized.

The curve in Fig. 2 shows the absorption data presented in curve (*a*) of Fig. 1, here replotted as a function of the incident photon energy. Reference will be made to the contents of this plot in conjunction with Skinner's[17] results on the intensity distribution of the $L_{2,3}$ emission band of Si.

2. $M_{2,3}$ Spectra of Germanium

Reports have recently appeared[18,19] on the studies of the $M_{2,3}$ emission bands of various transition elements of the iron group and nearby elements. Corresponding absorption measurements[20–22] in the vicinity of the $M_{2,3}$ edge have also been carried out in the case of Fe, Ni,

[15] V. P. Barton and G. A. Lindsay, Phys. Rev. **71**, 406 (1947).

[16] See reference 7 for a summary.

[17] H. W. B. Skinner, Trans. Roy. Soc. (London) **239**, 95 (1940).

[18] Skinner, Bullen, and Johnston, Phil. Mag. **45**, 1070 (1954).

[19] E. M. Gyorgy and G. G. Harvey, Phys. Rev. **87**, 861 (1952); **93**, 365 (1954).

[20] D. E. Carter and M. P. Givens, Phys. Rev. **101**, 1469 (1956).

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

[22] J. E. Johnston, Proc. Cambridge Phil. Soc. **35**, 108 (1939).

Cu, and Zn. An extrapolation of the existing data on the $M_{2,3}$ emission edges of the elements V to Zn, indicated that the corresponding edge in Ge should fall at about 100 A. Actually the emission spectrogram revealed a characteristic double-peaked intensity distribution extending from 102 A to 108 A, while in absorption the discontinuity appeared at about 101.5 A.

The first order Ge $M_{2,3}$ emission band was superposed on a background of continuous radiation. Because of the relatively high atomic number of Ge, it is believed that in the main the background radiation consists of the x-ray continuum appearing in the first order. This background may also contain shorter wavelengths, which appear in higher orders of diffraction. It may also include x-rays (of all wavelengths) scattered by the grating. (A relatively intense background radiation is known to accompany the M emission spectra belonging to the metals of the $3d$ transition group. However, the continuum is feeble in the case of the K and L bands of the light metallic elements.)

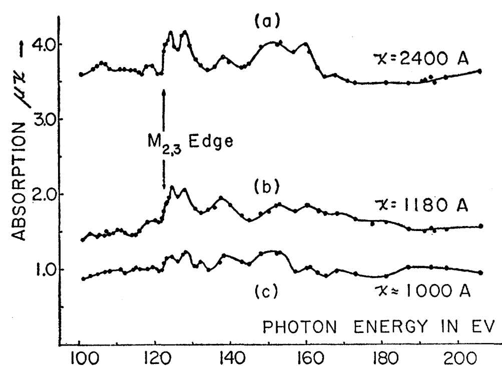

FIG. 3. $M_{2,3}$ absorption spectrum of Ge. The foils used in obtaining the data for curves (a) and (b) were presumably crystalline in nature. Curve (c) shows the results for an amorphous sample. In each case, x, the value of the absorber thickness is indicated on the graph.

Similarly, the characteristic absorption by the $3p$ electrons of Ge appears as a small discontinuity in the general background absorption by the $3d$ and valence electrons whose binding energies are comparable. In the presence of a large background absorption, it is necessary to select the absorber thickness so as to achieve the maximum difference in transmitted intensity on either side of the discontinuity. Assuming that near the edge the background absorption can be accounted for by a constant coefficient μ_0, a simplified calculation leads to the result that x_{opt}, the optimum absorber thickness, should be approximately equal to $1/\mu_0$. From an experimental estimate of μ_0, the calculated value of x_{opt} is seen to fall in the neighborhood of 1500 A.

Sample absorption curves showing the behavior of μx in the vicinity of the Ge $M_{2,3}$ edge are given in the plots of Fig. 3. Curves (a) and (b) depict the results for two different thicknesses of crystalline absorbers,

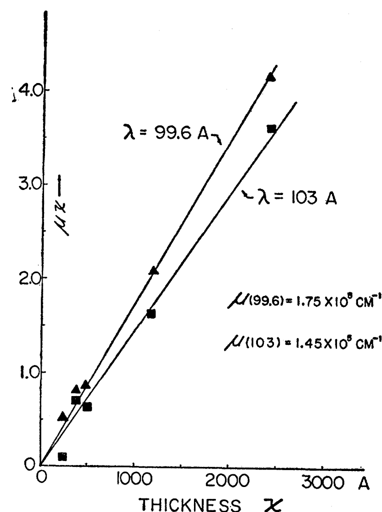

FIG. 4. A plot of μx *versus* x, the thickness of the Ge absorber. The points represented by triangles give the values of μx for incident radiation of $\lambda = 99.6$ A located on the short-wavelength side of the edge. The corresponding information at $\lambda = 103$ A, on the long-wavelength side of the edge, is shown by the squares. The values of μ deduced from the slopes are indicated on the graph.

while curve (c) shows the measurements for a granular or amorphous sample approximately 1000 A in thickness. In the case of the crystalline samples, whose thicknesses were not very different from x_{opt}, the $M_{2,3}$ edge may be recognized as the most prominent abrupt change in μx. The discontinuity is spread over a 2-ev range of incident photon energies and is centered at 123 ev. The location of the edge is also apparent in curve (c). However, without the data on crystalline absorbers it would not have been feasible to identify the feature with certainty since the jump in μx at this photon energy is not much different from other fluctuations which are present in the absorption curve. The values of μx in curves (a) and (b) are the averages of several reductions. Though the absorption on the high-energy side of the edge appears somewhat irregular in the case of curve (a), several secondary absorption maxima occurring at photon energies of 128, 138, 152, and 159.5 ev are present in all three curves and must be regarded as repeatable.

Measurements were also made on somewhat thinner absorbers. As a check on the consistency of the data, the magnitude of μx was plotted as a function of absorber thickness x, for two wavelengths, $\lambda = 99.6$ A and $\lambda = 103$ A, located, respectively, on the high- and low-energy side of the edge. The graph is shown in Fig. 4. The resulting plots are linear and pass through the origin. The departures observed for samples of small thickness are understandable, since these sample thicknesses must be regarded only as reasonable estimates. The values of μ, at 99.6 A and 103 A, are found to be 1.75×10^5 cm^{-1} and 1.45×10^5 cm^{-1}, respectively.

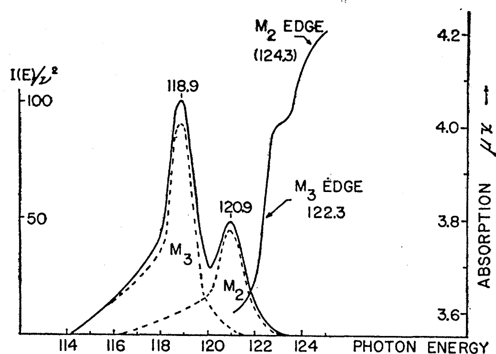

FIG. 5. The $M_{2,3}$ emission and absorption spectra of Ge. The dotted curves show the component M_2 and M_3 emission bands. The ordinates of the individual bands are in the ratio of two to one. The indicated positions of the M_2 and M_3 absorption edges were located by the method described in the text.

Three spectrograms revealed the well-resolved M_2 and M_3 emission bands. The result of the reduction of microphotometer traces is reproduced in Fig. 5, in which the relative intensity distribution within the $M_{2,3}$ band is plotted as a function of the energy of the emitted photon. For theoretical reasons,[7] the ordinate actually represents the quantity $I(E)/\nu^2$, where E is the photon energy and ν its frequency. The intensity within the band was found by applying a constant correction for the underlying continuum whose intensity was comparable to that of the band. This mode of correction may lead to unsatisfactory results since the background intensity is not necessarily uniform over the width of the band. Furthermore, the shape of the band, particularly at low intensities, depends sensitively on the magnitude of the correction subtracted out. Consequently, the appearance of the band at high and low energies may be in error and in particular it is difficult to evaluate the high-energy limit accurately.

DISCUSSION OF RESULTS

The emission and absorption processes which underlie the observations depicted by the curves in Figs. 2, 3, and 5 are associated with transitions into and from the $L_{2,3}$ and $M_{2,3}$ bound states (for Si and Ge, respectively). In each case the emission bands correspond to the radiation emitted when a valence band electron drops into a vacant inner level. In the absorption process, the final state of the photoelectrically ejected electron is a level in the conduction band. For the semiconductors of interest, there must be an energy gap between the filled and empty bands. If $h\nu_q$ is the minimum energy difference between the inner state and the state of lowest energy in the conduction band, then photons whose energies are in excess of $h\nu_q$ may be absorbed (subject to selection rules) by electrons populating the inner state q. For less energetic photons, the absorption process may involve valence electrons.

The experimental results may be interpreted with the aid of the schematic partial energy level diagrams shown in Fig. 6. For clarity, widths and separations of levels are not drawn to scale. For the emission bands, limiting values of photon energies for a given band are represented by the adjacent pair of downward arrows. Upward arrows of magnitude equal to $h\nu_q$ designate the onset of absorption. The sources of information not derived from the present measurements are given under the caption to Fig. 6.

1. Emission Bands: Widths and Shapes

On the basis of the j and l values of the initial states, the observed emission spectrum should consist of two overlapping intensity distributions whose ordinates are in the ratio of two to one. Skinner's[17] results for the L_2 and L_3 silicon bands indicate the value of 3 for the L_3/L_2 intensity ratio. In the case of Ge, the observed $M_{2,3}$ emission band shown in Fig. 5 can be resolved into component M_2 and M_3 intensity plots of the same shape if corresponding ordinates in the individual curves are taken in the ratio of two to one. (A somewhat arbitrary procedure is involved in the resolution, consequently the addition of the component curves as shown in Fig. 5 does not quite reproduce the observed intensity variation.) In either case, the absence of a large intensity anomaly may be construed to mean that the de-excitation by an Auger process of the $j=\frac{1}{2}$ level relative to the $j=\frac{3}{2}$ level is not favored. (This does not preclude the possibility of an Auger process in which one of the two valence electrons makes a transition into a vacant $j=\frac{1}{2}$ or $j=\frac{3}{2}$ state, while the second is ejected into the conduction band. The effect of such a process would be to increase the width of each inner level.)

The Ge M and Si L emission bands differ considerably in shape and width. According to the dipole selection rules, the shape of the observed intensity distribution should be related to $N_{s+d}(E)$ partial level density function since, in each instance the final state is a p state. The "reduced width" of the Si L bands is equal to 16.7±1 ev, and the intensity over the low-energy portion of the band rises as $E^{\frac{3}{2}}$, as is found to be the case in the L spectra of the preceding metallic elements, Mg and Al. On the high-energy side of the peak, the emission intensity falls off more gradually, a behavior which is characteristic of semiconductors.

Because of the background correction and tailing effects, the shape of the Ge M bands cannot be determined with certainty at the extremities of the spectrum. The band shape is asymmetric except in the region of the peak. The band width at half maximum is 1.3 ev. This figure includes the width of the M level. The terminations cannot be defined sharply, and the region near cutoff shown in the plot of Fig. 5 represents the average of two reductions. An over-all width of about 7 ev is indicated by inspection of the individual M_2 or M_3 emission curves. This must correspond to the spread in energy of the admixture of valence

states having s and d symmetry. Unfortunately, no information is available for the Ge $L_{2,3}$ bands which should be comparable with the $M_{2,3}$ bands in shape and width.

The measurements of Bearden and Shaw[23] on the Ge $K\beta_2$, $K\beta_5$ lines (as reproduced by Beeman and Friedman[24]) show that the K band, as observed experimentally, has a full width of about 4 ev (at half-maximum) which includes the influence of the width of the K level. (The width of the K level is not known, but its value may be estimated to be 2 ev by extrapolation from the widths of neighboring elements.) The K band reflects the characteristics of $N_p(E)$, the partial level density of p states within the valence band, so that the energy spread of p states must be a few ev. The existing evidence therefore points to the conclusion that the valence band of Ge is narrower than that of Si—a feature which represents an intrinsic difference between the electronic level structure of the two semiconductors. Results derived by Herman[6] show that the wave function belonging to the highest state in the valence band has the character of atomic p orbitals with some admixture of d orbitals. If the contributions coming from the admixture of d states are sufficiently intense so as to be detected, then the observed width of the M bands and the width of the valence band should be equivalent. In any case, the results derived from the study of K and M valence spectra must be regarded as complementary information of an experimental nature.

2. Estimation of the Energy Gap

If the electronic band structure of a substance has an energy gap between filled and empty states, absorption should begin at a wavelength which is shorter than the wavelength corresponding to the end of the emission spectrum. However, the actual observation of the limiting wavelengths is complicated by a number of factors. These include (1) the lack of a sharp drop at the emission edge arising from characteristics of the valence band structure and a usually negligible temperature broadening, (2) the total width (radiation and Auger) of the inner level involved, and (3) instrumental characteristics such as the finite line width of the spectrograph and the density of lines emitted by the source used for the absorption measurements. In addition, frequently the doublet character of the x-ray levels produces an overlapping of two individual emission and absorption edges. Difficulties may also arise from the presence of satellite bands, background continuum and self-absorption by the target.

Ordinarily in the soft x-ray region the instrumental "window" can be made sufficiently narrow (half-width approximately 0.05 ev) so that the direct observation of the gap is obscured mainly by the intrinsic width of the inner levels. In the case of Si and Ge, the inner level separations are comparable to the width of forbidden energies.

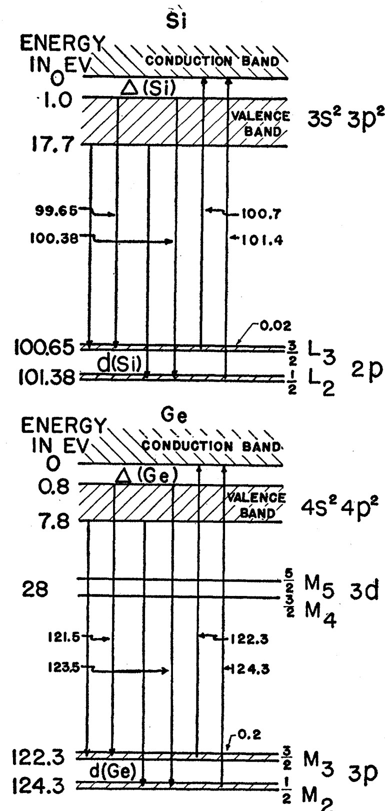

Fig. 6. Partial energy level diagram for Si and Ge. The lowest level of the conduction band is taken as the zero of energy. All numerical values are expressed in ev. Widths and separations not drawn to scale. The data representing the limiting transitions associated with the L_2 and L_3 valence bands of Si are taken from Skinner.[17] The indicated widths of inner levels must be regarded as estimates. The term values for the $M_{4,5}$ levels of Ge are taken from J. C. Slater, Phys. Rev. **98**, 1039 (1955).

An examination of the energy diagram in Fig. 6 indicates that $\Delta+d$ is equal to the energy interval between the L_3 emission edge and the L_2 absorption limit. Thus, the energy gap may be calculated if the spectral positions corresponding to these two edges can be established. In Si, Skinner[17] has located the L_2 and L_3 emission edges on the basis of small but sharp drops in the intensity near the high energy end of the band. His observations imply that it is reasonable to assume a width of about 0.02 ev for the L_2 and L_3 levels.

By introducing a number of simplifying assumptions, Richtmyer, Barnes, and Ramberg[25] have shown that in the neighborhood of an absorption limit, the frequency dependence of the absorption coefficient assumes the

[23] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).
[24] W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).
[25] Richtmyer, Barnes, and Ramberg, Phys. Rev. **46**, 843 (1934).

form

$$K(\nu)=C'\left\{\frac{1}{2}-\frac{1}{\pi}\arctan\left(\frac{\nu_0-\nu}{\Gamma_E/2}\right)\right\},$$

where ν is the frequency of the incident photon, Γ_E the width of the x-ray level and ν_0 is the frequency corresponding to the energy difference between the lowest state in the conduction band and the center of gravity of the inner state of width Γ_E. By adjusting the parameters C' and Γ_E, it is possible to find a curve of the above form which fits the observed absorption curve closely and thereby determine the value of Γ_E. The width of the absorption limit is defined as the frequency interval intercepted by ordinates whose magnitudes are equal to $\frac{1}{4}$ and $\frac{3}{4}$, respectively, of the asymptotic value C'. This interval is equal to Γ_E.

For Si, Γ_E is known independently so that one can predict the widths of the individual L_2 and L_3 edges. Here $\Gamma_E\approx 0.02$ ev, hence the widths of the individual absorption curves are correspondingly narrow. The observed absorption curve for Si (see Fig. 2) is found to be a superposition of steeply rising L_3 and L_2 components whose intensities are in the ratio of two to one and whose centers are shifted by the L_3-L_2 interval. The instrumental resolving power was more than adequate to show the individual edges. However, because of the insufficient density of the spectral lines, it was not possible to obtain sufficiently closely spaced values of of $\ln(I_0/I)$ so as to determine the structure of the $L_{2,3}$ edge with assurance. On the other hand, the observed discontinuity has an over-all spread of about 0.8 ev, which is nearly the separation of the L_2 and L_3 levels in agreement with expectation.

By taking into account the intensity ratio, and by assuming abrupt rises at each edge, the position of the L_2 edge was located at 101.4 ev. The L_3 edge in emission is at 99.65 ev. Hence $\Delta(\text{Si})+d(\text{Si})=1.75$ ev or $\Delta(\text{Si})\approx 1.0$ ev. Conductivity and Hall coefficient measurements give the value of 1.12 ev for the gap; while optical absorption data yield[26] the value of 1.19 ev for $\Delta(\text{Si})$.

If the width of the M_3 level in Ge is taken as 0.2 ev, it is possible to reconstruct the observed shape of the initial portion of the absorption curve for Ge (see Fig. 5) quite accurately assuming the simple arctangent form. This process yields the value of 122.3 ev for the position of the M_3 edge. In addition, if the width of the M_2 level is also taken as 0.2 ev, it is possible to match the observed shape over its entire rising portion by combining a second arctangent curve with the first one in the appropriate ratio. The M_2-M_3 interval determined in this manner has the value of 1.5 ev. The value of the same interval deduced from the peak-to-peak separation of the individual M_2 and M_3 emission bands is 2.0 ev. The latter value must be considered as a reliable measure of the interval in question. The source of the discrepancy is probably associated with the process in which the theoretical M_2 curve, having the simple arctangent form, is combined with the asymptotic portion of the corresponding M_3 curve. This portion of the M_3 curve derives its shape from the underlying assumption relative to the uniformity of the density of states—an assumption which is probably invalid in the case of Ge. Indeed, the fluctuations in the observed absorption curve just beyond the edge lend support to this view. Therefore, the location of the M_2 edge cannot be established independently but is best determined from more reliably known quantities such as the M_2-M_3 separation and the position of the M_3 edge.

However, over the region which follows the onset of absorption, the observed shape must be that of the M_3 absorption curve alone, since contributions from the M_2 edge first become effective at about 2 ev beyond the M_3 edge. Consequently the position of the M_3 edge (at 122.3 ev) was arrived at by fitting an arctangent curve to the portion which corresponds to the initial rise in absorption. The estimated termination of the M_3 band occurs at 121.5 ev; this leads to $\Delta(\text{Ge})\approx 0.8$ ev. For Ge, Fan[26] lists the values of 0.74 ev and 0.77 ev as derived from electronic and optical measurements.

The preceding spectroscopic procedure for evaluating the gap utilizes limiting transitions into and from an inner state with $l=1$. The energy interval labeled as the "gap" corresponds to the energy difference between a level near the top of the valence band and a level near the bottom of the conduction band. The wave functions belonging to these states in the electronic band must possess either s or d symmetry, but the states involved need not necessarily correspond to the highest valence of lowest conduction levels.

In the existing theoretical models, the wave function of the lowest state in the conduction band is constructed from atomic s orbitals while the highest state in the valence band has the mixed character of s and d states. If the theoretical description represents the situation in the real crystal, then, in principle, the energy difference between corresponding emission and absorption edges as evaluated in the present case should give the width of forbidden energies.

Similar qualifications accompany the method followed in determining the gap from optical absorption data. Here the selection rule requires that $\mathbf{k}$ remain unchanged. In Si and Ge, the top of the valence band corresponds to $\mathbf{k}=0$, whereas the bottom of the conduction occurs at a different value of $\mathbf{k}$. As a result the observed gap may not represent the energy interval between the lowest conduction and highest valence levels.

The relevant numerical information derived from the emission and absorption spectra of Si and Ge is summarized in Table I.

[26] See the article by H. Y. Fan in *Solid State Physics* (Academic Press Inc., New York, 1955), Vol. 1, p. 307.

3. Additional Comments

The M_2-M_3 energy interval obeys the spin doublet law and should be essentially independent of Z. For the preceding elements V to Zn, the magnitude of this interval[18] shows a slow increase from 0.9 ev at V to 2.5 ev at Zn. The value of 2.0 ev for the M_2-M_3 interval in Ge is not unreasonable. High accuracy cannot be claimed either for the present determinations or those quoted for the neighboring elements of smaller Z. For elements of higher Z, such as Rb the magnitude of the interval is ≈ 10 ev and shows a slow increase with increasing Z.

The spectrograms obtained for the purpose of studying the emission band of Ge contain additional information which with reasonable certainty can be interpreted as $M_1 \rightarrow M_{2,3}$ and $M_2 \rightarrow M_{4,5}$ or $M_3 \rightarrow M_{4,5}$ intrashell transitions. The M_1 emission band in Ge is expected to fall in the vicinity of 70 A. However, as in the case of the transition elements of the iron group, no emission band was observed corresponding to electron jumps from the valence band to the $3s$ level. It is likely that radiationless transitions of the type $M_1 \rightarrow M_2 V$ or $M_1 \rightarrow M_3 V$ materially reduce the probability of $M_1 \rightarrow V$ radiative transitions.

Bearden and Shaw,[23] while examining the K lines of the elements extending from Ti to Ge, have observed that at Cu($Z=29$) the $K \rightarrow N_{2,3}$ and the $K \rightarrow M_{4,5}$ lines still form an unresolved doublet. The electronic transitions characterizing these lines are designated as valence$\rightarrow 1s$ and $3d \rightarrow 1s$, respectively. (The latter is not an electric dipole transition.) At Zn ($Z=30$) and at Ge ($Z=32$), the two lines appeared as distinct, although for the intervening element Ga ($Z=31$), the $K \rightarrow M_{4,5}$ line is not in evidence. These observations imply that beginning with Zn, the $3d$ states no longer form a part of the valence band but appear as distinct $M_{4,5}$ levels below the valence band.

In addition, in the case of Ge, Gwinner[27] has identified the x-ray transitions from the $M_{4,5}$ levels into the L_2 and L_2 levels. It was therefore possible to predict the spectral location (≈ 450 A) of the $M_{4,5}$ emission band of Ge. Accordingly the available spectrograms were examined in this spectral region but no trace could be found of the valence to $3d$ transitions. As is true for the K spectrum, such an emission band would have reflected the characteristics of $N_p(E)$, the partial level density of p states and would have confirmed the distinctness of the $3d$ levels.

[27] E. Gwinner, Z. Physik **108**, 523 (1938).

TABLE I. Numerical information derived from Si $L_{2,3}$ and Ge $M_{2,3}$ absorption and emission spectra. All quantities are expressed in ev.

	Emission edges		Absorption edges		Width of valence band	Gap
	L_3 or M_3	L_2 or M_2	L_3 or M_3	L_2 or M_2		
Silicon	99.65	100.38	100.7	101.4	16.7	1.0
Germanium	121.5	123.5	122.3	(124.3)	7.0	0.8

Several reasons might be advanced for our failure to detect the $M_{4,5}$ emission spectrum. In order to excite the $M_{2,3}$ bands, the x-ray tube was operated at a potential of 1200 volts, which is 12 times the threshold voltage required for the ionization of the $M_{2,3}$ levels. The $M_{4,5}$ levels are expected to fall some 27 ev below the top of the valence band, so that the energy of the electrons bombarding the Ge target was 45 times the excitation energy of the $M_{4,5}$ levels. This circumstance may have reduced the ionization probability of the levels in question. The de-ionization of the $M_{4,5}$ levels by an Auger process involving valence electrons may further decrease the chance of radiative transitions. Because of the energies involved, such Auger transitions may be favored over the analogous process involving the de-excitation of the $M_{2,3}$ states. Instrumentally, the reflecting power of the grating as well as the sensitivity of the emulsion response of the plates (Ilford *Q-I*) used, are known to drop off significantly in this spectral region. Or again the intensity of the $M_{4,5}$ spectrum could have been appreciably reduced owing to enhanced absorption at the target by impurity traces or by the Ge itself. Finally, there is a possibility that the $3d$ levels, though distinct, are separated from the valence band by an energy interval which is less than 27 ev. In this case the emission band could have fallen outside the spectral range covered by the spectrograph used in this study.

On the high-energy side of the Ge $M_{2,3}$ edge there are a series of absorption maxima. The positions of these structures, measured in ev from the edge, occur at 5.7, 15.7, 29.7, and 37.2. Marton and Leder[28] have measured the energy losses of 30-kv electrons passing through thin films of Ge. They report two characteristic loss values of 16.0 ev and 30.1 ev, which are in close agreement with the positions of two of the peaks observed in the fine structure of the absorption spectrum.

The authors wish to thank Professor E. L. Jossem for valuable suggestions and helpful discussions.

[28] L. Marton and L. B. Leder, Phys. Rev. **94**, 203 (1954).