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Electronic Structure of $AgInSe_2$ and $CuInSe_2$

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We report electroreflectance and photoluminescence studies of the chalcopyrite compounds $AgInSe_2$ and $CuInSe_2$. Observation of photoluminescence at low temperatures at the same energy as the direct energy gaps located by electroreflectance measurements confirms that both compounds have direct band gaps. At 300 °K, the values for the energy gaps are 1.24 and 0.96 eV, respectively. The spin-orbit splittings of the uppermost valence bands as observed in electroreflectance measurements are considerably less than expected for *p* levels, a result which we attribute to ∼ 17% hybridization of Ag 4*d* levels, and ∼ 34% hybridization of Cu 3*d* levels, with the otherwise *p*-like valence bands. An ultraviolet electroreflectance structure observed in $CuInSe_2$ may result from transitions from the *d* levels themselves to the lowest conduction-band minimum. The crystal-field and spin-orbit parameters for the uppermost valence bands of $CuInSe_2$ disagree with values found in a recent energy-band calculation ignoring *d* bands, a calculation which also predicted that $CuInSe_2$ has an indirect energy gap. We also observe an anomalous temperature dependence of the energy gap in $AgInSe_2$. Whereas the energy gap in CdSe (the binary analog of $AgInSe_2$) decreases by approximately 80 meV as the temperature increases from 77 to 300 °K, the energy gap of $AgInSe_2$ is independent of temperature over this range within experimental error (± 5 meV).

I. INTRODUCTION AND CONCLUSIONS

The uppermost valence bands of a I-III-VI_2 compound are profoundly influenced by the proximity of noble-metal *d* levels in the valence band.[1,2] One consequence of the resulting hybridization of the valence-band wave functions is a reduction of the spin-orbit splitting observed in the ternaries relative to the values for the binary analogs, due to a partial cancellation of the positive spin-orbit parameter for *p* levels and the negative spin-orbit parameters for *d* levels. The direct energy gaps observed in I-III-VI_2 compounds are low relative to the energy gaps in the II-VI compounds by amounts up to 1.6 eV due to a repulsion of the anion *p* levels and the noble-metal *d* levels.

$AgInSe_2$ and $CuInSe_2$ are of special interest in this connection on several grounds. The large spin-orbit splitting (~0.4 eV) characteristic of Se leads to a large spin-orbit splitting in these ternary compounds, so that the three valence bands derived from *p*-like Γ_{15} levels in zinc-blende compounds are well resolved. Consequently, the effects on the band structure due to the substitution of Cu for Ag are readily determined. Furthermore, a recent energy-band calculation ignoring *d* bands has predicted that $CuInSe_2$ has an indirect energy gap ~0.3 eV below the direct gap. This would be a very surprising result, since all I-III-VI_2 compounds which we have studied to date have proved to have direct band gaps, and the binary analogs ZnSe and CdSe have direct energy gaps.

In this paper, we report results of electroreflectance measurements for $AgInSe_2$ and $CuInSe_2$ at 77 and 300 °K. For both compounds, we observe three valence bands derived from the *p*-like Γ_{15} level of zinc-blende compounds under the simultaneous influences of spin-orbit coupling and the noncubic crystalline field. The observed spin-orbit splittings are considerably less than expected for *p* levels, a result which we attribute to ~17% hybridization of Ag 4*d* levels and ~34% hybridization of Cu 3*d* levels, with the otherwise *p*-like valence bands. An ultraviolet electroreflectance structure observed in $CuInSe_2$ may result from transitions from the *d* levels themselves to the lowest conduction-band minimum.

The crystal-field and spin-orbit parameters measured for $CuInSe_2$ are in considerable disagreement with the theoretical values recently reported.[3] Furthermore, at low temperatures, we observe photoluminescence at the same energy as the direct energy gap found from the electroreflectance measurements, proving therefore that $CuInSe_2$ has a direct energy gap. However, this gap is reduced by ~1.2 eV from its binary analog $Zn_{0.5}Cd_{0.5}Se$. We conclude that the proximity of Cu *d* levels strongly influences the energy-band structure of I-III-VI_2 compounds containing Cu, and must be included in a realistic energy-band calculation.

Similar photoluminescence experiments show that $AgInSe_2$ has a direct energy gap as well. The value of the energy gap is only 0.5 eV below that of CdSe, its binary analog. Apart from a ~17% hybridization with Ag 4*d* levels, the uppermost valence bands in $AgInSe_2$ are equivalent to those which would occur in a cubic CdSe compressed to achieve the built-in distortion of $AgInSe_2$. Nonetheless, we observe an anomalous temperature dependence of the energy gap in $AgInSe_2$. Whereas the energy gap[4] of CdSe decreases by approximately 80 meV as the temperature increases from 77 to 300 °K, the energy gap of $AgInSe_2$ is independent of temperature within experimental error (± 5 meV). Since the physical and electrical properties of $AgInSe_2$ and CdSe are otherwise very similar, this observation is clearly at odds with the usual explanation that the temperature dependence of the energy gap in a semiconductor is dominated by self-energies associated with phonon scattering.

II. CRYSTAL GROWTH

$CuInSe_2$ and $AgInSe_2$ crystallize in the chalcopyrite structure (symmetry $I\bar{4}2d = D_{2d}^{12}$), which is an ordered superstructure of zinc blende. Starting materials were spectrographically 99.999% pure. Melts were prepared by slowly heating stoichiometric amounts to temperatures of 1050 °C for $CuInSe_2$ and 950 °C for $AgInSe_2$ in silica boats contained in evacuated and sealed silica ampoules. The temperature of the furnace was then lowered at a rate of about 2 °C/h. Crystallization of $CuInSe_2$ occurred at ~ 980 °C and $AgInSe_2$ at ~ 780 °C. Nucleation occurred at the end of the boat and crystals were obtained by directional freezing. Generally the silica boats were broken due to the thermal contraction of $AgInSe_2$ and $CuInSe_2$. The lattice constants were determined to be $a = 6.09$ Å, $c = 11.71$ Å for $AgInSe_2$, and $a = 5.78$ Å, $c = 11.62$ Å for $CuInSe_2$. Note that $CuInSe_2$ has a built-in elongation $[(c/2a > 1)]$ in contrast to most other chalcopyrite crystals which have built-in compressive distortions $[(c/2a < 1)]$. As previously reported,[5] the conductivity of $CuInSe_2$ can be either n or p type depending upon annealing conditions, whereas only n-type conductivity has been observed in $AgInSe_2$. Most of the results reported for $AgInSe_2$ were obtained from samples doped with P during growth. Nominally undoped $AgInSe_2$ typically has resistivity of less than 0.1 Ω cm. Phosphorous acts as an acceptor in $AgInSe_2$, and can result in samples with room-temperature resistivity of several hundred Ω cm.

III. EXPERIMENTAL TECHNIQUES

Room-temperature-electrolyte electroreflectance[6] measurements were performed on $AgInSe_2$ using 1-molar KCl in water. Such measurements were not possible in $CuInSe_2$ since the band gap lies at longer wavelengths than the infrared cutoff of water. Low-temperature electroreflectance measurements on $AgInSe_2$ and $CuInSe_2$ employed a metal-insulator-semiconductor (MIS) structure consisting of successive evaporations of $CuGaS_2$ (insulator) and Au layers each ~ 100 Å thick. Soldered indium contacts were Ohmic for both $CuInSe_2$ and $AgInSe_2$ and were also used to contact the Au. $CuGaS_2$ was chosen as an insulator since it is easy to evaporate at relatively low temperatures. The absorption of the $CuGaS_2$ film becomes appreciable at wavelengths shorter than ~ 3500 Å. The MIS packages were too leaky at room temperature to permit electroreflectance measurements. Some data were also obtained at 77 °K using a Au Schottky barrier on $AgInSe_2$. All samples for electroreflectance measurements were Syton[7] polished to remove surface damage.

The optical apparatus for electroreflectance measurements consisted of a $\frac{1}{2}$-m-focal-length Bausch and Lomb monochromator chosen for its large numerical aperture (f4.4). For measurements at wavelengths longer than ~ 0.5 μ, a Sylvania 150-W, 24-V dc tungsten halogen lamp No. FCS was used. In this region, an EGG SGD-444 silicon photodetector was used with a 1-MΩ load resistor. A Bausch and Lomb xenon light source and an EMI 9558 photomultiplier were used at wavelengths shorter than ~ 0.5 μ. Al + MgF coated plane and spherical mirrors were used throughout. HR, HN 32, and HNPB polaroids were used to polarize the incident light.

Low-temperature electroreflectance and photoluminescence experiments used Janis stainless-steel Dewars. For variable-temperature measurements, a "Supervaritemp" Dewar was used permitting measurements between 2 and 300 °K. The temperature was measured with a calibrated platinum resistor and a GaAs diode. The excitation source for the photoluminescence experiments was either a 50-mW He-Cd laser at 4416 Å or a 50-mW He-Ne laser at 6328 Å. The photoluminescence was dispersed by a $\frac{3}{4}$-m spectrometer and detected by a cooled S-1 photomultiplier ($AgInSe_2$) or a cooled PbS detector ($CuInSe_2$).

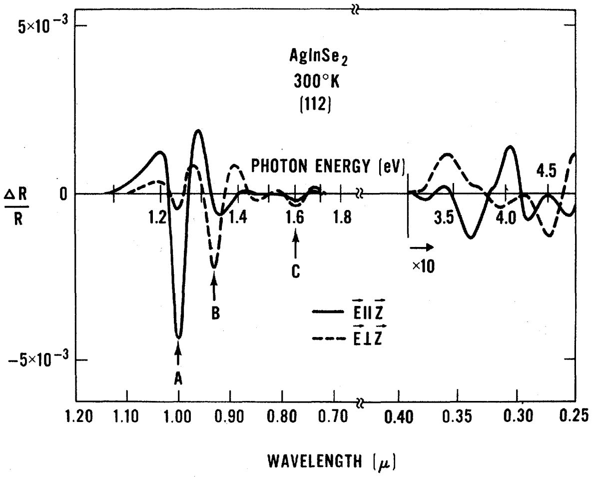

FIG. 1. Room-temperature-electrolyte electroreflectance spectrum of $AgInSe_2$.

IV. EXPERIMENTAL RESULTS

A. $AgInSe_2$

In Fig. 1, we show the room-temperature-electrolyte electroreflectance spectrum of $AgInSe_2$. On account of the (112) orientation, $\vec{E} \parallel \vec{z}$ is only nominal, and at most $\frac{2}{3}$ of the intensity is along the $\vec{z}$ axis (the optic axis). By analogy with earlier studies[1,8] of II-IV-V_2 and I-III-VI_2 compounds, we attribute the A, B, and C structures in Fig. 1 to transitions to a single conduction band from three closely spaced valence bands derived from the *p*-like Γ_{15} level in zinc-blende compounds. The lowest-energy gap in $AgInSe_2$ is ~0.5 eV lower than the energy gap[6] of CdSe, its binary analog. Precise values for the energy gaps determined from the data in Fig. 1, using the theory of Aspnes and Rowe,[9] are listed in Table I. The value of lowest direct energy gap at room temperature (1.238 eV) is close to the value (1.22 eV) found by Lerner[10] in earlier optical measurements. The crystal-field and spin-orbit parameters deduced from these valence-band splittings, in a manner previously described,[11] are listed in Table I. The crystal-field splitting parameter is large and negative due to the large compressive distortion of the $AgInSe_2$ lattice $[2-(c/a)=0.084]$. The spin-orbit parameter is considerably less than that observed[6] in CdSe (0.42), a feature we shall discuss in more detail in Sec. V.

As shown in Fig. 1, no electroreflectance structure is observed between 1.7 and 3.3 eV. At energies above 3.3 eV, several poorly resolved structures are observed. These may correspond to the E_1 transitions observed in this energy region for CdSe.[6]

At 77 °K, the electroreflectance spectrum of $AgInSe_2$ is considerably sharper, as shown in Fig. 2. The values of the energy gap deduced from these data are listed in Table I, together with the valence-band parameters derived from the data. We notice that the lowest-energy gap is independent of temperature within experimental error. The consequences of this anomalous behavior will be discussed in Sec. V.

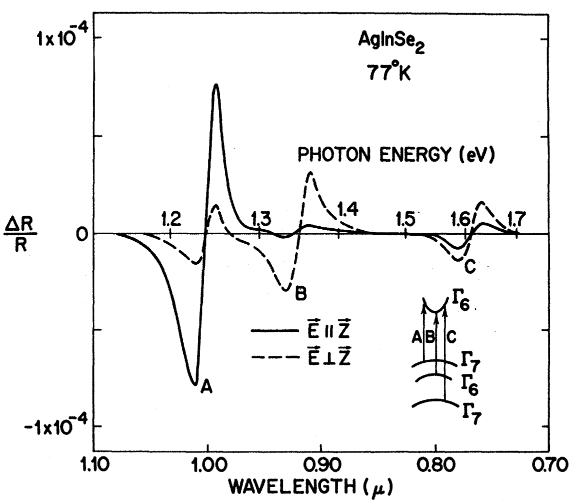

FIG. 2. Electroreflectance spectrum of $AgInSe_2$ measured at 77 °K using an Au Schottky barrier.

The photoluminescence and reflectivity spectra of $AgInSe_2$ at 2 °K are shown in Fig. 3. The weak anomaly which is observed in reflectivity at 1.245 eV is attributed to the lowest-energy exciton. The photoluminescence spectrum consists of a few lines near 1.240 eV and a broad band near 1.19 eV. The shoulder near 1.245 eV is believed to result from decay of the free exciton, whereas the other lines and the band at 1.19 eV are attributed

TABLE I. Valence-band structure.

Crystal	T (°K)	Energy gaps (± 0.005 eV) A	B	C	Valence-band parameters (eV) Δ_{cf}	Δ_{so}
$AgInSe_2$	77	1.237	1.345	1.608	−0.143	0.298
	300	1.238	1.328	1.595	−0.121	0.298
$CuInSe_2$	77	1.038	1.042	1.273	+0.006	0.233

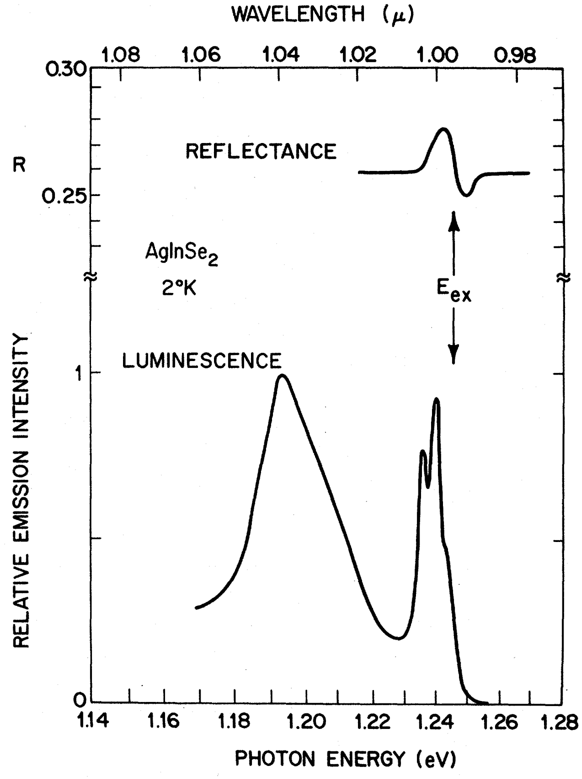

FIG. 3. Reflectance and photoluminescence of $AgInSe_2$ near the lowest direct energy gap.

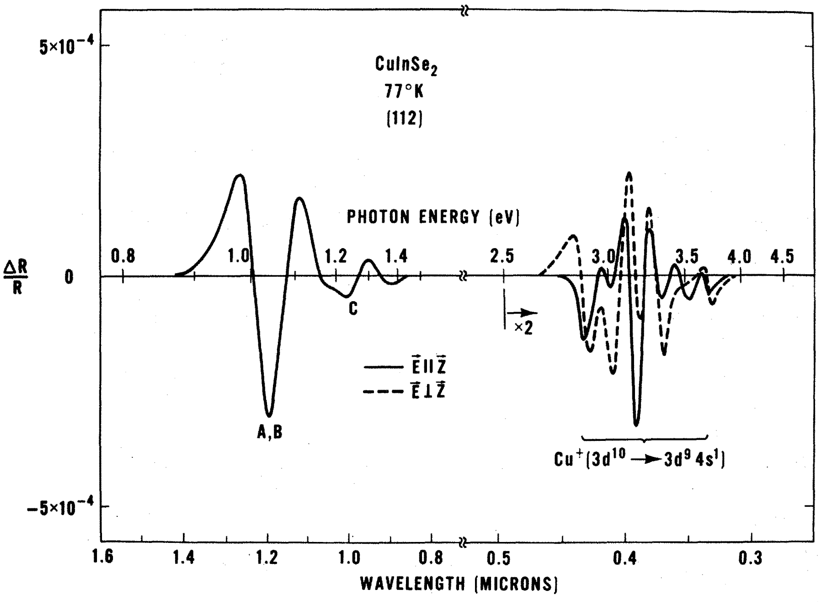

FIG. 4. Electroreflectance spectrum of CuInSe$_2$ measured at 77 °K using a metal-insulator-semiconductor package.

to impurities. The observation of luminescence near the energy of the lowest direct energy gap indicates that there are no lower-lying indirect energy gaps.

B. CuInSe$_2$

The electroreflectance spectrum of CuInSe$_2$ measured at 77 °K is shown in Fig. 4. Since the built-in compressive distortion of this compound is small (actually slightly elongated), the crystal-field parameter should be small and the electroreflectance spectrum should be polarization independent. As expected, two polarization-independent structures are observed in Fig. 4 and are labeled A, B, and C, respectively. Using the theory of Aspnes and Rowe,[9] the energy gap of CuInSe$_2$ deduced from the data in Fig. 4 is 1.013 eV at 77 °K, which is ~1.3 eV less than the energy gap in the binary analog Zn$_{0.5}$Cd$_{0.5}$Se. Due to the lack of any polarization dependence to these structures, the splitting of 0.23 eV is attributed to the spin-orbit parameter. This splitting is much less than the corresponding spin-orbit splitting[6] of CdSe (0.42) or ZnSe (0.43), which comprise the binary analog.

Despite the nearly cubic lattice constants of CuInSe$_2$ and the polarization independence of the A, B, and C structures, we observe a strongly polarization-dependent spectrum in the 3- to 4-eV region. As discussed elsewhere,[2] this structure may result from transitions to the lowest conduction-band minimum from valence-band states derived from Cu 3*d* levels. It is difficult to exclude the possibility that this spectrum is derived from the E_1 transitions in II-VI compounds. However, the superficial features of this structure in CuInSe$_2$ are quite different from those of the ultraviolet structure observed in II-IV-V$_2$ crystals which are related to E_1 transitions in III-V compounds.[12]

In another sample, the A, B, and C structures were considerably sharper than shown in Fig. 4. As can be seen in Figs. 5 and 6, the C structure is well separated from the A, B doublet and, in addition, the splitting of the A, B doublet is resolved. From these data we determine a spin-orbit parameter of 0.233 eV. Note that the structure

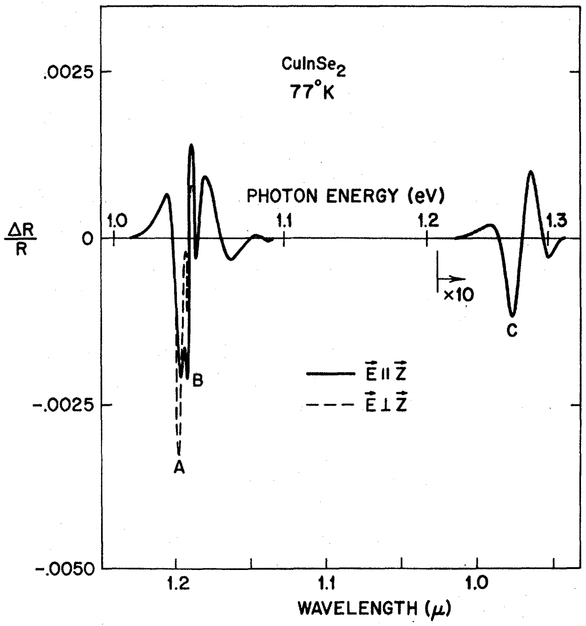

FIG. 5. Electroreflectance spectrum at 77 °K for a selected sample of CuInSe$_2$, for which the A, B, and C peaks are well resolved.

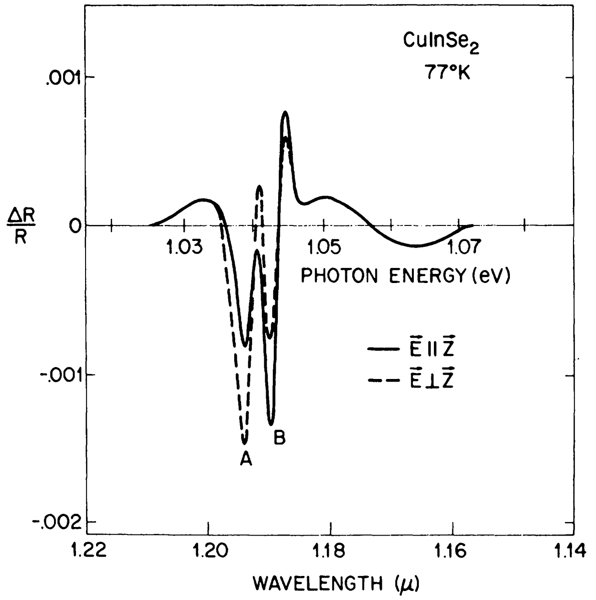

FIG. 6. High-resolution electroreflectance spectrum near the A and B structures in $CuInSe_2$.

at the lowest-energy gap (A in Figs. 5 and 6) is predominantly polarized $\vec{E} \perp \vec{z}$. This behavior has never before been observed in a chalcopyrite compound, but is the expected result for a crystal with a built-in dilation $[(c/2a) > 1]$ rather than a compression as is the usual situation. The measured splitting of the A and B peaks is 3.8 meV which indicates a crystal-field parameter of 6 meV.[13]

In Fig. 7, we show the photoluminescence spectra of $CuInSe_2$ measured at 2 and 77 °K for energies near 1 eV. The observation of photoluminescence at the energy of the lowest direct energy gap determined from electroreflectance measurements indicates that there are no lower-lying indirect energy gaps. Hence, both $AgInSe_2$ and $CuInSe_2$ have direct energy gaps as do all other I-III-VI_2 compounds we have studied.

V. DISCUSSION

A. *p-d* Hybridization

As mentioned in Sec. IV, the valence-band spin-orbit parameters observed in $AgInSe_2$ (0.298) and $CuInSe_2$ (0.233) are considerably less than those observed[6] in ZnSe (0.43) and CdSe (0.42) which comprise the binary analogs. We have shown elsewhere[1,2] that this behavior is observed in other I-III-VI_2 compounds containing Cu or Ag, and we have suggested that it results from a hybridization of Cu and Ag *d* levels with the *p* levels on the other atoms. The hybridization reduces the experimental values for Δ_{so} below the values observed in the binary analogs since the negative Δ_{so} characteristic of *d* levels tends to cancel the positive Δ_{so} of *p* levels. Using the simple approximation to the hybridization given in Ref. 1, we find that the spin-orbit parameters observed in $CuInSe_2$ and $AgInSe_2$ indicate *d*-like characters of 34% and 17%, respectively, for the uppermost valence bands. These hybridizations are qualitatively consistent with the larger downshift of the energy gap for $CuInSe_2$ as compared with $AgInSe_2$.

From the valence-band parameters derived from the splittings of the A, B, and C electroreflectance structures, the polarization ratios of these structures can be predicted by a single quasicubic model.[11] Using the values summarized in Table I, the quasicubic model predicts a polarization ratio $I_{\parallel}/I_{\perp} \sim 9$ for the A peak of $AgInSe_2$ at 77 °K. For comparison, the experimental value deduced from the data in Fig. 2 is ~ 5. This discrepancy probably results from a breakdown of the quasicubic model due to the admixture of *d*-like wave functions into the uppermost valence bands. On the other hand, the quasicubic model gave good agreement with experiment for the polarization dependence of the A peak in $AgGaSe_2$ which also has ~16% hybridization of Ag 4*d* levels into the uppermost valence bands.[14]

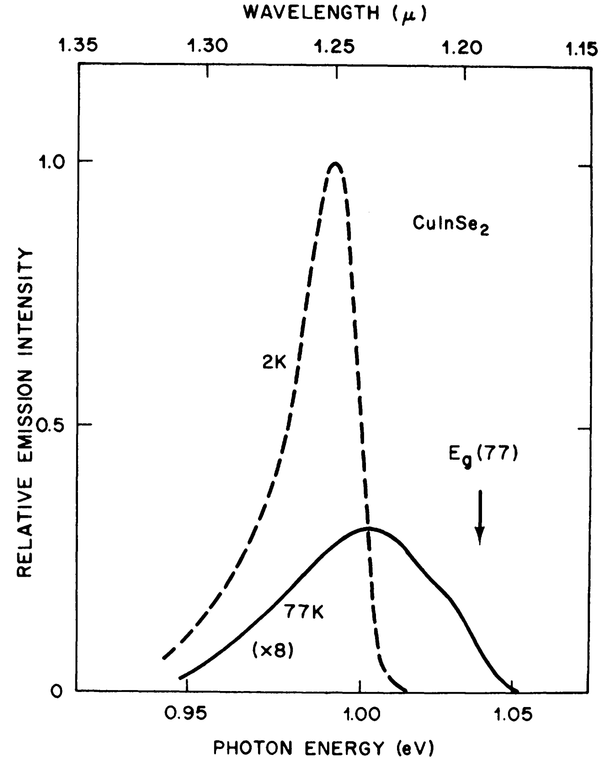

FIG. 7. Photoluminescence spectra of $CuInSe_2$ at 2 and 77 °K. The arrow indicates the value of the lowest direct energy gap located in electroreflectance measurements at 77 °K.

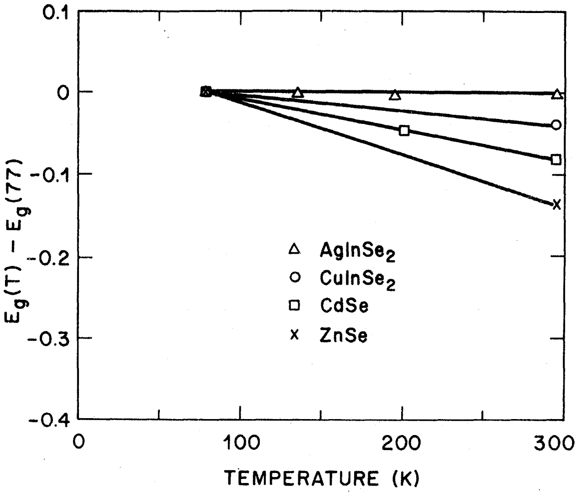

FIG. 8. Temperature dependences of the energy gaps for AgInSe$_2$, CuInSe$_2$, ZnSe, and CdSe. Data for the binary compounds are taken from Refs. 4 and 6. The room-temperature band gap in CuInSe$_2$ was estimated from the shift of the absorption edge between 77 and 300 °K. The data for AgInSe$_2$ were obtained by measuring the spectrum of the sample in Fig. 2 as a function of temperature.

B. Comparison with Theory

A recent energy-band calculation[3] has predicted that CuInSe$_2$ has an indirect energy gap ~ 0.3 eV below the lowest direct energy gap. In Sec. IV B, we showed that our observation of photoluminescence at the energy of the lowest direct energy gap indicates that there are no lower-lying indirect energy gaps. Other predictions of the calculation are also in disagreement with experiment. The theoretical Δ_{so} of 0.48 eV is to be compared with our observed value of 0.23 eV, and the theoretical Δ_{cf} of 0.04 eV is to be compared with our observed value of 0.006 eV. From this comparison we conclude that the proximity of Cu *d* levels profoundly influences the energy-band structure of CuInSe$_2$ and must be included in any realistic energy-band calculation.

C. Energy-Gap Temperature Dependence

In Fig. 8 we show the temperature dependences of the energy gaps of the chalcopyrite compound CuInSe$_2$ and AgInSe$_2$, as well as those of CdSe and ZnSe, which comprise the binary analogs. It is apparent that the temperature dependences for the ternaries are anomalously low, especially for AgInSe$_2$, for which no variation is observed within experimental error (± 5 meV). This effect cannot be explained by a decrease with temperature of the crystal-field splitting, since it is apparent from Table I that Δ_{cf} decreases only by 22 meV between 77 and 300 °K, which would tend to increase the energy gap by only ~ 14 meV.

Theoretical calculations[15] of the temperature dependence of the energy gap in GaAs have shown that ~ 10% of the observed variation results from the lattice dilation with increasing temperature and ~ 90% results from electronic effects. Hence, the observation in AgInSe$_2$ could be explained by a lattice *contraction* with increasing temperature at a rate ~ 10 times larger than the dilation observed in GaAs. Although the temperature dependence of the lattice constants of AgInSe$_2$ has not been measured, it is considered extremely unlikely that such a peculiar dependence would occur.

The energy gap of CdSe, the binary analog of AgInSe$_2$, decreases by approximately 80 meV as the temperature increases from 77 to 300 °K, yet we find no variation of the energy gap in AgInSe$_2$. Since the physical and electrical properties of AgInSe$_2$ and CdSe are very similar, this observation is clearly at odds with the usual explanation[16] that the temperature dependence of the energy gap in a semiconductor is dominated by self-energies associated with phonon scattering.

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