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Exciton–phonon spectra and energy band structure of CuGaSe₂ crystals

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Abstract. The excitonic reflectivity spectra and the wavelength derivative reflection spectra have been investigated. The $n = 1$, $n = 2$ and $n = 3$ states of the A, B and C exciton series are determined. The exciton binding energies and exact values of the band gaps of all three intervals $\Gamma_7^{V_1}-\Gamma_6^{C_1}$, $\Gamma_6^{V_2}-\Gamma_6^{C_1}$ and $\Gamma_7^{V_3}-\Gamma_6^{C_1}$ have been calculated. Data on the splitting due to the crystal-field and the spin–orbit interaction are determined as well.

1. Introduction

The CuGaSe₂ (CGS) compound, which belongs to the I–II–VI₂ group, crystallizes into the chalcoyrite structure with the space group $I42d$ (D_{2d}^{12}). There is much research interest in materials of this group and, as a result of this, an expected application in optoelectronic devices. In some materials, stimulated radiation is observed [1, 2]. Generation of the second harmonic at 10.6 μm [3] and generation of IR radiation in the region 4.6 and 12 μm [4] have been obtained.

At the same time, materials are attractive for investigation of the band structure [5–8]. The energy band structure is calculated as the nearest analogue of zincblende [9]. Together with this, a reduction in the band gap and spin–orbit splitting values is revealed and is stronger than expected in terms of analogues. For CGS, the band gap is reduced by approximately 1 eV and the spin–orbit splitting is reduced from 0.45 to 0.23 eV compared with its analogue ZnSe [10–13]. These effects are explained by the hybridization of p and d states, determined by the valence band in the centre of the Brillouin zone [11, 14]. For more exact determination of this contribution, it is essential to determine experimentally values of the band gap between three upper valence bands V_1 , V_2 and V_3 and the lowest conduction band C_1 . At present, these parameters are estimated from the $n = 1$ lines of the exciton states [11, 14]. The exciton binding energies are not known.

In this work, the excitonic reflectivity spectra and the wavelength derivative reflection (WDR) spectra have been investigated. The states $n = 1$, $n = 2$ and $n = 3$ of the A, B and C exciton series are determined. The exciton binding energies and more exact values of the band gaps of all three intervals ($\Gamma_7-\Gamma_6$, $\Gamma_6-\Gamma_6$ and $\Gamma_7-\Gamma_6$) have been calculated. The magnitudes of the splitting due to the crystal-field and spin–orbit interaction are determined as well. In the polarization $E \perp c$, transitions into the band $n = 1$ of the A excitons with the absorption and the emission of the Γ optical phonons of the Brillouin zone centre have been revealed. For the polarization $E \parallel c$, in the continuum region of the B exciton series, transitions with the emission of the Γ optical phonons have also been revealed.

2. Experimental procedure

The crystals, grown by the iodine transport method of pulling the ampoule, are plates with an approximately $2.5 \text{ cm} \times 1.0 \text{ cm}$ mirror surface and $300\text{--}400 \text{ }\mu\text{m}$ thickness. Surfaces of some plates were parallel to the c axis. WDR spectra were measured using MDR-2 spectrometers with light strength 2:1. The size of the $1200 \text{ rulings mm}^{-1}$ ($0.2\text{--}0.6 \text{ }\mu\text{m}$) and $600 \text{ rulings mm}^{-1}$ ($0.6\text{--}1.0 \text{ }\mu\text{m}$) diffraction gratings was $140 \text{ mm} \times 140 \text{ mm}$, and the focal distance was -400 mm . The mirror vibrated at about 73 Hz near the exit slit and produced approximately $3\text{--}5 \text{ \AA}$ wavelength modulation. The modulated signal was recorded with a FEU-62 photomultiplier with a phase-sensitive detector. During the WDR measurements, the samples were immersed in liquid nitrogen.

3. Results and discussion

The $82 \pm 2 \text{ K}$ reflectivity spectrum for the CGS crystals is shown in figure 1. For the polarization $E \parallel c$, the $n = 1$ excitonic line at the energy 1.797 eV is revealed. The $n = 1$ line of the B exciton series reveals itself weakly in this polarization. For the polarization $E \perp c$, the $n = 1$ line of the A excitons is not displayed. The $n = 1$ line of the B excitons at 1.797 eV and the C excitonic line at 1.983 eV are revealed. The exciton parameters are reported in table 1.

Table 1. Parameters of the WDR excitonic spectra in CGS crystals.

Series	Previous results [11]		Present work	
	Exciton state	Energy (eV)	Exciton state	Energy (eV)
A	$n = 1$	1.729	$n = 1$	1.748; (1.711 ^a)
			$n = 2$	1.844
			$n = 3$	1.857
			$n = \infty$	1.867; $R = 0.0936$
			$\Gamma_7^{V_1} - \Gamma_6^{C_1}$	
B	$n = 1$	1.813	$n = 1$	1.833; (1.797 ^a)
			$n = 2$	1.898
			$n = 3$	1.9104
			$n = \infty$	1.920; $R = 0.086$
			$\Gamma_6^{V_2} - \Gamma_6^{C_1}$	
C	$n = 1$	2.016	$n = 1$	2.050; (1.983 ^a)
			$n = 2$	2.088
			$n = \infty$	2.114; $R = 0.064$
				$\Gamma_7^{V_3} - \Gamma_6^{C_1}$

^a Values of the reflectivity peaks at 87 K .

The WDR spectra have been measured in the region of the ground state and the excited states (figure 2). The $n = 1, 2$ and 3 lines of the A and B exciton series and the fine structure accompanying these lines are revealed in the spectra. Binding energy calculations of the excitons and band gap values for all three bands are calculated from the level positions of the $n = 2$ and $n = 3$ lines. For the C excitons series, the band parameters have been determined from calculations of the line energy positions $n = 1$ and $n = 2$ (the $n = 2$

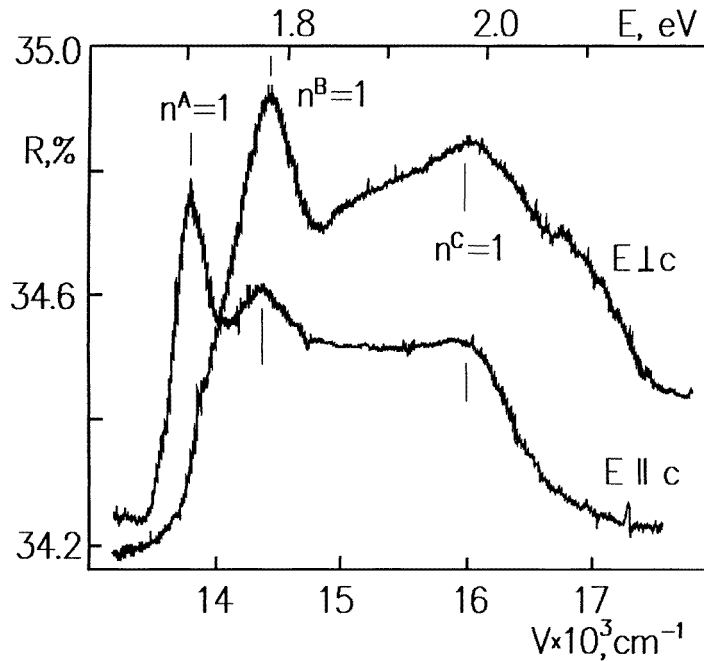


Figure 1. Exciton reflectivity spectra of the CGS crystals at 87 K.

line is very weak). The calculation shows that the binding exciton energies for the A, B and C series are 93.6 meV, 86 meV and 64 meV, respectively. The reflectivity and WDR spectrum measurements in polarized light (figures 1 and 2) show that the $n = 1$ excitonic line of the A series is permitted in the polarization $E \parallel c$ and is forbidden in the polarization $E \perp c$. In WDR spectra, for the polarization $E \perp c$ the $n = 1$ line of the A series is revealed. With the long-wavelength part of the $n = 1$ line, there are weaker peaks a_1 , a_2 and a_3 due to direct transitions in the excitonic band with an absorption of the E_{LO}^3 , E_{LO}^1 and $E_{LO}^1 + E_{LO}^3$ phonons, respectively. In the short-wavelength part of the $n = 1$ line of the A series, there are e_1 - e_4 bands due to a transition in the exciton band with the phonon emissions E_{LO}^2 , E_{LO}^1 and so on (figure 2 and table 2). The type and symmetry of the shared phonons are determined as of the nearest corresponding version to the energy of the Γ optical phonons. The longitudinal and transverse frequencies of phonons determined by the IR reflection in [15, 16] are presented in table 2.

In the polarization $E \parallel c$ the $n = 1$ line of the B exciton series has a low intensity like the reflectivity spectra (figure 1) and WDR spectra (figure 2). The $n = 1$ line of the B excitonic series appears as the forbidden line. This has been shown in previous work [11, 14]. In the energy region larger than the $n = 1$ energy position of the B excitonic series, there are $n = 2$ and $n = 3$ lines of the A and B excitons. In the continuum region of the B exciton series, there are c_1 - c_6 bands, which we explain as phonon sharing in the transition $\Gamma_6^{V_2} - \Gamma_6^{C_1}$. The c_1 band is due to the $\Gamma_6^{V_2} - \Gamma_6^{C_1}$ transition with E_{LO}^5 phonon emission, the c_2 band to that with E_{LO}^1 or B_{2LO}^1 and the c_3 band to that with $E_{LO}^1 + B_{2LO}^2$. The energy position and the identification of the bands revealed are shown in figure 3 and table 3. In the energy region between the principal state and the continuum of the B exciton, the transitions in the

Table 2. Energy and frequencies of phonons determined by the IR reflection and WDR in the environment of the A excitonic transition in the primary state.

Data on the IR reflection [15, 16]					Symbol for $\Delta R/\Delta\lambda$ peaks	Energy of peaks (eV)	Energy of phonon (meV)	Type and symmetry of shared phonons	Values of energy phonon from IR data (meV)
Mode	ν_{LO} (cm^{-1})	ν_{TO} (cm^{-1})	ν_{LO} (meV)	ν_{TO} (meV)					
E^1	277	255	34.3	31.6	a_3	1.694	54	$+(E_{LO}^1 + E_{LO}^3)$	52.8
E^2	186	180	23.1	22.3	a_2	1.714	34	$+E_{LO}^1$	34.3
E^3	149	145	18.5	17.9	a_1	1.783	18	$+E_{LO}^3$	18.5
E^4	109	105	13.5	13.0	$n^{Aex} = 1$	1.748	Without phonon transition		
E^5	90.9	88.2	11.3	10.9	e_1	1.770	22	$-E_{LO}^2$	23.1
E^6	66	64.5	8.2	7.9	e_2	1.783	35	$-E_{LO}^1$	34.3
B_2^1	273	257	33.8	31.9	e_3	1.794	46	$-(E_{LO}^1 + E_{LO}^5)$	45.6
								$-(B_{LO}^2 + B_{2LO}^3)$	45.7
B_2^2	188	127	23.3	15.7					
B_2^3	96	86	11.9	10.7					

Table 3. Energy of the features of the WDR spectra in the continuum range of the B excitonic series for the $E \parallel c$ polarization.

Symbol for peak $\Delta R/\Delta\lambda$	Energy of transitions (eV)	Phonon energy (meV)	Type of shared phonons	Energy of phonon combination (meV)
E_g^B	1.920	$\Gamma_6^{V_2}-\Gamma_6^{C_1}$	Without phonon transition	
C_1	1.931	11	E_{LO}^5	11.3
			B_{2LO}^3	11.9
C_2	1.950	30	E_{LO}^1, B_{2LO}^1	34.3; 33.8
C_3	1.978	58	$E_{LO}^1 + B_{2LO}^2$	57.6
C_4	1.985	65	B_{2LO}^1	67.6
C_5	2.013	93	$2E_{LO}^1 + E_{LO}^2$	91.9
			(B_{2LO}^2)	
C_6	2.020	100	$2E_{LO}^1 + B_{2LO}^1$	102.4

$n = 1$ exciton band with phonon emissions and the $\Gamma_6^{V_2}-\Gamma_6^{C_1}$ band–band transitions with the phonon absorption should be revealed. We suppose that these bands are veiled by a sharper change in the reflectivity spectra due to transitions into excitonic excited states.

4. Spin–orbit splitting in CuGaSe₂ crystals

The calculation of the energy band structure for crystals of the I–III–IV₂ group is made with the approximation that they are analogues of the zincblende structure (ZnSe and other) [9, 11, 14]. In the I–III–IV₂ structure, provided that the crystal field $\Delta_{cf} < E_g$, spaces between the $\Gamma_7^{V_1}-\Gamma_6^{V_2}$ and $\Gamma_6^{V_2}-\Gamma_7^{V_3}$ energy levels are denoted E_1 and E_2 respectively. These values are deduced from the Hamiltonian matrix and have been determined using the relation

$$E_{1(2)} = \frac{1}{2}(\Delta_{so} + \Delta_{cf}) \left[\frac{1}{4}(\Delta_{so} + \Delta_{cf})^2 - \frac{2}{3}\Delta_{so}\Delta_{cf} \right]^{1/2}. \quad (1)$$

The splitting $\Gamma_7^{V_1}-\Gamma_6^{V_2}$ of the upper valence bands is determined only by the fact that the level position of the $n = 1$ lines is equal to 0.085 eV, which completely corresponds to the

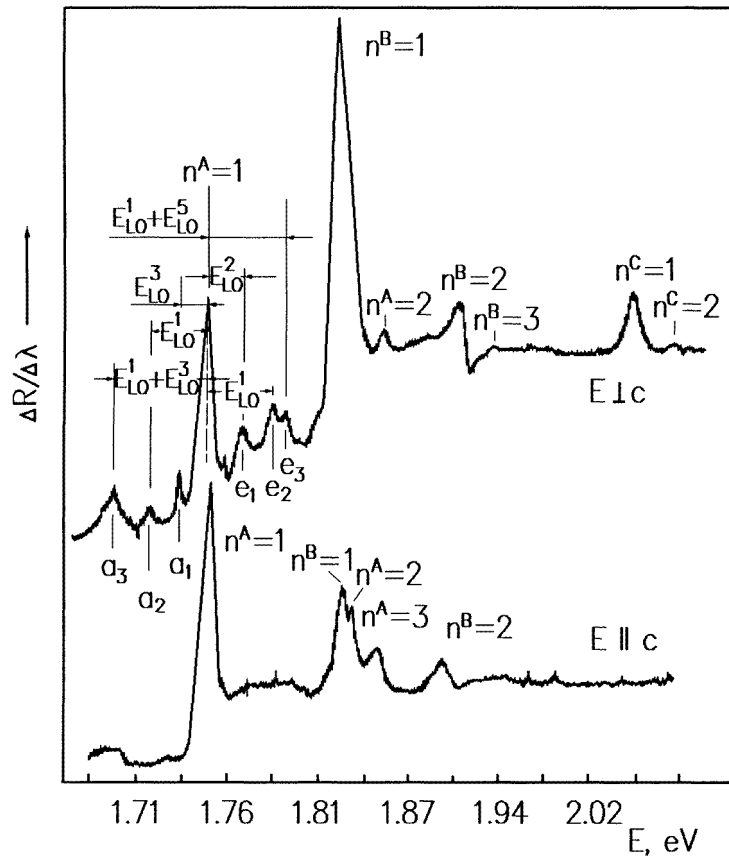


Figure 2. WDR spectra of CGS in the exciton region at 77 K and the model of the transitions with the phonon sharing in the $n = 1$ exciton band.

result (0.084 eV) of [11, 14]. However, taking into consideration the difference between the binding energies of the A and B excitons, it turned out that the $\Gamma_7^{V_1}$ and $\Gamma_6^{V_2}$ bands are split only by 53 meV ($\Delta E_g^{B-A} = E_g(\Gamma_6^{V_2} - \Gamma_6^{C_1}) - E_g(\Gamma_7^{V_1} - \Gamma_6^{C_1}) = 53$ meV). The same is revealed for the V_2 and V_3 bands. The splitting of these bands estimated by the $n = 1$ line position is equal to 0.217 eV, but the result of [11] is 0.203 eV. Taking into account the binding energies of the B and C excitons, the values of the band splitting $\Gamma_6^{V_2} - \Gamma_7^{V_3}$ is equal to 0.194 eV ($\Delta E_g^{B-A} = E_g(\Gamma_7^{V_3} - \Gamma_6^{C_1}) - E_g(\Gamma_6^{V_2} - \Gamma_6^{C_1}) = 0.194$ eV). Thus, using energy intervals between the bands determined by consideration of the binding energy of excitons, we have calculated the true values of $\Delta_{cf} = 55$ meV and $\Delta_{so} = 170$ meV. It should be pointed out that the values of $\Delta_{cf} = 55$ meV and $\Delta_{so} = 170$ meV give rise to the splitting of the bands: $\Gamma_7^{V_1} - \Gamma_6^{V_2} = 53$ meV, and $\Gamma_6^{V_2} - \Gamma_7^{V_3} = 194$ meV (figure 4).

For compounds of the group I-III-IV₂, it is suggested [11, 14] in that p-d hybridization influence on the spin-orbit splitting is determined using the relation

$$\Delta_{so} = \alpha \Delta_p + (1 - \alpha) \Delta_d \quad (2)$$

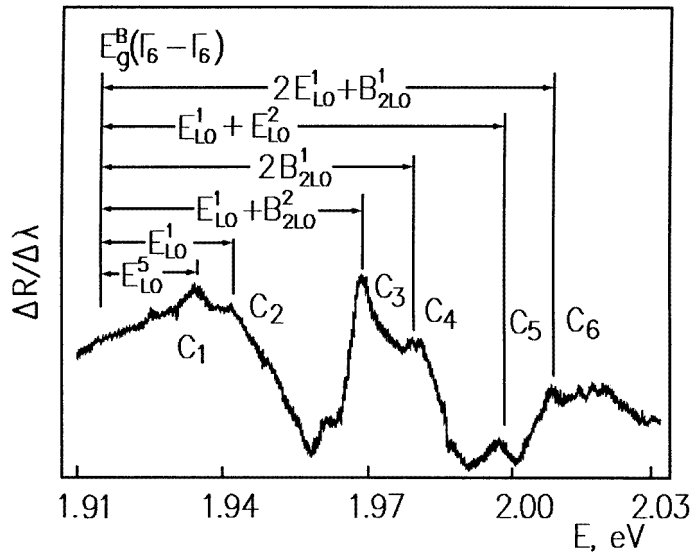


Figure 3. WDR spectra in the region from 1.9 to 2.1 eV for the polarization $E \parallel c$ and the model of the $\Gamma_6^{V_2}-\Gamma_6^{C_1}$ transition with Γ phonon emissions. (Spectra have been strengthened with respect to figure 2 by a factor of about 20.)

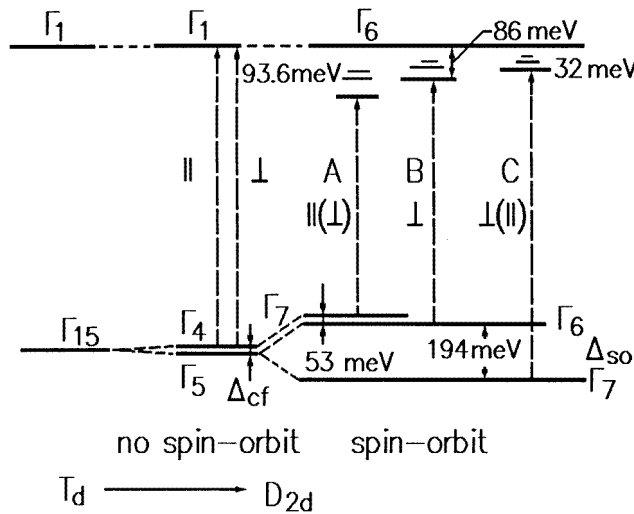


Figure 4. Energy band structure near the Brillouin zone centre showing the transition from zincblende to chalcopyrite.

where, for Cu atoms, $\Delta_p = 0.43$ is the spin-orbit splitting of p states, and $\Delta_d = -0.13$ eV is the negative spin-orbit splitting of d levels; α is the percentage of p states in the upper valence bands. In [11], α is equal to 0.36. Without considering the A, B and C exciton binding energies, we have obtained $\alpha \simeq 0.29$.

Table 4. Comparison of the scattering values of the CGS valence bands reported in the present work with those observed by the different workers.

Reference	Δ_{cf} (eV)		Δ_{so} (eV)		p–d hybridization (% p state)
	Quasi-cubic model	Experiment	Quasi-cubic model	Experiment	
[14]	0.05	0.09	0.43	0.23	36
[11]	0.05	0.084	0.43	0.203	24
Our data without Rydberg	0.05	0.085	0.43	0.217	29
Our data with Rydberg	0.05	0.055	0.43	0.170	13

Since the binding energies of the A, B and C exciton series differ, then for Δ_{cf} , Δ_{so} and α a correction is made (table 4). The value of the crystal field is estimated as

$$\Delta_{cf} = -\frac{3}{2}b(2 - c/a) \quad (3)$$

where a and c are the crystal lattice constants and b is the deforming potential of the lattice which is equal to 1.0 for I–III–VI₂ chalcopyrites [11, 14]. Taking into consideration that, for CGS, $c/a = 1.964$ ($a = 5.62 \text{ \AA}$; $c = 11.01 \text{ \AA}$), then the value $\Delta_{cf} = 0.054 \text{ eV}$. As is seen, the result agrees with Δ_{cf} determined from excitonic spectra (0.055 eV). The contribution of d states in the upper valence bands is about 13%.

References

- [1] Tell B, Shay J L and Kasper H M 1971 *Phys. Rev. B* **4** 2463
- [2] Tell B, Shay J L and Kasper H M 1972 *Phys. Rev. B* **6** 3008
- [3] Chemla D S, Kupcek P I, Robertson D S and Smith R C 1971 *Opt. Commun.* **3** 29
- [4] Hanna D C, Rampal V V and Smith R C 1973 *Opt. Commun.* **8** 151
- [5] Poplovnoi A S and Poliganov Y I 1971 *Izv. Akad. Nauk SSSR, Neorg. Material* **7** 1706
- [6] Rife J C, Dexter R N, Bridenbaugh P M and Veal B W 1977 *Phys. Rev. B* **16** 4491
- [7] Turowski M, Kisiel A and Tomlinson R D 1983 *Nuovo Cimento D* **2** 2064
- [8] Bacevicz R, Durant I R, Ciszek T F and Deb S K 1987 *Ternary and Multinary Compounds* ed S K Deb and A Zunger (Pittsburgh, PA: Materials Research Society) p 155
- [9] Jaffe J E and Zunger A 1983 *Phys. Rev. B* **28** 5822
- [10] Bondar I V, Bologa A P and Korzun B V 1982 *Phys. Status Solidi b* **109** K31
- [11] Tell B and Bridenbaugh P M 1975 *Phys. Rev. B* **12** 3330
- [12] Bondar I V, Bologa A P and Lukovski A I 1982 *Cryst. Res. Technol.* **17** K109
- [13] Horig W, Moller W, Neumann H, Reccius E and Kuhn G 1979 *Phys. Status Solidi b* **92** K1
- [14] Shay J L, Tell B, Kasper H M and Schiavone L M 1972 *Phys. Rev. B* **5** 5003
- [15] Syrbu N N 1995 *Opt. Spectrosc.* **79** 249
- [16] Andriesh A M, Syrbu N N, Iovu M S and Tazlavan V E 1995 *Phys. Status Solidi b* **187** 83