p-d hybridization of the valence bands of $Ag_xCu_{1-x}GaSe_2$ compounds

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Abstract. Polycrystalline compounds of Ag$_x$Cu$_{1-x}$GaSe$_2$ were grown by the Bridgman method. x was varied from 1.0 to 0.0 at intervals of 0.2. The optical absorption spectra of these six samples were measured using a photoacoustic spectrometer. From these spectra we determined the A, B and C transition energies of Ag$_x$Cu$_{1-x}$GaSe$_2$ as functions of the silver concentration x. The transition energies E_A and E_C relative to transition energy E_B were used to obtain both the spin–orbit splitting of the valence bands in a cubic field and the crystal-field splitting of the valence bands in the absence of spin–orbit interaction as functions of x. Furthermore, we estimated the fractional p-like character of the uppermost valence bands for various x, under the assumption that the d levels of Ag and Cu contribute to the spin–orbit splitting according to x.

1. Introduction

Considerable interest has been shown in the chalcopyrite compounds and their alloys because of their possible technological application in the areas of solar energy conversion, light-emitting diodes and non-linear optical materials, etc [1–3]. There are two major groups in the chalcopyrite compounds. One group consists of II–IV–V$_2$ compounds, which are the analogues of III–V zincblende binary compounds. The other group consists of I–III–VI$_2$ compounds, which are the analogues of II–VI zincblende binary compounds.

Hopfield [4] developed the quasi-cubic model to explain the properties of the wurtzite compounds. This quasi-cubic model regards the crystal-field splitting in the wurtzite compounds as equivalent to the splitting produced by a uniaxial trigonal stress applied to the zincblende compounds. The strain Hamiltonian [5, 6] is formally the same for both the trigonal distortion appropriate to the wurtzite compounds and the tetragonal distortion appropriate to the chalcopyrite compounds. This was first pointed out by Rowe and Shay [7], and they thus extended the quasi-cubic model to the chalcopyrite compounds.
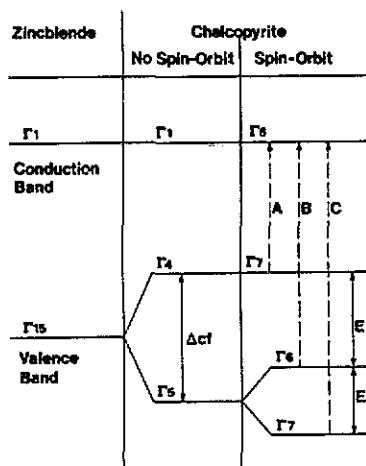
Figure 1. The band structure of chalcopyrite compounds derived from zincblende compounds having a $\Gamma_{15} \rightarrow \Gamma_1$ energy gap.
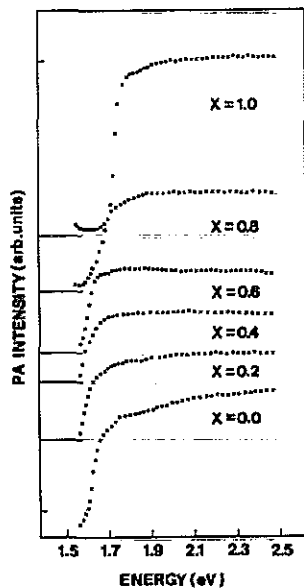

Figure 2. The photoacoustic spectra for $Ag_xCu_{1-x}GaSe_2$ normalized against a carbon-black standard.

Within this extended model, the triple degeneracy of the Γ_{15} level in the zincblende compounds is removed owing to the action of the tetragonal crystal field giving a non-degenerate Γ_4 level, which lies above the doubly degenerate Γ_5 level as shown in figure 1. If we consider the spin–orbit interaction, the Γ_5 level splits into two levels, Γ_6 and Γ_7, and the non-degenerate levels Γ_1 and Γ_4 are transformed into the levels Γ_6 and Γ_7, respectively. Three absorption structures are thus expected to occur in the chalcopyrite compounds originating from the transitions between the conduction band Γ_6 and the split valence bands Γ_7, Γ_6 and Γ_7. The crystal field and spin–orbit parameters of these compounds can be estimated from the experimental observation of these three transitions.

This theory can be satisfactorily applied to the II–IV–V$_2$ chalcopyrite compounds. In the case of the I–III–VI$_2$ chalcopyrite compounds, the observed energy gaps are substantially smaller than those of the respective binary analogues. The observed spin–orbit parameters are also smaller than either the theoretical values or the splittings observed in the binary analogues. It has been pointed out [8] that both of these anomalies result from a hybridization of the p-like valence bands with noble metal d levels a few electronvolts below. The chalcopyrite compounds containing Cu atoms show a stronger p–d hybridization effect than those containing Ag atoms. This means [9] that the larger hybridization implies that the d bands are not far below the p levels.

In this study we investigate the optical absorption spectra of $Ag_xCu_{1-x}GaSe_2$ quaternary chalcopyrite compounds in order to obtain the three transitions from the split valence bands to the conduction band. From these three transitions we calculate the crystal-field and spin–orbit parameters within the extended quasi-cubic model mentioned earlier. We also estimate the amount of p–d hybridization and wish to explore the consistency of $Ag_xCu_{1-x}GaSe_2$ compounds for various silver concentrations x in the p–d hybridization as well as in the crystal-field parameter.
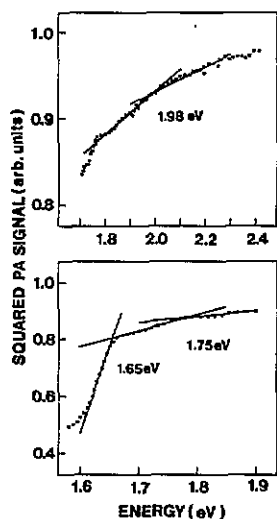
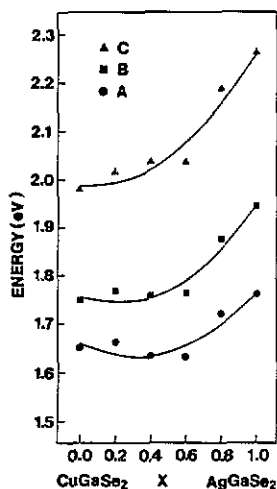**Figure 3.** Typical plots of the square of the signal intensity as a function of photon energy for $CuGaSe_2$.

Figure 4. The A, B and C transition energies of $Ag_xCu_{1-x}GaSe_2$: ●, E_A; ■, E_B; ▲, E_C; ——, best-fitted curve with a quadratic equation of x.

2. Experimental details

$Ag_xCu_{1-x}GaSe_2$ compounds were grown by the Bridgman method with values between $x = 1.0$ and $x = 0.0$ at intervals of 0.2. The stoichiometric mixture of the elements Ag, Cu, Ga and Se at a given x was sealed in a quartz ampoule evacuated to a pressure of about 10^{-4} Torr. Such ampoules were heated to about 1100 °C at a rate of about 15 °C h^{-1}, held for 75–95 h and cooled to the annealing temperature of about 600 °C at a rate of about 6 °C h^{-1}. After annealing for 2–3 d, they were cooled to room temperature over 1 d. The materials grown as mentioned above were polycrystalline compounds.

The lattice parameters of these six compounds were determined from the x-ray powder diffraction pattern, and the optical absorption spectra of the $Ag_xCu_{1-x}GaSe_2$ compounds in powder form were measured by photoacoustic techniques at room temperature. The photoacoustic signal amplitudes were measured as a function of wavelength using an EDT Research model OAS 400 photoacoustic spectrometer. These spectra were normalized against that of a carbon-black standard, and they are shown in figure 2.

3. Results and discussion

Typical examples of the square of the signal intensity as a function of incident photon energy are plotted in figure 3 in order to illustrate how various transition energies were measured. The A, B and C transition energies in figure 1 were determined by the positions of either the knee in the squared spectra or the crossing point of the best-fitted lines if the knee shape is less apparent. The measured values of the A, B and C transition

Table 1. Room-temperature valence band parameters of $Ag_xCu_{1-x}GaSe_2$ compounds.

	Energy gaps (eV)			$-\Delta_{cf}$ (eV)	Δ_{so} (eV)
x	E_A	E_B	E_C		
0.0	1.65	1.75	1.98	0.13	0.26
0.2	1.66	1.77	2.02	0.14	0.28
0.4	1.63	1.76	2.04	0.17	0.32
0.6	1.63	1.76	2.04	0.17	0.32
0.8	1.72	1.88	2.19	0.21	0.36
1.0	1.76	1.94	2.26	0.23	0.37

energies in this manner are listed in table 1 and plotted in figure 4. As a function of x each transition energy shows downward bowing, and the quadratic functions which best fit the data are found to be

$$E_A = 1.66 - 0.18x + 0.28x^2 \tag{1}$$

$$E_B = 1.76 - 0.14x + 0.32x^2 \tag{2}$$

and

$$E_C = 1.99 - 0.026x + 0.30x^2. \tag{3}$$

In the quasi-cubic model developed by Hopfield [4] and extended by Rowe and Shay [7], the crystal field splitting Δ_{cf} and the spin–orbit splitting Δ_{so} can be determined using the splittings observed between the three uppermost levels of the valence band. If E_1 and E_2 are the energies of the Γ_7 levels relative to the Γ_6 level as shown in figure 1, then

$$E_{1,2} = -\tfrac{1}{2}(\Delta_{cf} + \Delta_{so}) \pm \tfrac{1}{2}[(\Delta_{cf} + \Delta_{so})^2 - \tfrac{8}{3}\Delta_{cf}\Delta_{so}]^{1/2} \tag{4}$$

which determines Δ_{cf} and Δ_{so}. The results are also included in table 1.

The crystal-field and spin–orbit splittings, which are plotted in figure 5 as functions of x, show linear relations with x.

$$-\Delta_{cf} = 0.12 + 0.10x \tag{5}$$

and

$$\Delta_{so} = 0.26 + 0.11x. \tag{6}$$

This means that the behaviour of the negative value of the crystal-field effect is very similar to that of the spin–orbit effect in the $Ag_xCu_{1-x}GaSe_2$ compounds.

As the compressive lattice distortion $2 - c/a$ increases with increasing Ag content as shown in figure 6, the non-cubic crystal-field parameter Δ_{cf} is also expected to become more negative. In figure 7 the observed crystal-field parameters for $Ag_xCu_{1-x}GaSe_2$ compounds are shown as a function of their respective built-in lattice compressions. The data can be fitted by

$$\Delta_{cf} = \tfrac{3}{2}b(2 - c/a) - 0.11 \tag{7}$$

with $b = -0.42$. This value is smaller by a factor of about 2 than $b \simeq -1.0$ for the group of I–III–VI$_2$ chalcopyrite compounds [1]. The constant -0.11 is larger by a factor of about 2 than the value of -0.05 estimated from AgGaSe$_2$ and CuGaSe$_2$ [1]. Nevertheless, the
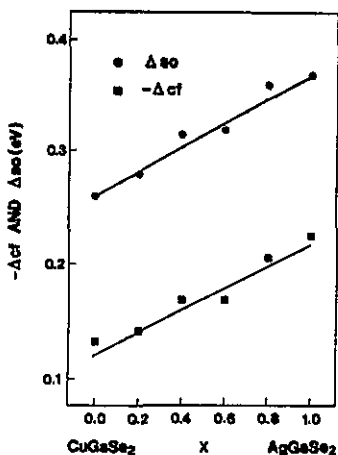
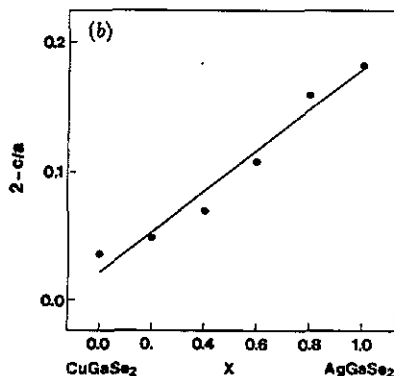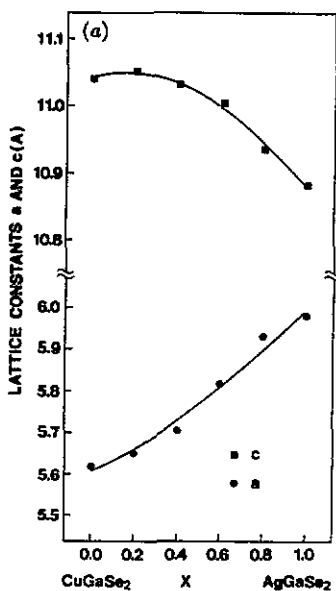**Figure 5.** The crystal-field and spin-orbit parameters for $Ag_xCu_{1-x}GaSe_2$: ●, Δ_{so}; ■, $-\Delta_{cf}$.

Figure 6. (*a*) The lattice parameters of $Ag_xCu_{1-x}GaSe_2$ as a function of x: ●, a; ■, c. (*b*) The lattice distortion $2 - c/a$ as a function of x.

$Ag_xCu_{1-x}GaSe_2$ compounds show a linear relationship for their crystal-field splittings to the lattice distortion parameters within the quasi-cubic model.

The hybridization of the d orbitals of the cations Ag and Cu with the p orbitals of the anion Se will reduce the spin-orbit splitting of the uppermost valence bands since the negative Δ_{so} of the d levels partially cancels the positive Δ_{so} of the p levels [1]. A linear model is considered to take into account the hybridization effect on the observed values of the spin-orbit splitting for the $Ag_xCu_{1-x}GaSe_2$ compounds, under the assumption that the d orbitals of Ag and Cu contribute to the spin-orbit splitting according to their compositions:
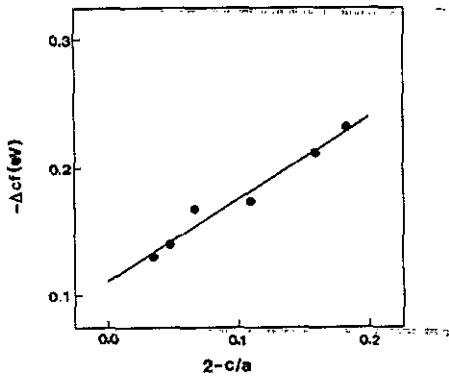
Figure 7. The observed crystal-field parameter as a function of the lattice compression.
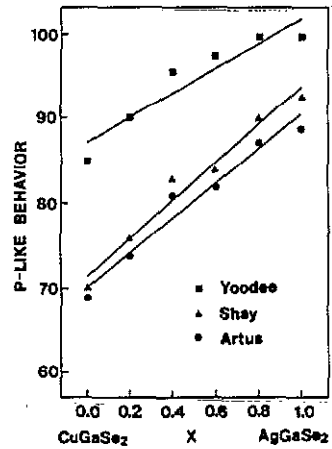
Figure 8. The percentage of the p-like behaviour of the uppermost valence bands for $Ag_xCu_{1-x}GaSe_2$: ▲, from [8]; ■, from [10]; ●, from [11].

$$\Delta_{so} = x[\alpha\Delta_p + (1 - \alpha)\Delta_d]_{Ag} + (1 - x)[\alpha\Delta_p + (1 - \alpha)\Delta_d]_{Cu} \qquad (8)$$

where Δ_p is the spin–orbit splitting observed in the p-like binary analogue, Δ_d is the negative spin–orbit splitting of the d levels and α is the percentage of the p-like character of the uppermost valence bands [8, 10, 11].

Shay *et al* [8] used the values of $\Delta_p = 0.42$ eV and $\Delta_d = -0.28$ eV for Ag, and the values of $\Delta_p = 0.43$ eV and $\Delta_d = -0.13$ eV for Cu. Yoodee *et al* [10] proposed another method to determine the spin–orbit splitting. In this case, the spin–orbit splitting of the p orbitals of the I–III–VI$_2$ compounds is calculated using the expression

$$\Delta_p = \tfrac{28}{26}[\tfrac{1}{16}\Delta_p(\text{I}) + \tfrac{3}{16}\Delta_p(\text{III}) + \tfrac{12}{16}\Delta_p(\text{VI})] \qquad (9)$$

where $\Delta_p(\text{I})$, $\Delta_p(\text{III})$ and $\Delta_p(\text{VI})$ are the spin–orbit splittings of the p orbitals of the atoms I, III and VI that make up the compound. In the case of the $Ag_xCu_{1-x}GaSe_2$ compounds, $\Delta_p(\text{Ag}) = 0.114$ eV, $\Delta_p(\text{Cu}) = 0.031$ eV, $\Delta_p(\text{Ga}) = 0.12$ eV and $\Delta_p(\text{Se}) = 0.286$ eV. The effects of the d orbitals of Cu and Ag are given by

$$\Delta_d = \tfrac{28}{26}\Delta_d(\text{I}) \qquad (10)$$

where $\Delta_d(\text{Ag}) = -0.55$ eV and $\Delta_d(\text{Cu}) = -0.152$ eV.

However, the above methods have disadvantages [11]: Shay *et al* [8] consider the values of the spin–orbit splittings of cations that do not constitute the compound, while Yoodee *et al* [10] take into account spin–orbit splittings of p orbitals of the noble metal that do not occur inside the valence band. In order to avoid these disadvantages, Artus and co-workers [11] proposed another method for calculating the spin–orbit splitting of the p orbitals in the I–III–VI$_2$ compounds. In this method, the spin–orbit splitting of the p orbitals in the I–III–VI$_2$ compounds is determined from that of the p orbitals in the atoms III and VI without taking into consideration the influence of the noble metal. The expression used in this method is

$$\Delta_p = \tfrac{28}{26}[0.2\Delta_p(\text{III}) + 0.8\Delta_p(\text{VI})]. \qquad (11)$$

The values used for the $Ag_xCu_{1-x}GaSe_2$ compounds are $\Delta_p(\text{Ga}) = 0.12$ eV and $\Delta_p(\text{Se}) =$

Table 2. Estimated p-like behaviour of the uppermost valence bands for $Ag_xCu_{1-x}GaSe_2$.

	Estimated p-like behaviour (%)		
x	[8]	[10]	[11]
0.0	70	85	69
0.2	76	90	74
0.4	83	96	81
0.6	84	97	82
0.8	90	100	87
1.0	93	100	89

0.37 eV. Equation (10) is used to evaluate the spin–orbit splitting of the d orbitals for these compounds with $\Delta_d(Ag) = -0.23$ eV and $\Delta_d(Cu) = -0.152$ eV.

Equation (8) can be used to estimate the p-like behaviour of the uppermost valence bands for the $Ag_xCu_{1-x}GaSe_2$ compounds from the values of Δ_p and Δ_d calculated by the methods mentioned above. The results are listed in table 2 and are shown in figure 8. As expected, the compounds containing more Cu atoms show a stronger p–d hybridization than those containing more Ag atoms, i.e. less p-like behaviour of the uppermost valence bands. The method proposed by Yoodee *et al* [10] estimates some-what larger p-like behaviour than the other methods do. A reasonably good linear relation of the p-like behaviour to x can be drawn in the $Ag_xCu_{1-x}GaSe_2$ compounds. This linear relation means that $\alpha \simeq \alpha_{Cu} + x(\alpha_{Ag} - \alpha_{Cu}) = \alpha_{Cu}(1 - x) + \alpha_{Ag}x$, that is to say, the $Ag_xCu_{1-x}GaSe_2$ compounds roughly have the amounts of the p-like character in their uppermost valence bands proportional to the respective Ag and Cu contents in the compounds.

Acknowledgments

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