Pressure dependence of the energy gap in some I-III-VI$_2$ compound semiconductors

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The shifts in the absorption edge with hydrostatic pressure have been measured for four ternary semiconductors. In all cases the energy gap increases with pressure. From the data the pressure dependence of the energy gap (dE_g/dP) was determined as 2.2 meV/kbar for AgGaS$_2$, 3.4 meV/kbar for CuGaS$_2$, 5.3 meV/kbar for AgGaSe$_2$, and 2.7 meV/kbar for AgInSe$_2$. These shifts are compared with the corresponding II-VI compounds and discussed. Some optical effects associated with the pressure-induced phase transitions in some of the I-III-VI$_2$ compounds and II-VI compounds are described and discussed.

INTRODUCTION

Ternary semiconducting compounds of the type I-III-VI$_2$ crystallize in the chalcopyrite structure[1] in which the bonding is tetrahedral, and hence they resemble the II-VI compounds in many respects. They appear to be promising candidates for many technological applications and therefore have been receiving much attention in recent years. Already an impressive body of knowledge has been accumulated on them.[2] They have been prepared in sufficient purity and in single-crystal form for determining transport and optical properties. In many cases electroreflectance, reflectivity,[3-5] and resistivity measurements[6,7] have been made and reliable values for the energy gap and mobility of carriers have been obtained. General features of their energy-band structure are also evolving.[8] It appeared to us worthwhile to study their behavior under pressure, particularly with regard to the change in their energy-band structure with hydrostatic pressure. Accordingly in the present study we have measured for the first time the pressure-induced shifts of the absorption edges in AgGaS$_2$, AgInSe$_2$, AgGaSe$_2$, and CuGaS$_2$ and from these data have evaluated the pressure dependence of the energy gaps. From the shift of the energy gap with pressure it is possible to estimate the $p-d$ hybridization contributions, by comparison with the shifts observed in the isoelectronic II-VI compounds. Further, the dE_g/dP data enable one to calculate the deformation potential for the valence–conduction band separation.

We have also made some qualitative observations on the changes in the light transmission characteristics, in some of the above materials and other related materials as a function of pressure, in a diamond anvil high-pressure apparatus. Evidence for a first-order structural transition has been obtained.

EXPERIMENTS AND RESULTS

Pressure was generated using a Harwood Intensifier with Plexol 262 as the pressure medium. The absorption measurements were carried out in a high-pressure cell provided with sapphire windows in conjunction with a Spex spectrometer (model No. 1500) over the wavelength range 1.1 –0.3 μm. The wavelength drive was electronically controlled to ensure accurate repetitive wavelength scanning, because of the small shifts observed under pressure. Polished single-crystal plates of the samples, about $\frac{1}{2}$ mm in thickness were used for the study. In Table I pertinent data on the materials are collected. Figure 1 shows the absorption coefficient as a function of wavelength in the case of AgGaSe$_2$ at different pressures up to a maximum of 7 kbar, the limit of the present study. The pressure-induced change in the energy gap was evaluated from the shift in the absorption edge, for AgInSe$_2$, AgGaSe$_2$, CuGaS$_2$, and AgGaS$_2$. These are plotted in Fig. 2. The values of the absorption edge reported here were typically analyzed at an optical density of about 1.0 for crystal thicknesses $\sim\frac{1}{2}$ mm. In all the materials the energy gap between the valence and the conduction bands increases with hydrostatic pressure.

DISCUSSION

In Table I the pressure coefficients of the absorption edge for a number of II-VI compounds are given for comparison. Among the ternaries studied, AgInSe$_2$ is isoelectronic with CdSe, and CuGaS$_2$ with ZnS. AgGaSe$_2$ and AgGaS$_2$ may be regarded as the corresponding (ZnCd) mixed selenide and sulfide. Comparing the pressure-induced shifts in II-VI compounds[9,10] with the corresponding ternaries, the II-VI compounds exhibit a larger

TABLE I. Electronic-band-structure parameters of interest for some II-VI compounds and the four I-III-VI$_2$ ternary semiconductors studied in the present investigations.

Substance	Color and Transparency	Energy gap (eV) at room temp. (300 °K)	dE_g/dP (meV/kbar)
AgInSe$_2$	black	1.24	+2.7
(CdSe)			(+3.7)
AgGaSe$_2$	black	1.80	+5.3
AgGaS$_2$	transparent light yellow	2.70	+2.2
CuGaS$_2$	transparent light red	2.50	+3.4
(ZnS)			(+5.7)
CdSe(wtz) [a,b]	black	1.63	+3.7
CdS(wtz) [b]	yellow	2.49(wtz) 1.7 (Znbl) [c]	+3.3
ZnTe(Znbl)		2.26	6.0
ZnSe(Znbl) [d]		2.57	+6.0
ZnS(Znbl) [d]	transparent colorless	3.54	+5.7
ZnO(wtz) [d]	transparent colorless	3.14	6.0

[a] wtz: wurtzite type.   [b] Reference 10.   [c] Znbl: zinc-blende type.   [d] Reference 9.

blue-shift.

All the materials studied have direct band gaps.[2] The uppermost valence bands are derived from a combination of the p orbitals of the anion with the noble-metal d orbitals, while the conduction band is derived from the s states of the cations. The tetrahedral crystal field splits the fivefold degenerate noble-metal d level into a threefold Γ_{15} and a twofold Γ_{12}, and these undergo further splitting due to spin-orbit interaction. The latter interaction also splits the p-like Γ_{15} valence-band state. It has been postulated that the p-like and d-like Γ_{15} states interact strongly in these materials and that this interaction raises the top of the valence band, leading to a reduction in the band gap. This effect known as p-d hybridization[11] is believed to be responsible for the smaller band gaps observed in the ternary compounds relative to their II-VI analogs[12,13] (see Table I). Apparently in II-VI compounds such an effect is absent or negligible. If this picture is valid, it would be natural to expect that pressure would promote a stronger overlap between the two Γ_{15} states involved, because of the reduced lattice constants,
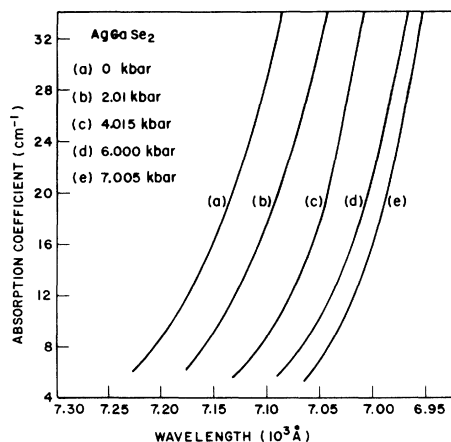

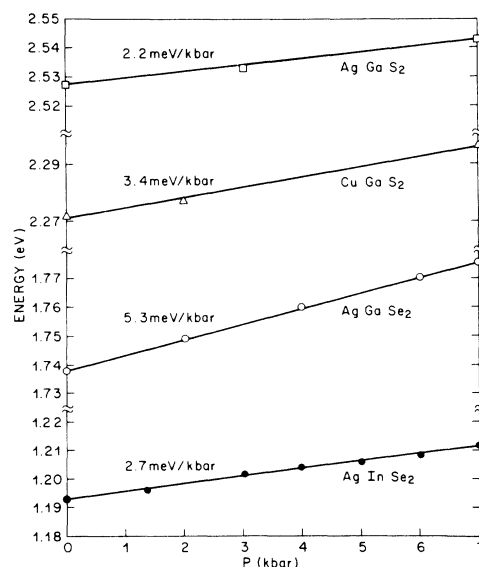FIG. 1. Shifts in the absorption edge with hydrostatic pressure for AgGaSe$_2$.

FIG. 2. Energy-gap change with hydrostatic pressure for four ternary I-III-VI$_2$ compounds.

and cause a reduction in the energy gap with pressure. However, experimentally the opposite behavior is observed in all these materials; the gaps increase with pressure. This leads to the conclusion that the bottom of the conduction band in the ternary semiconductors must be rising in energy with pressure, at least as rapidly as in the II-VI analogs, but the effect is partially compensated by the opposite effect expected from the increase in p-d hybridization. This probably is one reason why the pressure-induced energy gap shifts in II-VI compounds are larger.[9,10] However, there may be other causes contributing to the effect, but our present data do not allow any further quantitative evaluation.

OPTICAL OBSERVATIONS OF PHASE TRANSITIONS

We have studied $AgGaS_2$ and $CuGaS_2$ in the diamond anvil apparatus, since both materials exhibit transparency in the visible region and hence are amenable for making visual observation to very high pressures (up to 300 kbar). Single crystals of $AgGaS_2$ exhibit a light yellow color by transmission while crystals of $CuGaS_2$ have an orange color. When compressed in the diamond anvil apparatus and observed through a microscope, powdered $AgGaS_2$ at first appears opaque, but becomes gradually transparent, showing orange transmission. Near about 200-kbar pressure, a dark spot begins to appear in the center and the spot spreads with further increase in pressure. On slowly releasing pressure, the black region recedes and disappears. On examination after the pressure cycling, the compressed portion of the material appears deep orange and thus seems to have undergone an irreversible change in color. Likewise, $CuGaS_2$ powder which is initially opaque and brownish yellow exhibits a deep red transmission on compression, and a black spot develops in the center of the anvil at about 150-kbar pressure. As pressure is released the dark spot disappears. After pressure cycling, the compressed material is black and seems to have undergone a change in color. X-ray powder patterns taken immediately after the pressure treatment show that the Debye-Scherrer lines have become quite broad in both cases.

Irreversible shifts in the optical absorption edges after pressure cycling have been reported in many II-VI compounds,[9,10] viz., CdS, CdSe, ZnO, ZnTe. It has been shown by *in situ* high-pressure x-ray diffraction studies that in all these cases a transformation to the NaCl-type structure occurs at high pressure.[14-18] The large and abrupt red shifts[9,10] observed in the optical absorption studies of these materials are believed to be associated with the above transformation. On re-

leasing pressure the NaCl structure may be expected to revert to the zinc-blende type structure in the examples, viz., CdS, CdSe, ZnO, when the starting materials were originally in the wurtzite structure. The observed irreversible shifts would then correspond to this altered circumstance. Edwards and Drickamer[10] and Edwards *et al.*[9] have suggested that the irreversible shifts that they observed in their studies of the II-VI compounds may be due to metastable retention of the zinc-blende phase.

The reversible darkening observed in the ternary semiconductors $AgGaS_2$ and $CuGaS_2$ at high pressure may also be due to a transition to a ternary analog of the NaCl structure, and the color change in the material after pressure cycling may, in some way, be connected with the reversion of the NaCl-like phase to the zinc-blende structure, or to a heavily strained and partially disordered chalcopyrite phase. In the NaCl phase of I-III-VI_2 compounds, the cations should be completely disordered in the fcc lattice and on reversion to the low-pressure phase at ambient temperature, the material would have a strong tendency to stay in the disordered state. Hence reversion to the zinc-blende phase, or to a partially disordered, highly strained chalcopyrite phase may be expected. However, a positive identification of the dark high-pressure phase must be based on *in situ* high-pressure x-ray diffraction studies. Such a study on $AgInSe_2$,[19] and quenching studies,[20] have shown that the latter substance transforms to the NaCl-type structure above 25 kbar. It is for this reason we expect I-III-VI_2 compounds in general to transform to the NaCl-type structure at very high pressure.

We have also studied $CuAlS_2$ and ZnO in the diamond anvil apparatus. These crystals are colorless by transmission. On increasing pressure an opaque spot appears at about 150 kbar and spreads with further increase in pressure. On release of pressure the opaque spot clears up in both cases. Without x-ray diffraction data at high pressure, it is not possible to conclude with certainty whether the observed changes are due to a transition to the zinc-blende structure or to the NaCl-type structure. Further studies are in progress and will be discussed elsewhere.

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