Reflectivity of single-crystal GeS from 0.1 to 30 eV

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(Received 5 February 1976)

The reflectivity of single-crystal, orthorhombic GeS has been measured at 300°K for all three polarizations in the photon energy range 0.1–30 eV. Eleven distinct peaks or shoulders are observed, about half of which can be associated with known structure in the valence-band density of states. A Kramers-Kronig analysis was performed, giving the optical constants and energy-loss functions in the 0–25-eV range.

The binary IV–VI compounds formed with Ge, Sn, and Pb as cations and S, Se, and Te as anions form a very interesting class of semiconductors which can be divided into three groups according to crystal structure.¹ The well-known lead salts (PbS, PbSe, and PbTe) crystallize in a cubic (NaCl) structure, are very easy to produce both in bulk and epitaxial form, and have been extremely thoroughly studied.^{1,2} The tellurides of Ge and Sn have a rhombohedral structure at low temperatures, converting to cubic at $T=0^\circ\text{C}$ for SnTe and $T=400^\circ\text{C}$ for GeTe. These compounds have also been extensively studied,¹ though not as fully as the lead salts. The remaining four compounds, GeS, GeSe, SnS, and SnSe have an orthorhombic crystal structure (D_{2h}^{16}) and comprise the least-studied of the three groups. The lattice structure of these compounds can be considered either as a distortion of the NaCl structure or as a binary analog of the layered As structure. Even a casual macroscopic examination of GeS crystals reveals that they are, indeed, strongly layered since they exhibit an exceptionally easy cleavage similar to that of mica. Taking the c axis to be perpendicular to the cleavage planes, the lattice constants of GeS are¹ $a=4.30\text{ \AA}$, $b=3.65\text{ \AA}$, and $c=10.44\text{ \AA}$. Despite the obvious structural anisotropy of GeS, the most extensive previously reported reflectivity measurements³ (1.5–12 eV) were obtained using unpolarized radiation. Štourač *et al.*⁴ have measured the reflectivity of GeS for $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ (in our notation) but their measurements extended only over the range 0.5–4.8 eV and showed certain artifacts to be discussed later. In the present paper, we report the results of reflectivity measurements on single-crystal GeS at 300°K for all three principal polarizations in the photon energy range 0.1–30 eV.

Single crystals of GeS were grown by vacuum sublimation as described elsewhere.⁵ Samples used in the present study were undoped and had useable surface areas of the order of 1–2 cm². Measurements with $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ were performed on cleavage faces, the cleavage being done immediately prior to measurement by “peeling” a fresh surface with cellophane tape. Measurements with $\vec{E}||\vec{c}$ required the use of cut and polished faces perpendicular to the cleavage planes. Details of the sample preparation for $\vec{E}||\vec{c}$ measurements have been given elsewhere^{6,7} and will not be repeated here except to say that final polishing was done using Syton⁸ on polishing cloth. As will be evident from the uv reflectivities, the polished faces were definitely inferior to cleaved faces.

Because of the large range of photon energies covered, several different instruments were used in these measurements. The range 0.1–0.5 eV was measured using a Perkin-Elmer model 180 spectrophotometer. These measurements were extended into the visible region (0.5–2.5 eV) using a CARY model 17 spectrophotometer. The entire visible and near uv (1.7–4.5 eV) were measured on a modified version of the precision reflectometer described previously by Gerhardt and Rubloff.⁹ In the modified version of this instrument the light pipe is discontinuously stepped (rather than being continuously rotated) between sample and reference beams. During each sample or reference pause, the light intensity is measured using standard photon-counting techniques. The stepping and data processing are controlled by an on-line minicomputer. This system is believed to have an absolute midrange accuracy⁹ of $\pm 2\%$ and a relative accuracy of $\pm 0.002\%$. Where any disagreement existed, measurements made on other instruments were multiplied by constant

FIG. 1. Experimental reflectivities for GeS in all three principal polarizations at 300 K. Energy positions of the labeled peaks are given in Table I.

scaling factors to bring them into agreement with the Gerhardt reflectometer results in regions of overlap.

Finally, the uv reflectivity (4–30 eV) was measured using synchrotron radiation at the DESY facility. All measurements were made at normal or near-normal incidence using standard techniques.

The measured reflectivity is shown in Fig. 1 for all three polarizations of incident light. We find evidence for eight structural features (peaks or shoulders) for $\vec{E}||\vec{a}$ and nine each for $\vec{E}||\vec{b}$ and $\vec{E}||\vec{c}$. Features which occur at approximately the same energies are given the same labels and tabulated in Table I.

Earlier measurements of the absorption edge⁶ in GeS showed that the fundamental optical gap is $E_0 = 1.65$ eV at 300°K, the transitions being tenta-

tively identified as direct allowed for $\vec{E}||\vec{a}$ (and probably also for $\vec{E}||\vec{c}$) and direct forbidden for $\vec{E}||\vec{b}$. The absorption coefficient immediately above the edge is only 10^4 cm⁻¹ for $\vec{E}||\vec{a}$ and $\ll 10^4$ cm⁻¹ for $\vec{E}||\vec{b}$. Thus, one should not expect to find any structure corresponding to E_0 in the reflectivity and, with exceptions noted below, we find none. This is in contrast to the results of Štourač *et al.*⁴ who find an abrupt drop in reflectivity on passing through E_0 (indeed, this is by far the strongest feature in their entire reflectivity spectrum). We have occasionally observed similar “ E_0 ” structure but have found it to be highly sample dependent. This observation, combined with the shape of the structure (a decrease in reflectivity) and the fact that the absorption at E_0 is too weak to influence the reflectivity, leads us to conclude that the apparent E_0 structure is an artifact caused by re-

TABLE I. Energy values for the reflectivity peaks labeled in Fig. 1. Peaks which are too broad to be determined accurately are given in parentheses. The predicted peak energies are based on the density-of-states diagram in Fig. 2 as discussed in the text.

Reflectivity peak	Observed peak energy (eV) $\vec{E} \parallel \vec{a}$	$\vec{E} \parallel \vec{b}$	$\vec{E} \parallel \vec{c}$	Predicted peak energy (eV)
E_1	2.0	2.1	2.2	
E_2	2.8	2.7	2.5	
E_3	3.4	3.2	3.3	3.2–3.5
E_4	4.9	5.0	4.7	4.6–4.9
E_5	...	...	5.8	
E_6	6.6	6.8	6.3	6.3–6.6
E_7	...	8.9	...	
E'_7	...	...	9.4	
E_8	(10.6)	10.6	10.7	10.3–10.6
E_9	13.9	13.7	(14)	
E_{10}	16	(16.3)	...	15.0–15.3

flections from the back side of the sample in the transparency range below E_0 . All samples used in the present study were prepared from single-crystal ingots in such a way that their back sides preserved the curvature of the growth ampoule, thus minimizing back reflections. It should be noted, however, that this precaution is not necessarily sufficient for $\vec{E} \parallel \vec{a}$ and $\vec{E} \parallel \vec{b}$ measurements since the samples could still contain internal cleaves which would act as efficient back reflectors. This probably accounts for the sample dependence of the " E_0 " structure.

In the absence of any band-structure calculations for GeS, it is risky to speculate as to the detailed origins of the reflectivity peaks E_1 – E_{10} . A few semiquantitative assignments can nevertheless be made by comparing our results with recent ESCA measurements of Kemeny.¹⁰ Figure 2 shows a schematic diagram of the density of valence- and conduction-band states in GeS. The density of valence states is based on the above-mentioned ESCA measurements¹⁰ which show five clearly resolved peaks or shoulders at energies of $V_1=1.5$, $V_2=2.9$, $V_3=4.4$, $V_4=8.6$, and $V_5=13.3$ eV below the onset of the V_1 band. The V_1 – V_3 bands are associated (predominantly) with atomiclike $3p$ levels of S. The V_4 and V_5 bands originate from Ge($4s$) and S($3s$) levels, respectively.¹⁰ The density of conduction-band states is assumed to be relatively structureless (in analogy with calculations and measurements for the closely related Pb salts^{11–14}) and to consist of predominantly Ge($4p$)-like levels near the bottom of the band.

On the basis of Fig. 2, one expects structure in the reflectivity at energies $|V_i| + \Delta E$, where V_i is the position of the i th peak in the valence-band density of states and ΔE is an energy slightly larger than the band gap. Taking ΔE to be in the range 1.7–2.0 eV, we predict five peaks as given in the last column of Table I. It is seen that the predicted peaks associated with V_1 – V_5 are in good agreement with the measured peaks E_3 , E_4 , E_6 , E_8 , and E_{10} , respectively. The E_1 and E_2 peaks must be associated with transitions from the top of the valence band V_1 to low-lying conduction-band states. Peaks E_5 and E'_7 appear only in the $\vec{E} \parallel \vec{c}$ polarization and E_7 appears only for $\vec{E} \parallel \vec{b}$. All three of these peaks are sharp but weak. The E_9 peak is rather strong and lies at too low an energy to be associated with transitions from V_5 . We therefore assume that it originates from intra-atomic Ge($4s$)-Ge($4p$) transitions between V_4 and higher-lying conduction-band states. The data in the 1.7–4.5-eV range were sufficiently noise free to allow accurate numerical differentiation which revealed a considerable amount of apparent fine

FIG. 2. Qualitative representation of the densities of conduction and valence-band states in GeS along with the predominant atomiclike characters of the wave functions for each band.

FIG. 3. Results of a Kramers-Kronig analysis of the reflectivity spectra shown in Fig. 2. The solid lines represent ϵ_1 ; the dashed lines ϵ_2 ; and the dash-dot lines, the energy-loss function $\text{Im}(-1/\epsilon)$.

structure on the E_2 and E_3 peaks (approximately eight well-resolved peaks or shoulders in the 2.5–4.3-eV range). Further investigation will be required before this structure can be definitely attributed to the sample and not to slight asymmetries in the measurement system which were enhanced by differentiation. Finally, we would like to mention an unusual and unexplained feature found in the reflectivity near $\lambda_0 = 2.15\mu$. In the region between the band edge and λ_0 we found $R(\vec{E}||\vec{a}) < R(\vec{E}||\vec{b})$, while for $\lambda > \lambda_0$ we consistently measured $R(\vec{E}||\vec{a}) > R(\vec{E}||\vec{b})$. This reversal occurred fairly abruptly between 2.0 and 2.3 μ . Specific values for a typical sample were: at $\lambda = 2\mu$, $R(\vec{E}||\vec{a}) = 0.290$, $R(\vec{E}||\vec{b}) = 0.315$, at $\lambda = 2.15\mu$, $R(\vec{E}||\vec{a}) = R(\vec{E}||\vec{b}) = 0.310$; and at $\lambda = 2.3\mu$, $R(\vec{E}||\vec{a}) = 0.320$, $R(\vec{E}||\vec{b}) = 0.300$. This behavior is shown (somewhat exaggerated by the use of an energy rather than a wavelength scale) by the solid lines near the left-hand side of Fig. 1 [(a) and (b)]. Also shown are dashed lines representing smooth extrapolations which were

used in the Kramers-Kronig analysis discussed below.

Using the data shown in Fig. 1 a Kramers-Kronig analysis was performed and the results are shown in Fig. 3. The ϵ_1 curves for $\hbar\omega < 1.6$ eV are in excellent agreement with refractive-index measurements¹⁵ for $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$. No data are available for comparison in the $\vec{E}||\vec{c}$ case, but it is clear, both from the data in Fig. 1 and the Kramers-Kronig results in Fig. 3, that our $\vec{E}||\vec{c}$ data suffered severely from poor surface quality. Venghaus and Büchner¹⁶ (VB) have performed electron energy-loss measurements on thin GeS samples, and obtained the energy-loss function directly. From this they deduced ϵ_1 and ϵ_2 by Kramers-Kronig inversion. Our results are in quantitative agreement with theirs, aside from the following differences: (i) With the finer resolution available in optical spectroscopy, we were able to resolve structure not accessible by energy-loss measurements. In particular, we

observe considerable anisotropy in ϵ_1 and ϵ_2 , which VB were unable to find; and (ii) Our energy-loss function is smaller by a factor of 2–3 (in all three directions) than that obtained by VB. The peaks of our loss functions for $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ are at 18.3 and 18.1 eV, respectively, compared with an isotropic value of 18.45 eV reported by VB.

Finally, it is of interest to use our ϵ_2 data for $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ to estimate the semiempirical parameters E_0 and E_d of Wemple and DiDomenico's model for the electronic dielectric constant.¹⁷ These parameters are given by

$$E_0^2 = M_{-1}/M_{-3} \quad (1)$$

and

$$E_d^2 = M_{-1}^3/M_{-3}, \quad (2)$$

where the M_j 's are moments of ϵ_2 given by

$$M_j = \frac{2}{\pi} \int_0^\infty E^j \epsilon_2(E) dE. \quad (3)$$

Performing the indicated integrations gives $E_0 = 3.34$ eV, $E_d = 34.0$ eV for $\vec{E}||\vec{a}$; and $E_0 = 3.40$ eV, $E_d = 38.0$ eV for $\vec{E}||\vec{b}$. These numbers give an ex-

cellent representation of the refractive index and its dispersion¹⁵ when used in the formula¹⁷

$$n^2 - 1 = E_0 E_d / [E_0^2 - (\hbar\omega)^2]. \quad (4)$$

Owing to the poor quality of the $\vec{E}||\vec{c}$ data, no attempt was made to determine E_0 and E_d for this polarization.

ACKNOWLEDGMENTS

We are particularly indebted to M. Cardona for numerous suggestions and stimulating discussions, and to P. C. Kemeny for permission to quote the results of his ESCA measurements prior to publication. Kramers-Kronig results were independently checked by R. N. Dexter and J. C. Rife. We have also benefitted, during the course of this work, from discussions with U. Gerhardt, J. Lagois, H. J. Queisser, N. J. Shevchik, and H. Venghaus. The crystals used in this study were grown by E. Schonherr and W. Stetter. Finally, one of us (J.D.W.) would like to thank the Alexander von Humboldt Foundation for making possible a one-year visit at MPI-F.

*Work performed while on leave-of-absence from Bell Telephone Laboratories, Murray Hill, N. J. 07974.

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¹N. Kh. Abrikosov, V. F. Bankina, L. V. Poretskaya, L. E. Shelimova, and E. V. Skudnova, *Semiconducting II-VI, IV-VI, and V-VI Compounds* (Plenum, New York, 1969), Chap. II.

²Yu. I. Ravich, B. A. Efimova, and I. A. Smirnov, *Semiconducting Lead Chalcogenides* (Plenum, New York, 1970).

³V. V. Sobolev and V. I. Donetskikh, *Izv. Akad. Nauk. SSSR Neorg. Mater.* **8**, 688 (1972) [*Sov. Phys.-Inorg. Mat.* **8**, 599 (1972)].

⁴L. Štourač, M. Zavetova and A. Abraham, in *Proceedings of the 12th International Conference on the Physics of Semiconductors, Stuttgart, 1974*, edited by M. H.

Pilkun (Teubner, Stuttgart, 1974), p. 1012.

⁵E. Schönherr and W. Stetter, *J. Cryst. Growth* **30** (1975).

⁶J. D. Wiley, A. Breitschwerdt, and E. Schönherr, *Solid State Commun.* **17**, 355 (1975).

⁷J. D. Wiley, W. J. Buckel, and R. L. Schmidt, *Phys. Rev. B* **6**, 2489 (1975).

⁸Monsanto Chemical Corp.

⁹U. Gerhardt and G. W. Rubloff, *Appl. Opt.* **8**, 305 (1969).

¹⁰P. Kemeny (unpublished).

¹¹D. E. Aspnes and M. Cardona, *Phys. Rev.* **173**, 714 (1968).

¹²F. Herman, R. L. Kortum, I. B. Ortenburger, and J. P. Van Dyke, *J. Phys. (Paris) Suppl.* **29**, C4-62 (1968).

¹³G. Martinez, M. Schlüter, and M. L. Cohen, *Phys. Rev. B* **11**, 651 (1975); **11**, 660 (1975).

¹⁴M. Schlüter, G. Martinez, and M. L. Cohen, *Phys. Rev. B* **11**, 3808 (1975).

¹⁵J. Lagois (private communication).

¹⁶H. Venghaus and U. Büchner, *Phys. Status Solidi* (to be published).

¹⁷S. H. Wemple and M. DiDomenico, Jr., *Phys. Rev. B* **3**, 1338 (1971).