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Excitons and the Spin-Orbit Splitting in $CuGaS_2$

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From a study of the polarization properties in both reflectivity and absorption, the exciton parameters of $CuGaS_2$ were determined. From these parameters, an upper limit of 7 meV for the spin-orbit splitting of the uppermost valence band in $CuGaS_2$ was deduced.

I. INTRODUCTION

$CuGaS_2$ is probably the most interesting of the I-III-VI_2 compounds. It can readily be made p type and has a direct band gap in the green spectral range.[1] In our previous study of the band structure of $CuGaS_2$,[2] we concluded that the uppermost valence band was a doublet characterized by an apparent absence of spin-orbit splitting. This unusual result was attributed to the p-d hybridization of the uppermost valence band since the negative spin-orbit characteristic of Cu d levels would tend to cancel the positive contribution due to the p levels on the other atoms.[2,3]

We present polarized absorption and reflectivity studies in the vicinity of the lowest-energy exciton. These yield the exciton parameters which are subsequently employed to determine an upper limit to the spin-orbit–splitting parameter. The results obtained and the techniques employed are similar to those previously reported for $AgGaS_2$.[4]

II. DISCUSSION

Shay and co-workers[5] have shown that the uppermost valence band in the chalcopyrite compounds (symmetry D_{2d}) is derived from the p-like Γ_{15} level in zinc-blende compounds (symmetry T_d), as shown in Fig. 1. In the absence of spin-orbit interaction, the transitions are polarized either parallel (A) or perpendicular (B and C) to the z or optic axis. In the presence of spin-orbit interaction, the polarization of the A and C transitions becomes mixed. These mixing ratios can be predicted by the quasicubic model as described below.[5,6]

We have previously argued[2] that due to a strong admixture of Cu d bands into the otherwise p-like uppermost valence band, there is an apparent absence of spin-orbit splitting in $CuGaS_2$. This results in a near degeneracy of the B and C transitions. Whereas the spin-orbit splitting in the II-IV compounds CdS and ZnS is ~ 70 meV, it will be shown below that the spin-orbit splitting in $CuGaS_2$ is no more than 7 meV.

The A excitons are formed with a hole from the upper Γ_7 valence band and an electron from the Γ_6 conduction band. For an s-like hydrogenic exciton state (Γ_1), the relevant excitons are given by the product (for D_{2d} symmetry)[6,7]

$$\Gamma_1 \times \Gamma_6 \times \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5 ,$$

where the Γ_3 exciton is forbidden, Γ_4 is allowed for $\vec{E} \parallel \vec{z}$, and Γ_5 is allowed for $\vec{E} \perp \vec{z}$. Owing to the mixing, the lowest-energy exciton is still seen predominantly for $\vec{E} \parallel \vec{z}$, but becomes group theoretically allowed for $E \perp z$ (Γ_5). However, the oscillator strength for the Γ_5 exciton is reduced by the factor $(2 - 3\Delta E/\Delta_{so})^2$ with respect to the Γ_4 exciton, according to the quasicubic model.[5,6] Here ΔE is the splitting of the A from the B valence band (~ 120 meV), and Δ_{so} is the spin-orbit splitting. In the neighborhood of the lowest-energy transition, the absorption coefficient for $\vec{E} \perp \vec{z}$ should mirror that for $\vec{E} \parallel \vec{z}$, but with a magnitude reduced by the ratio of the oscillator strengths.[8]

III. RESULTS

A. Reflectivity

Reflectivity was obtained at 2 °K from natural surfaces using polarized light. These surfaces were commonly (112) planes, which for the chalcopyrite structure (D_{2d}) is equivalent to a (111) plane in zinc blende. For this orientation, $\vec{E} \parallel \vec{z}$ is only nominal since only $\frac{2}{3}$ of the intensity is along z. The exciton in reflectivity is seen only for $\vec{E} \parallel \vec{z}$ with an oscillator strength $\frac{2}{3}$ of its maximum value.

Figure 2 shows a computer fit for two uncoupled damped classical oscillators representing the exciton ground state and first excited state.[4,9] The long-wavelength reflectivity is taken to be ~ 25%, as estimated from room-temperature refractive-index measurements.[10] A good fit is obtained for the oscillator strength ($4\pi\beta$) of the excited state equal to one-eighth and a phenomenological damping constant (Γ) twice that for the ground state. The

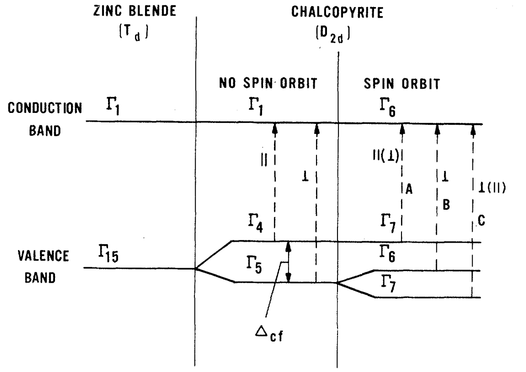

FIG. 1. Sketch of the band extrema at $\vec{k} = (0, 0, 0)$ showing the transition from zinc blende to chalcoprite. The selection rules, with respect to the optic axis, are indicated.

parameters obtained were $4\pi\beta_1 = 0.01$, $4\pi\beta_2 = 0.00125$, $\Gamma_1 = 1.5$ meV, $\Gamma_2 = 3$ meV, $E_1 = 2.501$ eV, $E_2 = 2.523$ eV, and $\epsilon_0 = 8.5$.

From the energy of the excited state (22 meV) above the ground state, the exciton binding energy in the hydrogenic approximation is 29 meV. Taking the static dielectric constant as 10,[11] the calculated exciton Bohr radius is ~25 Å, and the exciton reduced mass is $\sim 0.19 m_0$. These values are comparable to those obtained in II-VI compounds.[12] The oscillator strength, correcting for the (112) orientation, is $4\pi\beta = 0.015$, which is slightly larger than the equivalent for CdS (~0.012).[9,12]

B. Transmission

Polarized transmission spectra were obtained from samples of several growth runs. Selected samples from different runs exhibited the exciton absorption for $\vec{E} \perp \vec{z}$ (Γ_5 exciton). Good results (i.e., the sharpest exciton spectra) were obtained with natural surfaces, no two of which were ever parallel. In fact, one surface was usually quite irregular, but any polishing always broadened the exciton and gave the crystals a brownish appearance. Etching in warm concentrated 1:1 HCl + HNO_3 removed the discoloration and sharpened up the ground-state exciton line. However, the surfaces acquired a fuzzy appearance and the apparent absolute transmission and dichroism were greatly reduced. These complications made absolute transmission measurements and consequently the calculation of absorption coefficients difficult. The procedure finally employed was to polish a crystal and obtain an absolute transmission measurement at relatively long wavelength (i.e., 0.53 μ). The crystal was then subsequently etched to obtain relative measurements, using 0.53 μ as the calibration point.

During the course of investigating a number of samples, we observed the unexpected result that the broader exciton lines have greater integrated intensity. This suggests that the Γ_5 exciton is nearly forbidden (i.e., $\Delta_{so} \to 0$), and is turned on predominantly by an unknown factor, probably inhomogeneous strain. However, there is obviously a limit to the magnitude of the permissible inhomogeneous strain. On some samples, transmission was observed for energies greater than the ground-state exciton energy, but with no indication of an exciton absorption. These samples did not exhibit

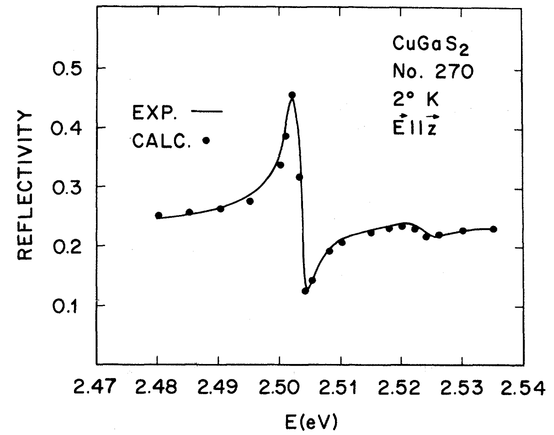

FIG. 2. Reflectivity spectra for $CuGaS_2$ at 2 °K including the ground state and first excited state. The parameters of the fit are given in the text.

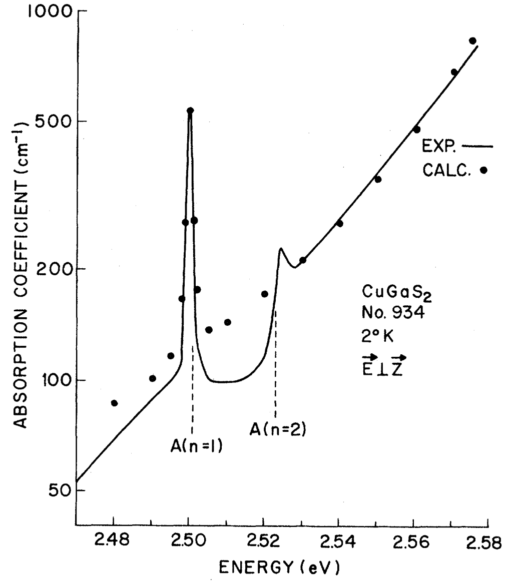

FIG. 3. Absorption spectra for $CuGaS_2$ at 2 °K. The energies of the exciton determined from reflectivity are indicated by dashed lines. The parameters of the fit (for the Γ_5 ground state and the B, C excitons at 2.62 eV) are given in the text.

a reflectivity anomaly.

The oscillator strength for the narrowest exciton line was determined, and by comparing this value to the oscillator strength obtained in reflectivity, an upper limit for the spin-orbit splitting can be determined. The absorption spectra for a $CuGaS_2$ sample polished and subsequently etched to a thickness ~ 0.01 cm is shown in Fig. 3. The $n=1$ state has a peak absorption of ~ 400 cm^{-1} above the background and a damping constant of 1.5–2 meV (full width at half-maximum). This damping constant is only slightly larger than the corresponding quantity determined from reflectivity, in contrast to our previous results on $AgGaS_2$.[4] The Γ_5 exciton energy is ~ 1 meV less than the Γ_4 exciton energy determined from reflectivity. The calculated oscillator strength for the Γ_5 ground state is $4\pi\beta = 6 \times 10^{-6}$ as shown in Fig. 3. The observed mixing ratio is therefore

$$\frac{I_\perp}{I_\parallel} = \frac{6\times 10^{-6}}{1.5\times 10^{-2}} = 4\times 10^{-4} .$$

Using the relationship $I_\parallel / I_\perp = (2 - 3\Delta E/\Delta_{so})^2$ with $\Delta E = -120$ meV, we obtain $\Delta_{so} \sim 7$ meV. As discussed above, this value for Δ_{so} represents the upper limit to the spin-orbit splitting. (This result assumes the validity of the quasicubic model, which was derived for p bands. The model may consequently require some modification due to the admixture of d bands.)

An additional absorption peak is seen near 2.524 eV which is within ~ 1–2 meV of the $n=2$ state determined from reflectivity. The rapidly varying background in the neighborhood of this absorption precludes precise determination of its oscillator strength and energy. It is presumably due to the $n=2$ state of the Γ_5 exciton. Also shown in Fig. 3 is the calculated absorption for two uncoupled classical oscillators showing the combined effects of the Γ_5 ground state and the B, C excitons at 2.62 eV. The parameters chosen for the B, C excitons were $4\pi\beta = 0.015$ and $\Gamma = 4$ meV. The oscillator strength was chosen to be the same as that determined from reflectivity for the A exciton, since the combined oscillator strength for $E \perp z$ should be equal to that for $E \parallel z$. The damping constant was chosen to obtain the best fit to the experimental data. The low-energy part of the fit ($E < 2.50$ eV) may be influenced by the above discussed difficulty in measuring absolute transmission. The high-energy section ($E > 2.53$ eV), has identical slope to that of the experimental curve. This indicates that the absorption in this region is due to the B, C excitons with perhaps a contribution due to the A continuum. The absorption in the energy interval between the $n=1$ and 2 exciton states appears anomalous and is not understood.

It should be mentioned that since the spin-orbit splitting is much less than the crystal-field splitting, the B and C excitons have nearly identical polarization properties. In addition, the B and C transitions should be split only $\frac{2}{3}$ of Δ_{so} (i.e., < 5 meV).[5] Consequently, due to the poor line shape of the B, C reflectivity,[1] a splitting of this magnitude could go undetected.

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[1] B. Tell, J. L. Shay, and H. M. Kasper, Phys. Rev. B **4**, 2463 (1971).

[2] J. L. Shay, B. Tell, H. M. Kasper, and L. M. Schiavone, Phys. Rev. B **5**, 5003 (1972).

[3] K. Shindo, A. Morita, and H. Kamimura, J. Phys. Soc. Jap. **20**, 2054 (1965).

[4] B. Tell, J. L. Shay, and H. M. Kasper, Phys. Rev. B **6**, 3008 (1972).

[5] J. L. Shay, E. Buehler, and J. H. Wernick, Phys. Rev. B **2**, 4104 (1970); J. E. Rowe and J. L. Shay, Phys. Rev. B **3**, 451 (1971).

[6] J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).

[7] See, for example, M. Tinkham [*Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964)] with the following equivalences for D_{2d}: $A_1 \leftrightarrow \Gamma_1$, $A_2 \leftrightarrow \Gamma_2$, $B_1 \leftrightarrow \Gamma_3$, $B_2 \leftrightarrow \Gamma_4$, and $E \leftrightarrow \Gamma_5$; for T_d: $T_2 \leftrightarrow \Gamma_{15}$.

[8] J. L. Shay and E. Buehler, Phys. Rev. Lett. **26**, 506 (1971).

[9] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).

[10] G. D. Boyd, J. H. McFee, and H. M. Kasper, IEEE J. Quantum Electron. **7**, 563 (1971).

[11] Estimated at room temperature by E. H. Turner (private communication).

[12] *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), p. 319ff.