Rev. 183, 798 (1969).

[17] D. C. Reynolds and T. C. Collins, Phys. Rev. 188, 1267 (1969).

[18] S. L. Hou and J. A. Marley, Jr., Appl. Phys. Letters 16, 467 (1970).

[19] W. C. Holton, A. R. Reinberg, R. K. Watts, and M. DeWit, J. Luminescence 1/2, 583 (1970).

[20] B. Tell, J. Appl. Phys. 41, 3789 (1970).

[21] B. L. Crowder and G. D. Petit, Phys. Rev. 178, 1235 (1969).

[22] N. O. Lippari and A. Baldereschi, Phys. Rev. Letters 25, 1660 (1970).

[23] P. Lawaetz (unpublished).

[24] O. F. Schirmer and D. Zwingel, Solid State Commun. 8, 1559 (1970).

[25] D. C. Reynolds and T. C. Collins, Phys. Rev. 185, 1099 (1969).

[26] G. D. Watkins, Phys. Rev. B 1, 4071 (1970).

[27] F. T. J. Smith, Met. Trans. 1, 617 (1970); Solid State Commun. 8, 263 (1970); 7, 1757 (1969); see also R. C. Wheelan and D. Shaw, Phys. Status Solidi 29, 145 (1968).

[28] J. Schneider and A. Räuber, Solid State Commun. 5, 779 (1967); K. Leutwein, A. Räuber, and J. Schneider, *ibid.* 5, 783 (1967).

[29] K. Nassau, C. H. Henry, and J. W. Shiever, *Proceedings of the Tenth International Conference on Semiconductors* (Cambridge U.P., New York, 1970), p. 629.

[30] R. A. Faulkner, Phys. Rev. 184, 713 (1969).

[31] G. H. Hershman and F. A. Kroger, J. Solid State Chem. 2, 483 (1970).

[32] E. M. Pell, J. Phys. Chem. Solids 3, 77 (1957).

PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Electrical Properties, Optical Properties, and Band Structure of $CuGaS_2$ and $CuInS_2$

B. Tell and J. L. Shay
Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

H. M. Kasper
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 20 May 1971)

Various optical and electrical properties of the I-III-VI_2 compounds $CuGaS_2$ and $CuInS_2$ have been studied. From the results of low-temperature luminescence and reflectivity, both crystals are determined to have a direct band gap. The band gaps at 2 °K are 2.53 eV for $CuGaS_2$ and 1.55 eV for $CuInS_2$. $CuInS_2$ has been made conducting both n and p type, while $CuGaS_2$ has been made p type only. Electroreflectance measurements have been performed in an attempt to determine the band structure. The highest valence band appears to be a doublet with a large admixture of Cu 3*d* wave functions.

I. INTRODUCTION

The I-III-VI_2 sulphides are ternary analogs of the familiar II-VI compounds ZnS and CdS. Very little is known of either the electrical or optical properties of this class of materials. They are tetrahedrally coordinated semiconductors which crystallize in the uniaxial chalcopyrite structure. Since some of these compounds display large birefringence, they are potentially interesting as nonlinear optical materials[1,2] as well as semiconductors. In the present paper, we have studied optical and electrical properties of melt-grown single crystals of $CuGaS_2$ and $CuInS_2$. We have determined that they are direct-band-gap materials which are capable of controlled doping. In addition, we present electroreflectance and photoreflectance studies in an attempt to understand the band structure. The only previous work on the present compounds was performed on powders and polycrystals.[3,4] Single crystals of other I-III-VI_2's have been briefly studied.[5,6]

Low-temperature optical studies show that in the wavelength vicinity of the absorption edge there are both sharp photoluminescence lines and reflectivity anomalies. The presence of reflectivity anomalies and luminescence at the same wavelength is unambiguous evidence that the crystals have direct energy gaps. These observations enable the determination of the band gaps at 2 °K to be 2.53 eV for $CuGaS_2$ and 1.55 eV for $CuInS_2$.

The band structure of these compounds is a complicated problem. As occurs in other copper compounds, the Cu 3*d* bands are expected to contribute appreciably to the highest valence band. The *d*-band mixing is probably responsible for the large downshift in the energy gap of the copper compounds (~1.5 eV) with respect to the II-VI analogs, and results in a valence-band structure unlike any previously observed in a "diamondlike" semiconductor.

Similar to the II-VI compounds, significant changes in electrical conductivity are achieved by annealing for relatively short times in one of the constitutent elements. The as-grown crystals vary from *p* type to semi-insulating. The semi-insulating crystals are readily made moderately conducting *p* type by annealing under maximum sulfur pressure. Annealing under minimum sulfur pressure (i.e., maximum cation pressure) yields *n*-type material in $CuInS_2$, but not in $CuGaS_2$. Some doping experiments were attempted, and the results will be described.

II. CRYSTAL GROWTH

Crystals of $CuGaS_2$ and $CuInS_2$ have been grown by slowly cooling melts of stoichiometric composition. The ingots obtained from a melt of $CuGaS_2$ heated to the softening point of fused silica were not homogeneous and consisted of crystals of orange and dark orange color. All crystals studied here formed a chalcopyrite-type phase. The lattice constants for the orange crystals, which crystallized first according to inspection, are $a = 5.328$ Å and $c = 10.462$ Å, and those for the dark crystals are slightly larger, $a = 5.351$ Å and $c = 10.484$ Å. Belova *et al.*[4] investigated quenched samples of the system $Cu_{1-x}Ga_{1+x/3}S_2$ and determined the phases present and their lattice constants. From their Fig. 1, compounds with the chalcopyrite structure form in the range $x = 0-0.13$, and disordered zincblende phases with vacancies form near $x = 0.75$ or $CuGa_5S_8$. Comparing the lattice constants of the orange and the dark crystals with their data, we conclude that the orange crystals are close to the composition $Cu_{0.88}Ga_{1.04}S_2$ or $x = 0.12$, and the dark crystals are close to stoichiometric $CuGaS_2$. The fact that the orange crystals form at the beginning of the crystallization process indicates that $CuGaS_2$ does not melt congruently. From the inspection of the ingots, we have the impression that we do not obtain under our conditions any intermediate phases between the orange and the dark crystals as reported for quenched samples by Belova *et al.* The melting temperature of $CuGaS_2$ lies near 1200 °C. $CuInS_2$ crystals were obtained in a similar way. Determination of the lattice constants of different spots of an ingot gave the same value $a = 5.52$ Å and $c = 11.13$ Å and did not indicate deviations from stoichiometry comparable to those found in $CuGaS_2$. The lattice constants obtained for both compounds are in satisfactory agreement with the results of Hahn *et al.*[7] The stoichiometry problems and the crystallization process are still under investigation, and a detailed report will be given elsewhere.

III. EXPERIMENTAL

The crystals studied in luminescence and reflectivity had either "as-grown" or irregularly cleaved faces. We have had little success observing excitons from surfaces which were mechanically polished and subsequently chemically etched. (Etches such as warm phosphoric acid and 1 : 1 $HCl-HNO_3$ were attempted.) The luminescence and reflectivity were obtained in an immersion Dewar with liquid nitrogen (77 °K), liquid hydrogen (20 °K), or liquid helium pumped below the λ point (2 °K).

For luminescence studies the excitation source was either a 50-mW He-Cd laser at 4416 Å ($CuGaS_2$), or a 50-mW He-Ne laser at 6328 Å ($CuInS_2$). The lasers were usually attenuated, since the sharpest lines were obtained with the minimum pump power. For reflectivity measurements, a well-apertured and attenuated 100-W tungsten-iodine source was employed. The light was focused and reflected off the crystal at the small angle from the normal. Band-pass filters (Corning 4-97 and 7-69) were employed to limit the wavelength range reflected from the sample. For both reflectivity and luminescence studies, the light was dispersed by a $\frac{3}{4}$-m Spex spectrometer and recorded photoelectrically. The maximum slit widths employed in the visible were ~1 Å ($CuGaS_2$) and ~2 Å in the infrared ($CuInS_2$).

Electrolyte electroreflectance[8] measurements were performed on oriented samples which had been annealed, as described below, in order to achieve sufficient conductivity. The surfaces were given a final preparation of fine polish and etch. In addition, photoreflectance measurements were performed at 77 °K using the 6328-Å laser line from the He-Ne laser or the 3511-Å line from the argon ion laser. Surfaces for photoreflectance were either as-grown or cleaved.

IV. ELECTRICAL PROPERTIES

The as-grown crystals of both $CuGaS_2$ and $CuInS_2$ varied from semi-insulating to moderately *p* type. The orange variety of $CuGaS_2$ was invariably semi-insulating, while the dark crystals often had measurable *p*-type conductivity. Annealing and doping experiments were performed in order to determine if the crystals could be made highly conducting *p* and/or *n* type.

It is well known that the electrical properties of II-VI compounds are greatly changed by variations in stoichiometry. For example, CdS is readily changed from low-resistivity *n* type to semi-insulating and vice versa by alternately annealing a sample under high S pressure and Cd pressure, respectively.[9] On the other hand, CdTe can be converted from *n* to *p* type and from *p* to *n* type by alternately annealing in Te and Cd, respectively.[10] Completely analogous to CdTe, $CuInS_2$ can be made highly conducting *p* type (~5 Ω cm) by annealing in S, and can be converted from *p* to *n* type by annealing under minimum S pressure. On the other hand, $CuGaS_2$ can also be made *p* type by annealing under maximum sulfur pressure, but minimum sulfur pressure yields only semi-insulating material ($\rho > 10^6$ Ω cm). $CuGaS_2$ can be readily made p type, while some compensation mechanism appears to limit the n-type conductivity. Such limits are well known in the wide-band II-VI compounds.

Annealing and diffusion experiments were performed by sealing an etched crystal (1 : 1 HCl + HNO_3) in a flamed-out quartz ampul (~ 1-in. length) which was then placed in the center of a 12-in. oven. The crystals were quenched to room temperature in a water bath. Anneals were carried out under maximum sulfur pressure or with maximum cation pressure. Since the vapor pressure over the cations (Cu, In, Ga) is apparently not large enough to prevent the crystals from partly decomposing, it was necessary to include powder of the crystal along with the cations. The experiments were performed at ~ 700 °C for times of 24–72 h. The crystals were typically ~ 0.25 mm thick.

All crystals were initially checked for conductivity type with a thermal probe. For moderately conducting crystals, Hall-effect and resistivity measurements were made at room temperature by the Van der Pauw technique.[11] Contacts were usually made with a Ga-In amalgam. These contacts were adequate for Van der Pauw measurements, although they were only strictly ohmic for n-type $CuInS_2$. In all cases, the carrier type determined from the thermal probe agreed with that determined from the Hall measurements. Typical mobility and resistivity results for $CuInS_2$ are given below. Starting with $CuInS_2$ No. 139 which was p type with initial resistivity ρ of $\sim 5\times10^3$ Ω cm and hole mobility μ of ~ 10 cm^2/V sec, a 30-h anneal in Cu + In (i.e., minimum S pressure) yielded n-type material of $\rho \sim 1$ Ω cm and $\mu \sim 200$ cm^2/V sec. Similarly, a 30-h anneal under maximum sulfur pressure gave p-type material with $\rho \sim 7$ Ω cm and $\mu \sim 12$ cm^2/V sec.

Anneals were also performed on $CuGaS_2$. For example, $CuGaS_2$ No. 124 had initial resistivity greater than 10^6 Ω cm, whose carrier type we were unable to determine. After annealing in Cu + Ga + powder (i.e., minimum sulfur pressure) the resistivity remained greater than 10^6 Ω cm. However, annealing under maximum sulfur pressure for 72 h at ~ 700 °C produced p-type material of $\rho \sim 0.4$ Ω cm and $\mu \sim 20$ cm^2/V sec. Dark material from boule No. 270 was also annealed, and qualitatively similar results were obtained. In addition, several doping experiments were performed on $CuGaS_2$. Specifically, Sn, Cd, and the halogens were diffused under minimum sulfur pressure, and Ge was added to a crystal during growth. The Ge-doped crystal was subsequently annealed under minimum sulfur pressure. The halogens would be expected to act as donors at sulfur sites, while Ge and Sn should be donors at a Ga site. Cd is probably amphoteric, being a donor on a Cu site and an acceptor on a Ga site. All attempts to obtain n-type material have been unsuccessful.

V. EXPERIMENTAL RESULTS

A. Optical Transmissions

Optical-transmission measurements at liquid-nitrogen temperature were performed from 2.5 μ to the band edge. The data were first obtained with a Cary spectrophotometer on unetched thick (0.25–0.5 mm) samples. Measurements in the absorption-edge region were also obtained using the Spex with slit widths of ~ 1 Å. For the latter measurements, the crystals were mechanically polished to ~ 150 μ and then etched in 1 : 1 HCl and HNO_3. The etching produced slightly diffuse surfaces which reduced the total transmission, but presumably yielded a more reliable shape to the absorption curve near the band gap.[12]

The optical-absorption–edge regions of orange $CuGaS_2$ and $CuInS_2$ are shown in Figs. 1 and 2, respectively. The long-wavelength region has low residual absorption, the transmission for both crystals being greater than 50% for wavelengths a few hundred Å longer than the energy gap. The transmission values quoted were obtained by extrapolating the values at longer wavelengths as obtained from the Cary. Both crystals exhibit a moderately sharp absorption edge, the transmission dropping to less than 0.01 of its long wavelength value within 0.05 eV of the lowest-energy exciton. The dark variety of $CuGaS_2$ has essentially the same

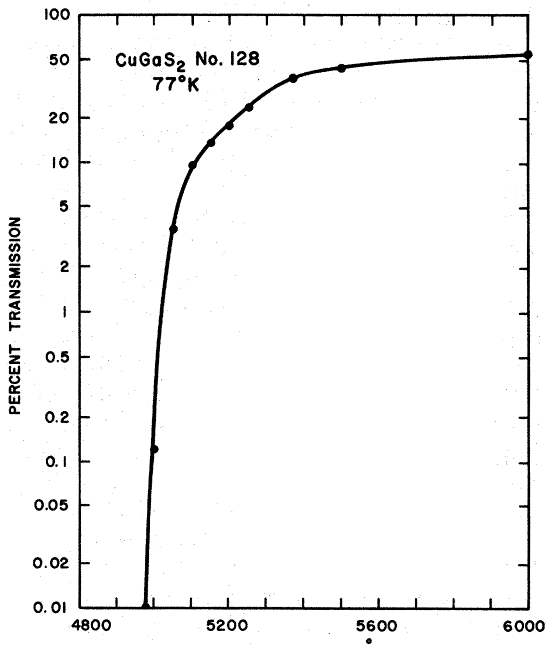

FIG. 1. Transmission spectra at 77 °K for a typical orange $CuGaS_2$ sample using unpolarized radiation.

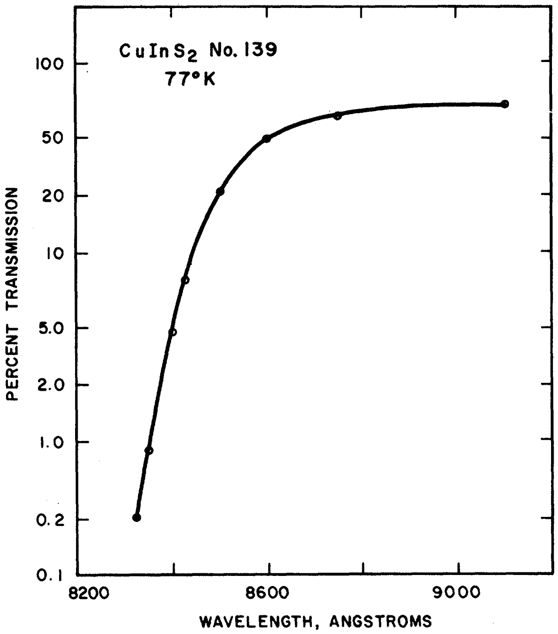

FIG. 2. Transmission spectra at 77°K for CuInS$_2$ using unpolarized radiation.

shape to the absorption edge, although the magnitude of the transmission is reduced an order of magnitude. In addition, the dark crystals have an infrared absorption band commencing near 0.8–0.9 μ. The nature of this extra absorption in the dark crystals is not presently understood.

B. Luminescence

The low-temperature luminescence appears qualitatively similar to the II-VI compounds. The highest-energy luminescence observed is identified as the decay of a free exciton with the hole belonging to the highest valence band. This is determined by comparison to the reflectivity data discussed below. Since luminescence is associated with the lowest-energy gap, and since reflectivity anomalies occur only at a direct gap,[13] the lowest gap is unambiguously direct in both CuGaS$_2$ and CuInS$_2$. At 2°K the spectra are dominated by sharp lines which are presumably excitons bound to impurities or defects. This is seen in Figs. 3 and 4 for CuGaS$_2$ and CuInS$_2$, respectively. (It should be mentioned that only selected CuInS$_2$ crystals exhibited such luminescence, whereas the selection was somewhat less critical for CuGaS$_2$.) We have also observed sharp-line photoluminescence from dark samples of CuGaS$_2$. The spectra obtained are richer and the lines narrower than the spectra shown in Fig. 3. However, the free exciton is not as pronounced, so that a spectrum from an "orange" crystal was chosen.

At liquid-nitrogen temperature, the impurity or defect luminescence is greatly reduced in magnitude relative to the free exciton as seen in Figs. 5 and 6. For this sample of CuInS$_2$ the bound excitons are not observed at N$_2$ temperature, while for CuGaS$_2$ the bound and free are of comparable magnitude. These results are consistent with an expected smaller binding energy for an impurity exciton with respect to the free exciton and with a smaller binding energy in a narrower gap material.

Both crystals often exhibit a broader emission at slightly longer wavelength. This emission appears analogous to the so-called "edge emission" in the II-VI compounds. That is, for CuGaS$_2$ at low excitation levels at 2°K, there is structure in this emission which could be phonon wings. The peak positions (at low excitation levels) vary from crystal to crystal even within the same boule. In addition, the spacings are irregular, suggesting that more than one phonon branch may be participating. At the highest excitation level the structure is obscured, and the peak shifts to shorter wavelength. On the other hand, "dark" samples apparently do not exhibit a broad emission, but instead a number of lines in the same wavelength region. For CuInS$_2$, structure is not always observed, although the peak shifts to shorter wavelength as the excitation is increased. The shift to shorter wavelength at high pump levels is indicative of a donor-acceptor pair recombination, since the distant pairs are more readily saturated.[14] The "edge emission" is also seen in Figs. 3 and 4.

C. Reflectivity

The reflectivity in the absorption-edge region

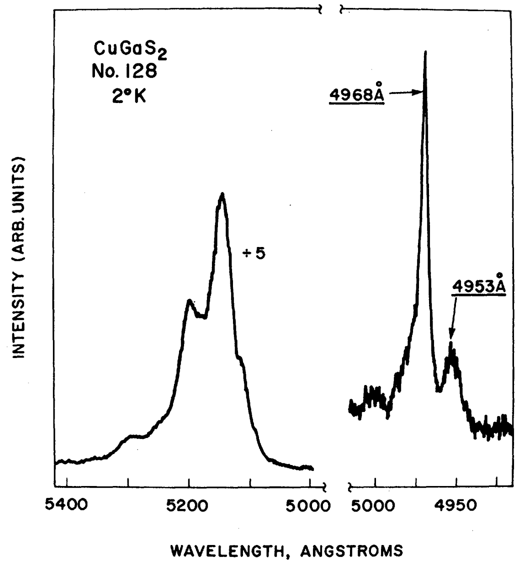

FIG. 3. 2°K luminescence spectra obtained from an orange CuGaS$_2$ crystal employing minimum excitation power. The luminescence attributed to the decay of the free exciton is at 4953 Å.

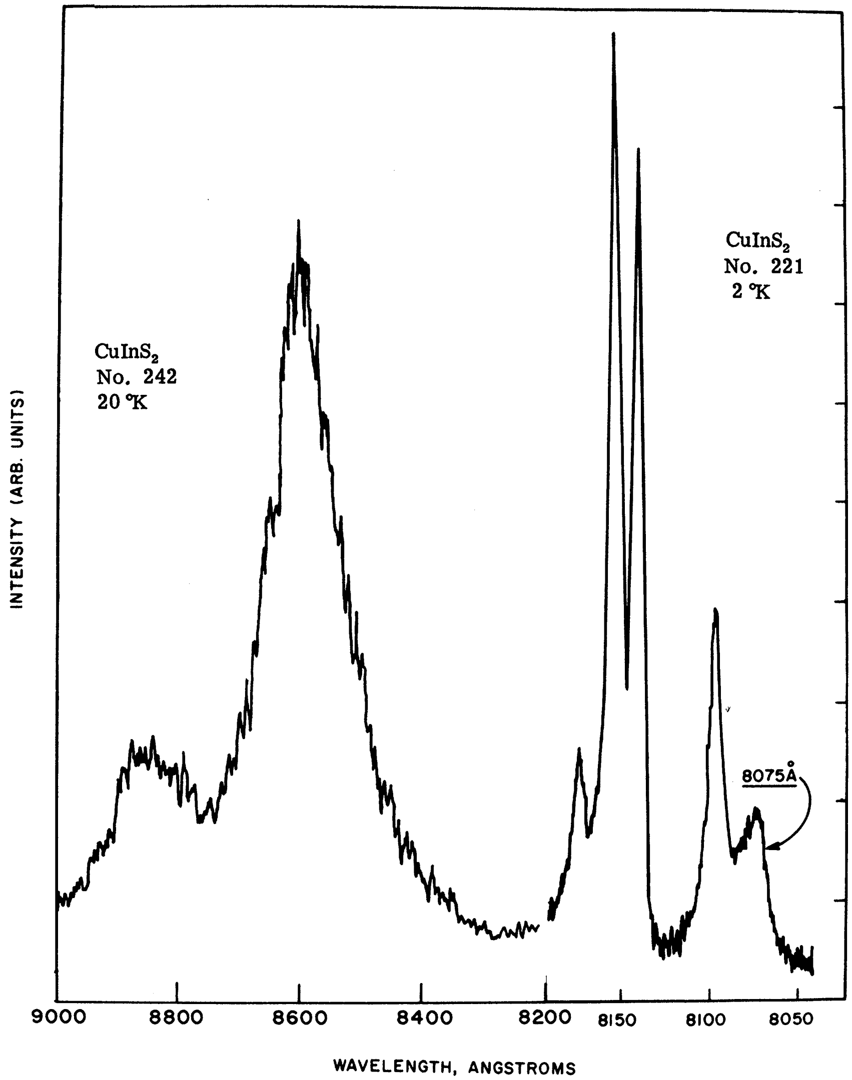

FIG. 4. Luminescence spectra obtained from two different samples of CuInS$_2$. (Note the break at 8200 Å.) Sample No. 221 did not exhibit any broad-edge emission. The free exciton is at 8075 Å, while the other lines are attributed to excitons bound to impurities or defects.

was studied at both 2 and 77 °K. Because of the strong dispersion in the dielectric constant in the neighborhood of a direct-gap intrinsic exciton, reflectivity anomalies occur similar to those observable in II-VI compounds. Typical reflectivity[13,15] curves obtained at 2 °K are shown in Figs. 7 and 8. The anomalies are not appreciably broadened at 77 °K, which indicates that imperfections rather than intrinsic effects give rise to the observed width. The observed width at 2 °K for CuGaS$_2$ is several times that for the *A* and *B* peaks in high-quality CdS platelets.[15] This probably explains the absence in reflectivity of the exciton excited states.

In principle, from a detailed analysis of the reflectivity curve, the oscillator strength, the damping, and the energy of the exciton can be determined. The position of the lowest-energy direct gap is then determined by adding the exciton binding energy to the exciton energy. The exciton energy lies close to the reflectivity maximum, its exact position depending on damping, etc.[15] For the present purposes it should be sufficient to take the exciton energy at the reflectivity maximum. (The wavelength of the maximum agrees well with the exciton as observed in luminescence.) For lack of a better method, the lowest-energy gap can then be estimated by adding a binding energy equal to that obtained for the II-VI compound of closest comparable band gap, i.e., 28 meV for CuGaS$_2$ and 10 meV for CuInS$_2$, using values obtained for CdS and CdTe, respectively.[13,15] For CuGaS$_2$ the reflectivity maximum occurs at ~ 4955 Å at 2 °K, and at 4958 Å at 77 °K. (Within experimental error, we have not observed any difference between the dark and the orange crystals.) For CuInS$_2$ the values are

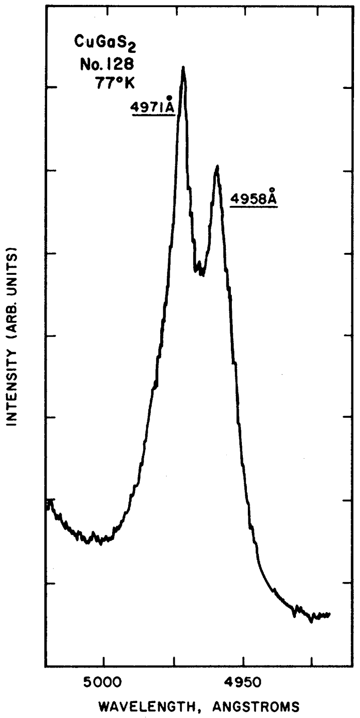

FIG. 5. 77 °K luminescence spectra for an orange CuGaS$_2$ sample. The free exciton is at 4958 Å.

8075 Å at 2 °K and 8068 Å at 77 °K. The lowest-energy gap is then 2.53 eV at 2 °K for CuGaS$_2$ and 1.55 eV at 2 °K for CuInS$_2$. The shift in the reflectivity maximum is quite small for temperatures less than 77 °K, and, in fact, appears to be negative for CuInS$_2$.

For both crystals a higher-energy reflectivity anomaly is observed at both 2 and 77 °K. These

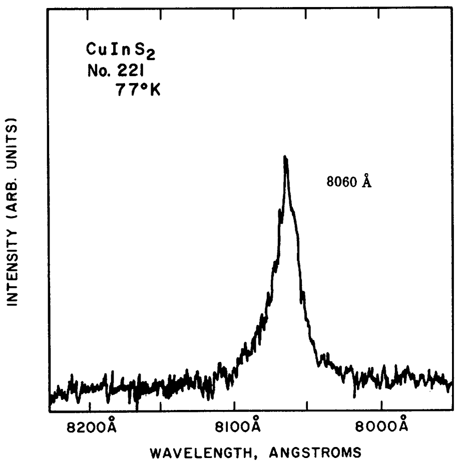

FIG. 6. 77 °K luminescence spectra for CuInS$_2$ sample showing only the free exciton.

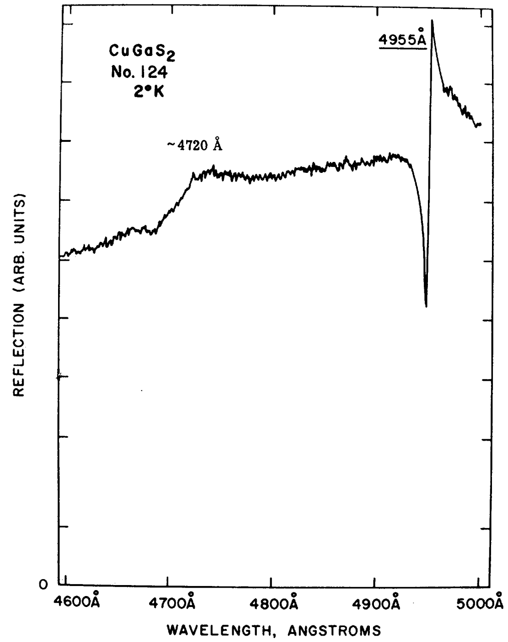

FIG. 7. 2 °K reflectivity spectra for CuGaS$_2$ for unpolarized radiation. The zero-reflectivity level is the bottom of the scale, while the flat region is estimated to be 20–25% reflection.

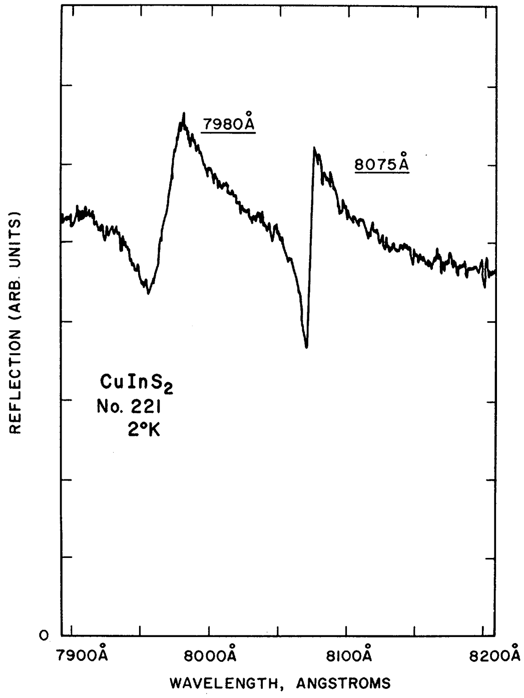

FIG. 8. 2 °K reflectivity spectra for CuInS$_2$ for unpolarized radiation. The zero reflectivity is the bottom of the scale, while the flat region is again in the 20–25% reflectivity range.

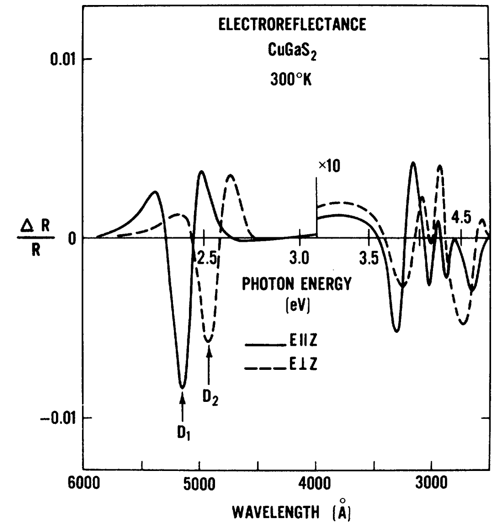

FIG. 9. Electrolyte electroreflectance spectra of $CuGaS_2$ for light polarized relative to the optic axis. D_1 occurs at ~ 2.40 eV and D_2 at 2.52 eV.

occur near 4720 Å in $CuGaS_2$ and 7980 Å in $CuInS_2$. This peak in $CuGaS_2$ is appreciably broadened due to auto-ionization.[15] In addition, the anomalies in $CuGaS_2$ are polarization dependent, whereas the dependence in $CuInS_2$ was too small to be observed. This is consistent with the electroreflectance and photoreflectance results.

D. Electroreflectance and Photoreflectance

When excitons can be observed, low-temperature exciton reflectivity is probably the best method for accurately determining energy gaps. It suffers, however, from the difficulty in determining structure more than roughly 100 meV above the lowest direct gap. Electroreflectance, on the other hand, produces strong reflectivity modulation in the neighborhood of excitons as well as higher-energy critical points of the energy-band structure.[8] Electroreflectance readily yields structure at critical points many volts above the lowest direct gap. In the present work electroreflectance yields structure at the lowest direct gaps consistent with the low-temperature reflectivity measurements, and in addition yields structure at considerably higher energies. However, only two peaks are observed near the lowest gap. This is shown in Fig. 9 for $CuGaS_2$. The structure near 2.5 eV is strongly polarization dependent with the lowest direct gap (D_1) polarized predominantly $E \parallel Z$, and the next gap (D_2) polarized $E \perp Z$. (Z is the optic axis.) The polarization dependence is indicative of a crystal field splitting. There is additional polarization-dependent structure in $CuGaS_2$ at energies near 3.5 eV, close to the band gap of the binary analog ZnS.

The electroreflectance spectra for $CuInS_2$ shown in Fig. 10 does not exhibit polarization dependence at the lowest gap (D_1, D_2) and again does not yield a third peak. There is also structure at higher energy near the band gap of the binary analog $Zn_{0.5}Cd_{0.5}S$.

Since electroreflectance peaks tend to be broad (compared to low-temperature reflectivity) and often have residual oscillations which can obscure other nearby weak structure, the failure to observe a third peak is not conclusive. Similarly, the absence of a third peak in reflectivity may be due to auto-ionization. For these reasons, we have also studied photoreflectance at 77 °K. As shown in Fig. 11, $CuGaS_2$ again exhibits two polarization-dependent peaks, and within a factor of ~ 800, there is no third peak within 0.5 eV of the lowest-energy exciton. Photoreflectance was also observed in $CuInS_2$, as seen in Fig. 12. The sample was an "as-grown" (112) face [equivalent of a (111) face in the zinc-blende system] for which locations of the principal axes were known. (This orientation allows a maximum of 65% of the intensity along Z, or 100% normal to Z.) Under these conditions the peaks at the lowest gap, as observed in reflectivity, were clearly resolved, but there was no apparent polarization dependence. A splitting in the absence of polarization dependence is suggestive of spin-orbit splitting. Any third peak within 0.3 eV of the lowest-energy exciton is at least 125 times weaker than the two peaks which are observed in Fig. 12. The broad bump near 1.60 eV is attributed to photoreflectance associated with band-to-band transitions.[16]

VI. DISCUSSION

The salient features of the direct energy gaps in

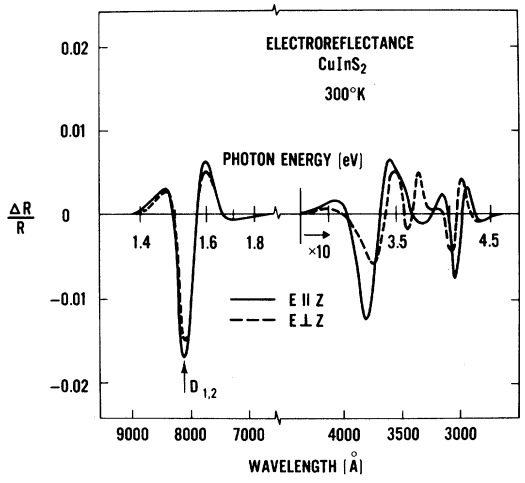

FIG. 10. Electrolyte electroreflectance spectra of $CuInS_2$ for light polarized relative to the optic axis. D_1 and D_2 occur at ~ 1.53 eV.

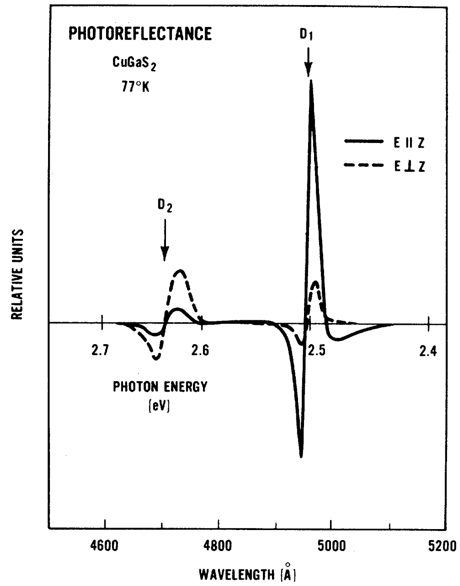

FIG. 11. Photoreflectance spectra of $CuGaS_2$ at 77 °K for light polarized relative to the optic axis. The optic axis is slightly out of the plane of the crystal, so $E \parallel Z$ is only nominal.

$CuInS_2$ and $CuGaS_2$ are qualitatively different from those in any known semiconductor. As previously mentioned, these direct energy gaps lie ~1.5 eV below the energy gaps in the binary analogs, in sharp contrast to II-IV-V_2 crystals in which the direct energy gaps lie within 0.3 eV of the energy gaps in the binary analogs.[17,18] One immediately suspects that the Cu 3*d* bands are perturbing the energy bands in these ternary sulphides, as they do in the copper halides. In CuCl, for example, the Cu 3*d* levels lie ~3 eV above the valence bands formed from the Cl 3*p* levels.[19] As a result, the energy gap of CuCl lies ~3 eV *below* the expected value obtained by extrapolating the energy gaps in the series GaP, ZnS, to CuCl. It is therefore plausible that the lowering of the energy gap in $CuInS_2$ and $CuGaS_2$ by ~1.5 eV relative to their binary analogs results from the influences of the 3*d* bands of copper.

The nature of the direct energy gaps in $CuInS_2$ and $CuGaS_2$ is qualitatively new in another essential way. For the II-IV-V_2 chalcopyrite compounds, the lowest direct energy gap is one of three closely spaced energy gaps derived from the $\Gamma_{15} \rightarrow \Gamma_1$ energy gap in zinc-blende crystals.[20,21] The triple degeneracy of the *p*-like Γ_{15} valence band in zinc-blende crystals is completely lifted in chalcopyrite crystals under the simultaneous perturbations of spin-orbit interaction and the uniaxial crystalline potential. In CuCl,[19] the 3*d* bands of Cu split into a threefold-degenerate Γ_{15} lying above a doubly degenerate Γ_{12}. The lowest-energy gap is therefore basically a triplet in CuCl, in III-V binary compounds, and in II-IV-V_2 compounds.[22] In both $CuInS_2$ and $CuGaS_2$, however, we find that the direct energy gap is not a triplet but is, in fact, a doublet. For example, in $CuGaS_2$ photoreflectance measurements at 77 °K (Sec. IV D) reveal that any third peak is at least 800 times weaker than the structure associated with the lowest energy gap. We therefore conclude that the valence-band maxima in $CuInS_2$ and $CuGaS_2$ are *not* derived from the *p*-like Γ_{15} valence bands in zinc-blende crystals nor derived from the Γ_{15} level of the copper 3*d* bands.

In light of the previous discussion, it is clear that a new energy-band model is needed to explain the doublet nature of the direct energy gaps of $CuInS_2$ and $CuGaS_2$. Several possibilities come to mind, none of which is entirely satisfactory. For example, it is possible that the twofold-degenerate Γ_{12} level of the copper 3*d* band lies above the Γ_{15} level of copper, opposite to the situation in CuCl. This model is unpalatable because the $\Gamma_{12} \rightarrow \Gamma_1$ transition is forbidden in the absence of spin-orbit interaction and because a transition metal in a tetrahedral environment usually results in a Γ_{15} level higher in energy than the Γ_{12} level. It is also possible that the direct energy gap may lie off $\vec{k}=0$ as occurs in silver halides, or the valence-band maximum at $\vec{k}=0$ may be a Γ_5 state derived from the X_5 valence band in zinc-blende crystals due to the mapping of the zinc-blende Brillouin zone into the smaller

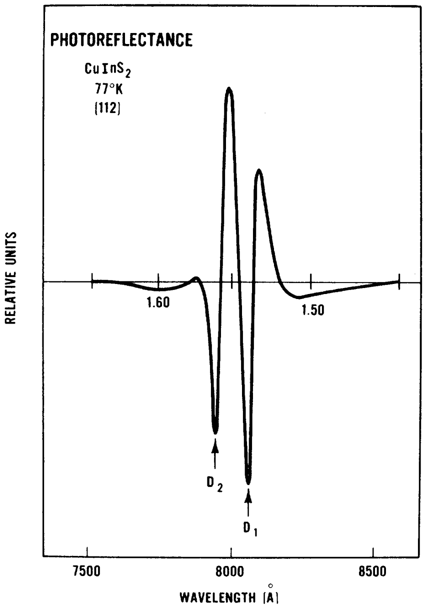

FIG. 12. Photoreflectance spectra of $CuInS_2$ at 77 °K for light polarized relative to the optic axis. Since the orientation is (112), $E \parallel Z$ is only nominal so, in fact, only two-thirds of the intensity is parallel to Z.

chalcopyrite Brillouin zone.[17,18]

In addition to the new direct energy gaps just discussed, in both $CuInS_2$ and $CuGaS_2$ we observe electroreflectance structure in the photon-energy region near the direct energy gaps in the binary analogs (3.25 eV in $CuInS_2$ and 3.75 eV in $CuGaS_2$). This structure is considerably broader than is usually observed at the direct energy gap in III-V and II-IV-V_2 compounds presumably due to autoionization.

Since we have observed two sets of valence bands in both compounds, the question arises as to which, if either, is mostly copper $3d$ levels. For comparison, in the series CuCl, CuBr, and CuI[23] the direct energy gap (average of spin-orbit–split levels) is essentially constant (3.2, 3.0, and 3.2 eV, respectively) because it is basically a $3d$-$4s$ transition on the copper atom. On the other hand, going from $CuInS_2$ and $CuGaS_2$, the lowest-energy gap increases 1.0 eV while the higher-energy structure increases by 0.5 eV. This comparison suggests that both sets of valence bands result from a strong admixture of Cu $3d$ level and p levels on the other atoms. This conclusion is only qualitative, and in no way explains the doublet nature of the direct energy gaps in these compounds.

VII. CONCLUSIONS

We have studied properties of two I-III-VI_2 compounds $CuGaS_2$ and $CuInS_2$, using several of the techniques which have proved fruitful in our present understanding of the II-VI compounds. Clearly, much remains to be done and understood concerning these materials. The present crystals are probably of comparable quality to melt-grown II-VI compounds, and should be capable of yielding interesting new physics, as illustrated by the unusual band structure observed. The practical application of these materials will probably depend on whether or not visible band-gap materials can be made usefully both n and p type. The defect chemistry of these materials holds more possibilities than the II-VI compounds, the implications of which have not yet been explored.

Note added in proof. Using polarized light ($E \parallel Z$), we have clearly observed in reflectivity the $n = z$ state of the lowest-energy exciton at 2 °K from dark $CuGaS_2$ crystals. The $n = 1$ state occurs at 4955 Å (2.502 eV) and the $n = 2$ state at 4914 Å (2.523 eV), giving a separation of 21 meV. The exciton binding energy is then 28 meV, yielding a band gap of 2.530 eV at 2 °K.

ACKNOWLEDGMENTS

We wish to thank R. A. Laudise and A. G. Chynoweth for their interest and suggestions in this work, and R. L. Barns for obtaining the lattice constants quoted in Sec. II. In addition, L. M. Schiavone and Mrs. A. A. Pritchard provided valuable experimental assistance.

---

[1] D. S. Chemla, P. J. Kupecek, D. S. Robertson, and R. C. Smith, Opt. Commun. 3, 29 (1971).

[2] G. D. Boyd, J. H. McFee, and H. M. Kasper, J. Quantum Electron. (to be published).

[3] For general review of I-III-VI_2 including CuGaS and $CuInS_2$ see L. I. Berger and V. D. Prochukhan, *Ternary Diamond-Like Semiconductors* (Consultants Bureau, New York, 1969), pp. 47ff.

[4] E. K. Belova, V. M. Koshkin, and L. S. Palatnik, Inorg. Mater. 3, 543 (1967).

[5] L. S. Lerner, J. Phys. Chem. Solids 27, 1 (1966).

[6] W. N. Honeyman, J. Phys. Chem. Solids 30, 1935 (1969).

[7] H. Hahn, G. Frank, W. Klingler, A. Meyer, and G. Storger, Z. Anorg. Allgem. Chem. 271, 153 (1953).

[8] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[9] F. A. Kroger, H. J. Vink, and J. van den Boomgaard, Z. Physik. Chem. (Leipzig) 203, 1 (1954); H. H. Woodbury, Phys. Rev. 134, A492 (1964).

[10] D. DeNobel, Philips Res. Rept. 14, 361(1959); 14, 430 (1959); M. R. Lorenz, B. Segall, and H. H. Woodbury, Phys. Rev. 134, A751 (1964).

[11] L. J. Van der Pauw, Philips Res. Rept. 13, 1 (1958).

[12] See, e.g., D. T. F. Marple, Phys. Rev. 150, 728 (1966).

[13] See, e.g., B. Segall and D. T. F. Marple, in *Physics and Chemistry of* II-VI *Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967), pp. 319ff.

[14] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. 133, A269 (1964).

[15] D. G. Thomas and J. J. Hopfield, Phys. Rev. 116, 573 (1959).

[16] J. L. Shay, Phys. Rev. B 2, 803 (1970).

[17] J. L. Shay, E. Buehler, and J. H. Wernick, Phys. Rev. B 2, 4104 (1970); 3, 2004 (1971).

[18] J. L. Shay and E. Buehler, Phys. Rev. B 3, 2598 (1971).

[19] K. S. Song, J. Phys. (Paris) 28, 195 (1967); J. Phys. Chem. Solids 28, 2003 (1967).

[20] J. L. Shay, E. Buehler, and J. H. Wernick, Phys. Rev. Letters 24, 1301 (1970).

[21] J. E. Rowe and J. L. Shay, Phys. Rev. B 3, 451 (1971).

[22] Our symmetry notation follows G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Stotz, *Properties of the Thirty-Two Point Groups* (MIT U.P., Cambridge, Mass., 1963), except for the following changes in the point group $T_d : \Gamma_{15} \longleftrightarrow \Gamma_5$, $\Gamma_{12} \longleftrightarrow \Gamma_3$.

[23] M. Cardona, Phys. Rev. 129, 69 (1963).