their results employing a model involving a three-center impurity system as we have done. However, because of the low magnetic fields involved, the interaction mechanism he considered was different from ours. It involved spin-orbit coupling of the donor atom mixing excited $3d$ states into $1s$ ground states.

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Optical Absorption in $GeSe_{0.75}Te_{0.25}$†

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$GeSe_{0.75}Te_{0.25}$ is a new IV–VI compound which has electrical properties similar to those of the degenerate semiconductors GeTe and SnTe. Optical absorption has been measured in single crystals of $GeSe_{0.75}Te_{0.25}$ grown by an iodine transport process. The measurements show a sharp absorption edge followed by a rapid rise in absorption at long wavelengths caused by the large free-carrier concentration (10^{20} holes cm^{-3}). The absorption edge is interpreted as the fundamental absorption edge of a semiconductor. It is concluded that $GeSe_{0.75}Te_{0.25}$ is a degenerate semiconductor which has a band gap considerably less than 0.82 eV.

I. INTRODUCTION

THE name $GeSe_{0.75}Te_{0.25}$ has been given to a new compound discovered in the Ge-Se-Te system.[1,2] It exists over a range of composition $0.65<x<0.85$; in the system $GeSe_xTe_{1-x}$. It is stable only below 400°C, decomposing by a solid-state reaction at higher temperatures to form GeSe and GeTe. It exists in at least two polytypic forms, the simplest of which has hexagonal lattice parameters $a=3.80$ Å and $c=15.62$ Å. The electrical properties of $GeSe_{0.75}Te_{0.25}$ (75-25) suggest that it is a degenerate semiconductor; $p=1\times10^{20}$ holes cm^{-3}, $\rho=1.5\times10^{-4}$ Ω cm, and $\mu_p=325$ cm^2/V sec (all at 300°K). The resistivity increases by less than a factor of 3 between 4.2°K and the solid-state transformation temperature near 400°C. The effective mass of the holes is quite low; a value of $m^*/m=0.09$ is obtained from the electric susceptibility. If it is assumed that there is one germanium vacancy for each two holes, then the compound is equivalent to $Ge(Se,Te)_{1.002}$.

The electrical properties of 75-25 are similar to those of GeTe,[3] SnTe,[4] and heavily p-type PbTe.[4] In order to better compare 75-25 with these other IV-VI semiconductors, we have measured optical absorption in a number of samples of 75-25. Because of the high carrier concentrations, such measurements are difficult unless thin samples can be obtained. Optical-absorption measurements on thin crystals of PbTe indicate a direct band gap of 0.32 eV.[5] Optical-absorption measurements on GeTe and SnTe single crystals are more difficult to perform, since these materials do not cleave readily. Optical absorption has been studied in thin films of SnTe,[6] and reflectance measurements have been made on single crystals[7] and thin films[8,9] of SnTe, and on single crystals[8] and thin films[8,9] of GeTe. Fortunately, 75-25 single crystals can be obtained in the form of thin, hexagonal plates, often 1–5 μ thick, thus permitting sufficient optical transmission for a study of the optical absorption edge.

II. EXPERIMENTAL

75-25 single crystals were obtained using an iodine vapor transport process.[2] The crystals grow in the form of thin plates with the c-axis perpendicular to the plates. Relatively thick (1–10 μ) crystals were used in the region of low absorption, while much thinner ones

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(0.1–1.0 μ) were required in the region of high absorption. The carrier concentration, and thus the Burstein shift, varies from one sample to another, and so a complete set of absorption measurements was made on each sample. Crystals could be grown which had any composition lying within the range of solid solution; the ones chosen for optical-absorption measurements were as close as possible to the composition $GeSe_{0.75}Te_{0.25}$, as shown by lattice-parameter measurements.[2] The absorption coefficient was measured for as thick a crystal as possible in order to minimize errors in measurement of crystal thickness. The crystal was then cleaved thinner and thinner with Scotch tape so that the measurements were extended to include the regions of higher absorption. A portion of the original crystal was used for measurements of reflectance, electrical resistivity, and carrier concentration. The optical measurements were performed with a Hilger-Muller monochromator for wavelengths greater than 1.5 μ, and a Van Cittert monochromator at shorter wavelengths. The electrical measurements were obtained by standard four-probe methods. Ohmic contacts to the samples were obtained with a small amount of conducting silver paste.

It is difficult to measure the thickness of a crystal precisely. The thickness of the hexagonal plates grown from the vapor varies from one part of the crystal to another, and decreases from the center of the crystal to the outside. When the exceedingly soft crystals are cut into a convenient shape for Hall measurements the crystal edges are badly distorted. Thus the thickness stated for a crystal is obtained by suitably averaging the measurements made at several points around the crystal as viewed with the calibrated eyepiece of a metallurgical microscope. Measurements dependent upon the crystal thickness are therefore uncertain to approximately 40%.

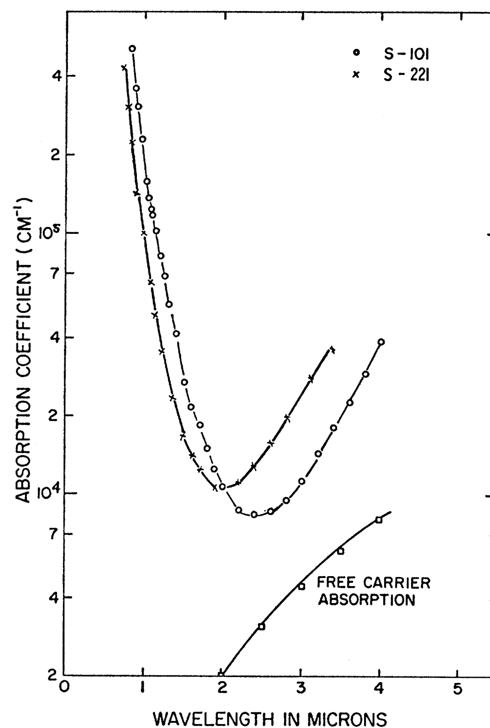

FIG. 2. Absorption coefficient versus wavelength for two single crystals of $GeSe_{0.75}Te_{0.25}$.

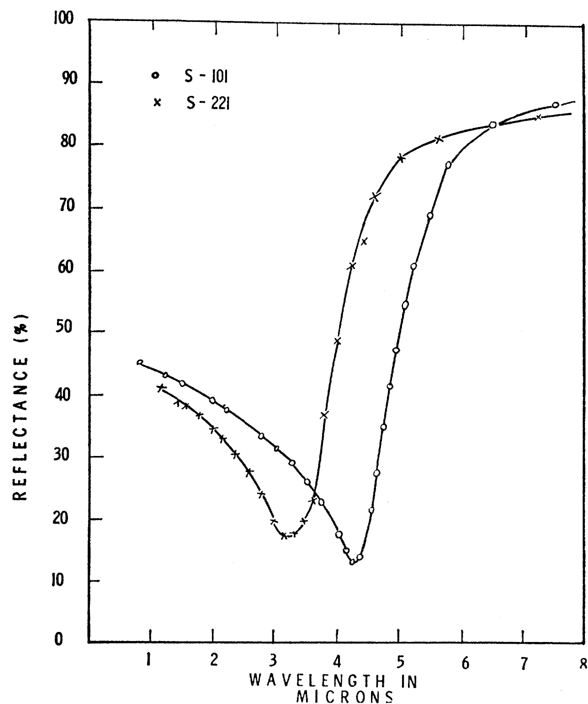

FIG. 1. Reflectance versus wavelength for two single crystals of $GeSe_{0.75}Te_{0.25}$.

III. RESULTS

The reflectance of two typical samples of 75-25 is shown in Fig. 1. The reflectance minimum for all 15 samples ranges from 3.2–4.2 μ. From all samples we obtained an average value of 0.09 for m^*/m, the electric susceptibility effective mass, and a value of 20.4 for ϵ, the high-frequency dielectric constant (see Ref. 2).

Figure 2 shows the results of absorption measurements for two samples. The absorption edge of sample S-101 is shifted to longer wavelengths by several tenths of a micron from that of sample S-221. The carrier concentration is 9×10^{19} holes cm^{-3} in S-101 and is 1.3×10^{20} holes cm^{-3} in S-221. Our interpretation of these absorption spectra is that the absorption edge at short wavelengths is due to direct transitions between valence and conduction bands, and that the rapid rise in absorption toward longer wavelengths is caused by the high free-carrier concentration in 75-25. A calculated free-carrier absorption curve is also shown in Fig. 2, assuming average values of $p=1\times10^{20}$ holes cm^{-3}, $\epsilon=19$, $m^*/m=0.09$, $\mu_p=325$ cm^2/V sec, and an

index of refraction of 4.5. The experimental and calculated curves are found to agree to within a factor of about 2. The absorption coefficient is always too large for the observation of indirect optical transitions. The absorption edge shifts towards shorter wavelengths as the temperature is decreased.

It is difficult to determine a value for the energy band gap from these data. The large number of holes present and their small effective mass should produce a Burstein shift of the absorption edge to an energy considerably greater than the smallest direct gap between conduction and valence band extrema. Because of this shift, a value for the energy band gap cannot be obtained by relating the absorption coefficient to some power of $(h\nu-E_g)$. The absorption edge is sometimes taken to be that point at which the slope of the absorption coefficient is a maximum.[10] In the present case, however, the slope is almost constant over a wide range of wavelengths and this result could not, because of the Burstein shift, be equated to the energy difference between conduction and valence band extrema.

In order to compare different samples, we chose the absorption edge to be that point at which the absorption coefficient is equal to 3×10^4 cm^{-1}. The results are 0.84 eV for sample S-101 and 0.98 eV for sample S-221. When the data from a dozen samples are compared, this apparent value of E_g ranges from 0.82 to 1.09 eV.

IV. DISCUSSION

The variation in the apparent values of E_g is presumably caused by the Burstein shift; samples with high carrier concentrations have the highest values of E_g. It is evident that the energy band gap in intrinsic material is less than 0.82 eV, and that the Burstein shift in some crystals is at least as large as $1.09-0.82=0.27$ eV. It is unfortunate that crystals are not available which have a wide range of carrier concentration so that the shape of the energy bands could be determined from the variation of effective mass. Attempts to prepare more intrinsic material by altering the stoichiometry or by compensating some of the excess carriers have succeeded in reducing the carrier concentration only to 5×10^{19} cm^{-3}. In the absence of such information only an estimate of the amount of the Burstein shift can be made. For a carrier concentration of 1×10^{20} holes cm^{-3} and an effective mass of $0.1m_e$ the Fermi level is 0.9 eV below the top of the valence band assuming a parabolic one-band model for the valence band. It is, however, unlikely that only one valence band need be considered, or that such a band could remain parabolic over such a range of energy. The electrical properties of GeTe (Ref. 11), SnTe (Ref. 12), and PbTe (Ref. 13) have been interpreted in terms of a complex valence band, consisting of two sub-bands mutually displaced by an energy separation of 0.3, 0.2, and 0.14 eV, respectively. From the present data we can only conclude that the separation between conduction and valence bands is less than 0.82 eV, probably by several tenths of an eV. The possibility that the bands overlap is unlikely, but cannot be excluded with the evidence currently available.

In conclusion, measurements of optical absorption in single crystals of $GeSe_{0.75}Te_{0.25}$ indicate what we believe to be the fundamental absorption edge of a semiconductor. On the basis of these data we conclude that $GeSe_{0.75}Te_{0.25}$ is a degenerate semiconductor having an energy band gap considerably less than 0.82 eV.

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