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Some properties of $AgAlTe_2$, $AgGaTe_2$, and $AgInTe_2$

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The valence-band structure and the semiconducting properties of the $AgXTe_2$ (X=Al, Ga, In) compounds have been studied. At 77 °K, $AgAlTe_2$ and $AgInTe_2$ have direct energy gaps located at 2.35 eV and 1.04 eV, respectively. $AgGaTe_2$ has a direct energy gap at 1.36 eV, which is probably the lowest energy gap. All three compounds can be made usefully *p* type, but only $AgInTe_2$ has been made *n* type.

I. INTRODUCTION

As a continuation of our previous work on the I-III-VI_2 ternary sulfides and selenides,[1] we have extended our studies to the $AgXTe_2$ (X=Al, Ga, In) compounds. These crystals are of interest, since they should exhibit the least hybridization of the noble-metal *d* levels with the anion *p* levels for any crystals in the I-III-VI_2 family. Furthermore, because of the large spin-orbit splitting characteristic of the Te atom, the crystal-field and spin-orbit effects should be well separated. The band structure of the $AgXTe_2$ compounds should consequently be quite similar to that of the binary analogs ZnTe and CdTe.

The electrical conductivity type of these crystals is also of some interest. Among the Cd and Zn II-VI compounds, only the tellurides can be made significantly *p* type, while only CdTe is usefully conducting both *n* and *p* type. In the I-III-VI_2 series, all Cu-containing compounds have been made *p* type, while the Ag sulfides and selenides were either *n* type or semi-insulating.[2] We have found that the Ag tellurides can be made *p* type, but that only the narrowest gap member $AgInTe_2$ (the analog of CdTe) can also be made *n* type. This is somewhat surprising in view of the fact that the bandgap of $AgGaTe_2$ is less (~ 0.2 eV) than that for CdTe.

These experiments were plagued by our inability to grow or to post-treat the tellurides to a quality comparable to that of the sulfides and selenides previously studied. It is possible that these crystals exist over a wide stability range, as suggested by existing phase diagrams.[3] A variation in sample stoichiometry could account for the poorer optical and electrical quality of these materials.

II. EXPERIMENTAL

Single crystals of the $AgXTe_2$ were grown from the melt. Stoichiometric amounts of the high-purity elements were contained in silica boats ($AgGaTe_2$, $AgInTe_2$) or graphite boats ($AgAlTe_2$) and sealed in evacuated silica ampoules. They were soaked for several hours at approximately 50 °C above the melting point, and then slowly cooled. Due to gradients in the furnace, nucleation occurred at the ends of the tube, and single-crystal sections grew by directional freezing. All crystals formed with the chalcopyrite structure with lattice constants consistent with those given in the literature.[4] The mechanical behavior of $AgGaTe_2$ was much superior to the other $AgXTe_2$ compounds, as large (1 cm × 1 cm × 0.1 cm) crack-free crystals could be readily obtained.

The conductivity of various as-grown $AgXTe_2$ crystals varied from moderately conducting *p* type to high-resistive *p* type. The samples often had macroscopic precipitates which reduced the optical transmission. These precipitates were presumably Te rich, since the optical transmission could usually be increased by vacuum anneals and decreased by Te anneals. The vacuum anneal also generally reduced the *p*-type conductivity for $AgAlTe_2$ and $AgGaTe_2$, while a Te anneal increased the *p*-type conductivity. The results for $AgInTe_2$ were less predictable. While the Te anneals increased the *p*-type conductivity, vacuum anneals could produce crystals which varied from conducting *n* type to conducting *p* type. Some samples could be made highly-conducting *n* type by anneals in a metal (e.g., Cd) overpressure at 400–500 °C, while other samples could not be made *n* type with similar treatments. Our starting material was not sufficiently characterized for any definitive explanation for these effects other than the above conjecture concerning the wide range of stoichiometry.

We had considerable difficulty with $AgAlTe_2$. Clear crystals (i.e., orange-red) would quickly become oxidized and turn opaque when exposed to air. We were not able to obtain large, solid, precipitate-free regions (0.5 × 0.5 cm) suitable for optical transmission or electrical measurements.

Both $AgGaTe_2$ and $AgInTe_2$ can be made *p* type with hole concentrations greater than 10^{17} cm^{-3} and with hole mobility in the range of 20–40 cm^2/V sec. *n*-type $AgInTe_2$, although apparently appreciably conductive, tended to be rather inhomogeneous,

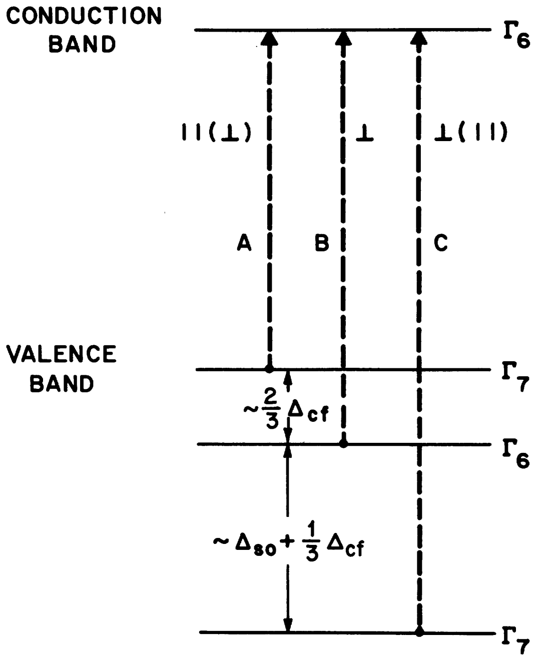

FIG. 1. Expected band structure for the AgXTe$_2$ compounds. For $\Delta_{so} \gg \Delta_{cf}$, the A-B separation is $\sim \frac{2}{3}\Delta_{cf}$ and the B-C separation is $\sim \Delta_{so}+\frac{1}{3}\Delta_{cf}$.

and measurements were limited to thermal probe. As mentioned above, measurements on AgAlTe$_2$ were also limited to thermal probe.

The crystals used for electroreflectance measurements were annealed in vacuum at temperatures between 400–600 °C. As previously mentioned, this treatment removed precipitates and decreased the conductivity. Although we obtained some data from the room-temperature electrolyte electroreflectance technique, the sample surfaces were rapidly attacked and degraded. Better data were obtained with metal-insulator-semiconductor (MIS) structures near liquid-nitrogen temperature, using techniques previously discussed.[5] In addition to electroreflectance, wavelength derivative spectra were obtained from freshly cleaved AgAlTe$_2$ surfaces at 77 ° K. This technique employed a 3-mm-thick fused silica vibrator (~ 20 Hz) near the exit slit of a $\frac{3}{4}$-m Spex spectrometer giving a modulation amplitude of ~ 3 Å.

Near-bandgap luminescence was also obtained from AgAlTe$_2$ and AgInTe$_2$ at 2 ° K. Several unsuccessful attempts were made to obtain near-bandgap luminescence from AgGaTe$_2$. The only luminescence usually observed from this compound was a band commencing at ~ 100 meV below the lowest direct energy gap. A few optical transmission measurements were obtained at room temperature and 77 ° K from both AgGaTe$_2$ and AgInTe$_2$.

For selected samples, optical transmission of ~ 50% could be obtained from 0.5-mm-thick crystals for energies 0.2 eV less than the direct energy gap.

III. RESULTS

A. AgGaTe$_2$

The results for AgGaTe$_2$ are presented first, since the energy-band data are the most complete. In Fig. 1, we illustrate the expected energy-band structure for the AgXTe$_2$ compounds. Due to the large spin-orbit effects associated with Te, we expect the valence-band splittings to be dominated by the spin-orbit interaction (Δ_{so}) with magnitude ~ 1 eV, as is the case for the binary compounds ZnTe and CdTe. Due to the noncubic nature of this crystal, we expect, in addition, a crystal-field splitting (Δ_{cf}) which is dominated by the uniaxial compression along the z or optic axis. In other chalcopyrite crystals, this splitting has been found to be represented by the formula $\Delta_{cf} = 1.5b(2-c/a)$, where b is a typical deformation potential and is approximately -1 eV,[1,6] and c and a are the measured lattice constants along the z axis and in the xy plane, respectively. This formula predicts a crystal-field splitting for AgGaTe$_2$ of 0.15 eV.

In Fig. 2 we show the 77 °K MIS electroreflectance spectra for AgGaTe$_2$. The A, B, and C transitions at 1.356, 1.472, and 2.26 eV are clearly resolved with polarization dependences consistent with the quasicubic model.[7] From the observed separation of the transitions, the spin-orbit and crystal-field splittings are calculated to be 0.84 eV and 0.165 eV, respectively.[7] The crystal-field splitting is in excellent agreement with the model

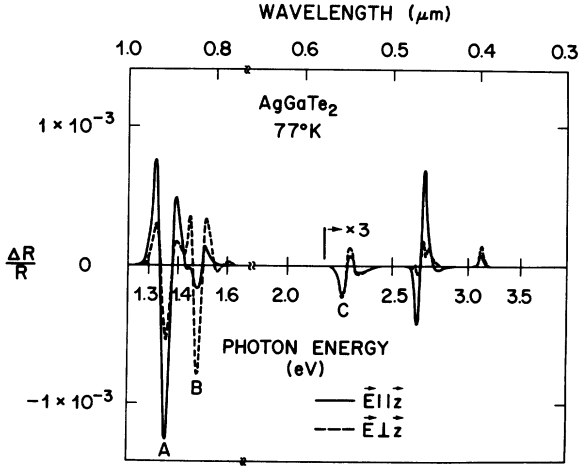

FIG. 2. 77 °K MIS electroreflectance spectra for AgGaTe$_2$ for light polarized with respect to the z or optic axis.

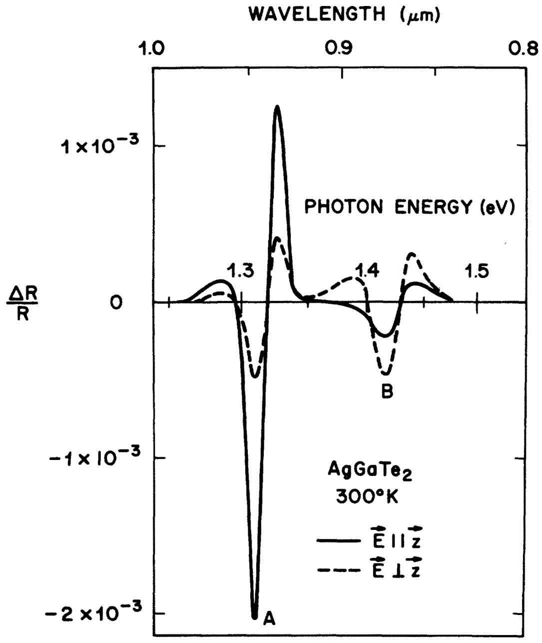

FIG. 3. Room-temperature electrolyte electroreflectance spectra for $AgGaTe_2$ for light polarized with respect to the z or optic axis.

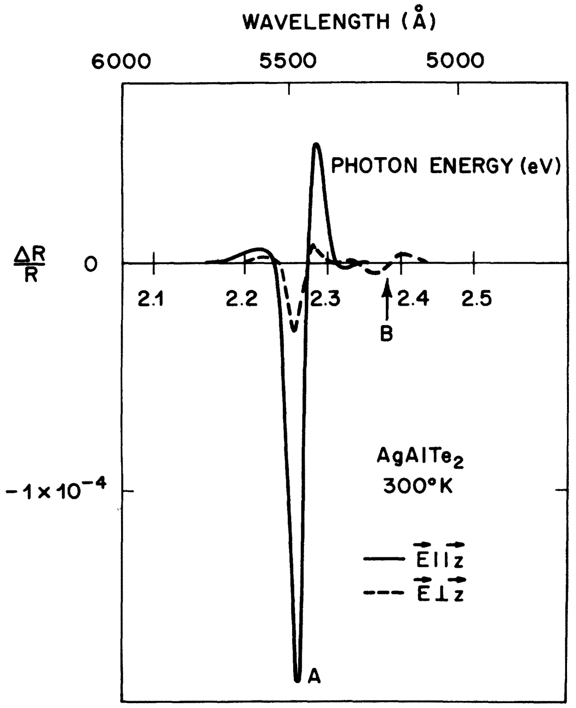

FIG. 4. Room-temperature electrolyte electroreflectance spectra for $AgAlTe_2$ for light polarized with respect to the z or optic axis.

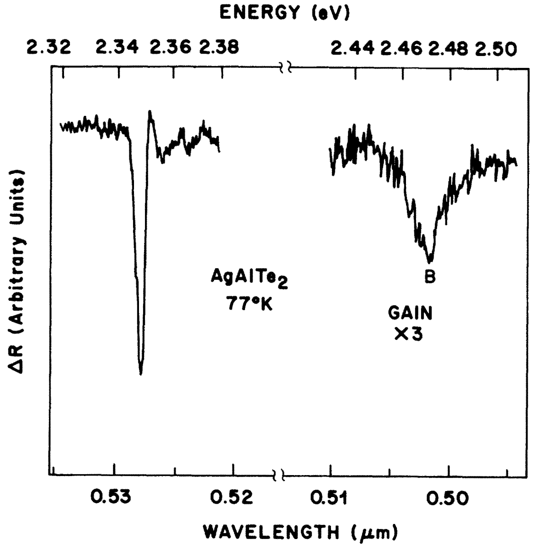

FIG. 5. 77 °K wavelength modulated reflectivity spectra for $AgAlTe_2$.

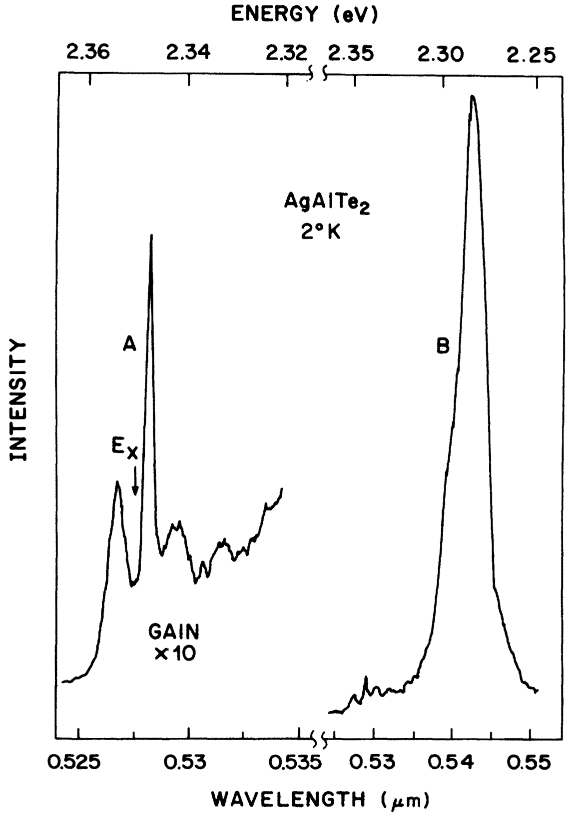

FIG. 6. 2 °K luminescence spectra for $AgAlTe_2$. Note break in the scale where the left-hand figure shows a higher resolution version in the neighborhood of the A exciton. The arrow marks the position of the exciton as determined from the wavelength derivative reflectivity.

which includes only the uniaxial compression. The spin-orbit parameter is only slightly less than the corresponding value for ZnTe and CdTe (~0.93 eV).[8] This indicates a smaller degree of hybridization of the Ag d levels with the anion p levels than occurs for the corresponding sulfides and selenides. This trend is consistent with previous work on the Cu halides.[9] Also seen in Fig. 2 is higher-energy structure, which may be related to E_1 transitions in the zinc-blende structure or d bands as previously discussed.[10,11]

In Fig. 3 we show the room-temperature electrolyte electroreflectance spectra of $AgGaTe_2$. Due to the deterioration of the surface by the electrolyte (several electrolytes were attempted with no great success) only the A and B transitions at 1.316 and 1.425 eV, respectively, could be observed. The A structure is shifted by only ~40 meV to lower energy from 77 °K to room temperature, which is consistent with the small temperature dependence of the energy gap previously observed in other crystals of this class.[1,5] From the A, B splitting, a crystal-field splitting of 0.155 eV is deduced. The difference in crystal-field splitting between room temperature and 77 ° K is within our error of determining energies from the electroreflectance spectra.

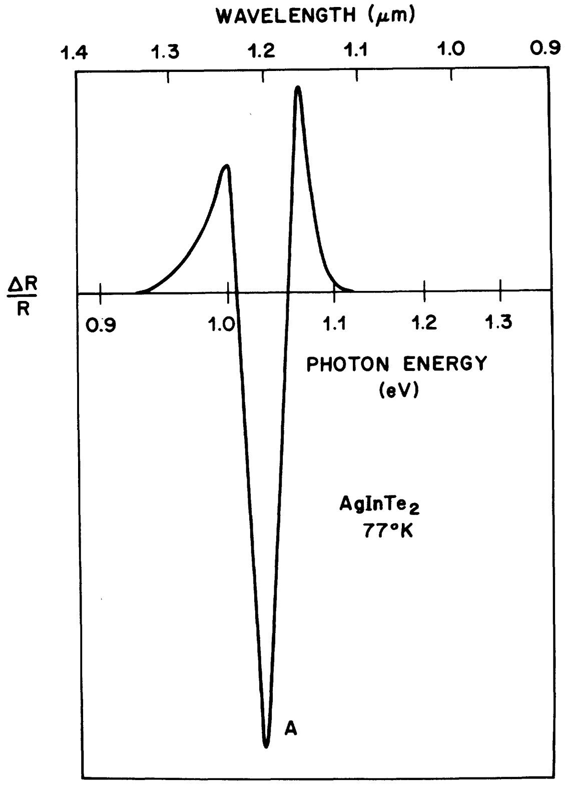

FIG. 7. 77 °K MIS electroreflectance spectra for $AgInTe_2$.

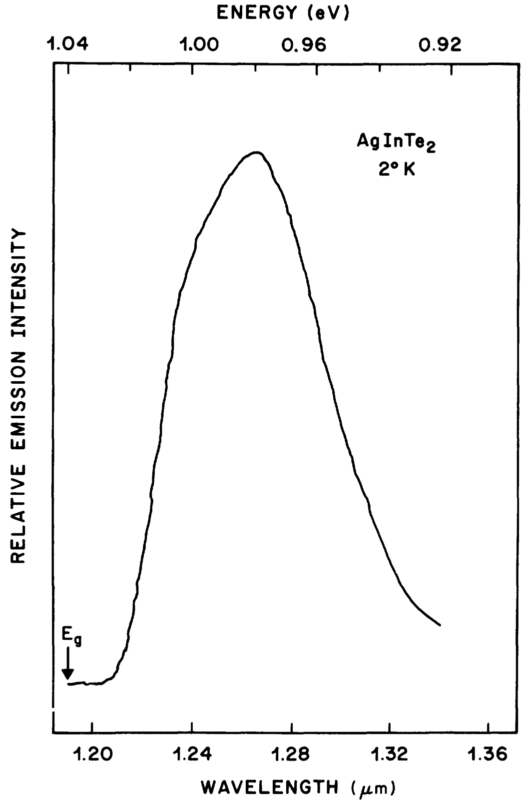

FIG. 8. 2 °K luminescence spectra for $AgInTe_2$. The arrow indicates the position of the energy gap as determined from the electroreflectance spectra.

We have made several attempts to observe near-bandgap low-temperature photoluminescence from both as-grown and annealed samples of $AgGaTe_2$. We have occasionally observed a moderately strong broad band [~50 meV full width at half-maximum (FWHM)] which commences near 1.0 μ (1.24 eV). The threshold is about 100 meV removed from the lowest direct energy gap. In addition, optical transmission measurements at 77 °K were performed on thin samples (~0.025 cm) which yield absorption coefficients of less than 10 cm^{-1} for wavelengths greater than 1.05 μ. Although we are unable to establish the presence of a direct energy gap, any indirect gap would have to be within ~100 meV of the direct gap.

B. $AgAlTe_2$

Despite the difficulties of working with $AgAlTe_2$, we have been able to establish its direct energy gap and to determine the crystal-field splitting. We have not been able to determine the spin-orbit splitting. Room-temperature electrolyte electroreflectance spectra exhibit the A and B structures at 2.27 and 2.38 eV, respectively, as seen in Fig.

TABLE I. Valence-band parameters of the $AgXTe_2$ compounds (in eV). The energies of the *A*, *B*, and *C* transitions and the calculated crystal-field (Δ_{cf}) and spin-orbit (Δ_{so}) parameters are given. Blanks indicate no available data.

	T(°K)	*A*	*B*	*C*	Δ_{cf}	Δ_{so}
$AgAlTe_2$	292	2.27	2.38		−0.16	
	77	2.35	2.47		−0.17	
$AgGaTe_2$	292	1.316	1.425		−0.155	
	77	1.356	1.472	2.26	−0.165	0.84
$AgInTe_2$	77	1.04				

4. The small magnitude of the *B* structure with respect to the *A* structure is partly the result of surface degradation. The observed splitting (0.11 eV) yields a value of −0.16 eV for the crystal-field splitting, assuming the same spin-orbit splitting as observed in $AgGaTe_2$. This value is in reasonable agreement with the simple formula for Δ_{cf} which predicts $\Delta_{cf} = -0.18$ eV.

At low temperatures, wavelength derivative reflectivity was obtained from freshly cleaved surfaces. The samples were not of sufficient quality to yield discernible exciton reflectivity anomalies, so that the higher sensitivity of the modulation technique was required. In Fig. 5 is shown a modulated reflectivity spectrum which exhibits two transitions at 2.35 and 2.47 eV. These transitions are presumably due to excitons associated with the *A* and *B* valence bands. The observed splitting of 0.12 eV yields a crystal-field splitting of −0.17 eV.

In Fig. 6 is shown a 2°K photoluminescence spectra of an unannealed freshly cleaved sample under He-Cd laser (0.44 μ) excitation. The left-hand section illustrates an expanded version of the higher-energy luminescence with the energy position of the *A* exciton indicated. The near coincidence of the wavelength derivative structure with the luminescence is strong evidence for a direct energy gap. Since the wavelength derivative was obtained at 77°K and the luminescence at 2°K, there is also very little shift in the energy gap below 77°K. This observation is also consistent with our previous results on other ternary semiconductors.[1,5] In the right-hand section of Fig. 6, a complete luminescence spectra is shown. The relative weakness of the high-energy lines with respect to the broad band is illustrated.

C. $AgInTe_2$

The room-temperature energy gap of this compound was previously determined from optical transmission measurements to be 0.96 eV.[12] We have performed MIS electroreflectance measurements at 77° K on unoriented samples and have observed a single structure near 1.04 eV, as seen in Fig. 7. From the simple relationship for crystal-field splitting, we expect an *A* to *B* separation of 40 meV. With our present crystals we have been unable to resolve this crystal-field splitting, or to determine the spin-orbit splitting parameter. There is also near-band-gap broad band luminescence observable at 2°K, as shown in Fig. 8. This provides reasonable evidence that $AgInTe_2$ is a direct-gap semiconductor with an energy gap of ~1.04 eV at low temperatures.

IV. CONCLUSIONS

This concludes our present study of the properties of the $AgXTe_2$ compounds. The band-structure results are summarized in Table I. $AgGaTe_2$, which is the most structurally adequate material, has a direct energy gap near 1.3 eV which is close to the energy being contemplated for optical-fiber communication systems. However, our inability to obtain *n*-type material and its apparent weak photoluminescence appears to eliminate this material from any such considerations. Perhaps an understanding of the stoichiometry of this material would change the above conclusion. On the other hand, $AgGaTe_2$ has a moderately large compression, and might have a sufficiently large birefringence to be useful for nonlinear optics. To our knowledge, there have been no studies of this aspect with regard to the $AgXTe_2$ compounds.

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