EXCITON SPECTRA OF CuInSe$_2$ CRYSTALS

L. Nemerenco

Technical University of Moldova, 277012, Stefan cel mare, bul. 168, Chisinau, Republic of Moldova

Abstract

The excitonic reflectivity spectra and the wave-length derivative reflection spectra have been investigated for CuInSe$_2$ crystals. The n =1, n =2 and n = 3 states of A, B and C exciton series are revealed and the contours of exciton lines (n=1) are calculated. The exciton binding energies and exact values of the band gaps of all three intervals Γ_7 (V$_1$) $-$ Γ_6 (C$_1$), Γ_6 (V$_2$) $-$ Γ_6 (C$_1$), Γ_7 (V$_3$) $-$ Γ_6 (C$_1$) have been also calculated. Data of the splitting due to crystal-field and spin-orbit interaction are determined. The parameters of excitons and energy bands for the region of interband interval minimum have been determined as well. The band model in the Γ, N and T points of the Brillouin zone is proposed.

The CuInSe$_2$ compound crystallizes into the chalcopyrite structure with the space group $D_{2d}^{12} = I\bar{4}2d$ [1]. Crystalline CuInSe$_2$ is a narrow band gap material (E$_g$ ~ 1.0 eV) with a direct band gap [2 - 4]. The energy band structure is calculated as the nearest analog of the zincblend [5]. In the region of minimum interzone interval the lines n = 1 of A, B and C excitonic series have been found [6]. The exciton excited state is not revealed and the exciton binding energies are not known. The CuInSe$_2$ compound is a prospective material for converters of solar energy. At the same time, this material prove to be of interest in further investigation of the band structure due to the existence of p and d hibridization states of upper valence bands in the center of the Brillouin zone.

In this paper, we present experimental results and contours calculation of the reflectivity spectra in the one-phonon region (50 – 600 cm^{-1}). Both phonon energy and dielectric constant values have been calculated in the paper.

In addition to that, exciton reflectivity spectra and the wave-length derivative reflection (WDR) have been investigated as well.

CuInSe$_2$ single crystals were grown by using the classical Bridgman method in the form of ingots with 30 mm in diameter and 60 –70 mm long. 15 x 25 mm^2 plates cut from ingots were used for measurement. IR reflectivity spectra were measured by KSDI-82 (50 – 250 cm^{-1}) vacuum spectrometer and SPECORD M – 80 (200 – 4000 cm^{-1}) with 0.2 cm^{-1} and 1 cm^{-1} spectral slits respectively.

In the reflectivity spectra of CuInSe$_2$ crystals, the structure of maximums due to exciton states is found in the region 1.0-1.1 eV. The 1.037 eV and 1.043 eV maxima are due to S-state of the A and B exciton series. The energy position of these reflection peaks corresponds to the results achieved in ref. [6], where n=1 lines of the A and B were observed at 1.038 eV and 1.042 eV, respectively. These data have been obtained from electroreflectance measurements at T = 77K.

In the CuInSe$_2$ WDR spectra the n=1 lines at 1.0369 eV of the A exciton and at 1.0431 eV of the B exciton are revealed. Polarizing dependences also correspond to the results reflected in Ref. [6].

In the short-wavelength region of spectrum, features are seen, which we ascribe to exciton excited states, namely the lines n=2 and n=3 of the A and B excitons series (Fig.1, Table 1). According to the energy position of n=1, n=2 and n=3 lines, both exciton binding energy and the minimum energy intervals responsible for excitonic states are determined. For A and B excitons the Rydberg constants are equal to 39.1 and 36.3 meV and band gaps are respectively equal to 1.0760 and 1.0794 eV.

In the high-energy region of spectrum two bands at 1.2864 and 1.3092 eV, which are due to C exciton series, can be found (Table 1, Fig.1).
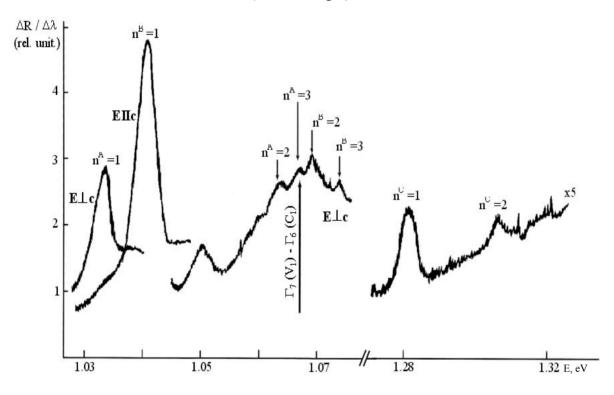

Fig.1. WDR spectra of CuInSe$_2$crystals for the exciton lines pf A, B, and C series at 77 K in the polarized light.

Assuming that the bands 1.2864 and 1.3092 eV are due to lines n=1 and n=2 of the C excitons, we obtain that the energy difference $n_1^B - n_1^A$ is equal to 6.2 meV and $n_1^C - n_1^B$ is equal to 0.243 eV (n_1^A, n_1^B and n_1^C - S-state energy position of the A, B and C). In work [6], $n_1^B - n_1^A$ is equal to 0.006 eV and $n_1^C - n_1^B$ is equal to 0.233 eV. As it is seen these values correspond to our data. The Rydberg constant and band gap for the C series is equal to 0.0304 and 1.3168 eV, respectively. The crystal-field and SO (spin orbital) splitting of the valence band is calculated from the relations:

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

were E_1 and E_2 are the intervals $\Gamma_7(V_1)$ - $\Gamma_6(V_2)$ and $\Gamma_6(V_2)$ - $\Gamma_7(V_3)$, respectively.

At present the splitting of upper valence bands $\Gamma_7(V_1)$ - $\Gamma_6(V_2)$ and $\Gamma_6(V_2)$ - $\Gamma_7(V_3)$ is determined from n =1 line energy levels for A, B and C excitons. Taking into account that E_1 is equal to 0.0034 eV and E_2 is equal to 0,2374 eV, we have calculated the "de facto" values

of Δ_{cf} = 0.0051 eV and Δ_{so} = 0,2367 eV. Thus, the given values Δ_{cf} and Δ_{so} result in the splitting of bands $\Gamma_7(V_1)$ - $\Gamma_6(V_2)$ equal to 0.0034 eV and $\Gamma_6(V_2)$ - $\Gamma_7(V_3)$ equal to 0.2374 eV (Fig. 2).

The splitting value due to the crystal-field is estimated according to the following equation:

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

where a and c serve as crystal lattice constant, b - deformation potential of lattice, which is equal to 1,0 for I-III-VI$_2$ chalcopyrites [5,6]. Taking into consideration the crystallographic data of CuInSe$_2$ [1] a = 5.78 Å and c = 11,62 Å the value Δ_{cf} is equal to 0,006 eV. At the same time, we can estimate the contribution of p state to upper valence bands from the following relation:

$$\Delta_{SO} = \alpha\Delta_P + (1-\alpha)\Delta_d$$

where for Cu atoms, Δ_p = 0,43 is the spin-orbit splitting of p states, and Δ_d = -0.13 eV is the negative spin-orbit splitting of d levels, a is the percentage of p states in upper valence bands. In the CuInSe2 crystals, the contribution of p-levels into the upper valence bands comprises 37%, while according to [6] it comprises 34 %.
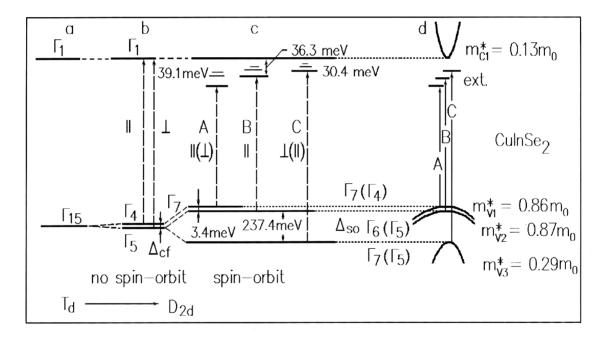

Fig.2. Energy band structure near the Brillouin zone center of CuInSe$_2$ crystals for D$_{2d}$ symmetry

The model of the medium with a spatial dispersion (SD) is being examined. This model takes into consideration the additional links between oscillators, which evoke the transmission of the excitation between them. Within the framework of the theory that takes into consideration SD and provided that the dead-layer (DL) effects of Hopfield and Thomas exist on the crystal boundary, where the Pecar's additional boundary conditions are feasible on the interior boundary, the dielectric permeability of the medium in the exciton resonance environment appears as the following:

$$\varepsilon\left(\omega,\vec{k}\right)=\varepsilon_f+\frac{2\varepsilon_f\omega_{LT}\omega_0}{\omega_0^2-\omega^2+\dfrac{h^2k^2}{2M}\omega_0-i\omega\gamma} \quad,$$

where ε_f is the background dielectric constant, which is due to contribution of all interaction mechanism except the examined oscillator, ω_0 is the transverse exciton frequency; $M = m_C^* + m_V^*$ is exciton translation mass; k is the wave vector; $\omega_{LT}=\omega_L-\omega_0$ is the longitudinal-transverse splitting; ω_L is the longitudinal exciton frequency.

Table 1. Parameters of exciton spectra in CuInSe$_2$ crystals

Series	Exciton state	Energy of peaks $\Delta R/\Delta\lambda$, eV	Exciton and band parameters
A	n = 1	1.0369	$\varepsilon^{II}=6.0$; $\varepsilon^{\perp}=6.86$ $\varepsilon_{midd}^{\Delta R/\Delta\lambda}=6.7$ $\mu=0.1183m_0$; M = $1m_0$ $m_{C1}^*=0.14m_0$ $m_{V1}^*=0.86m_0$, R = 0.0391
	n = 2	1.0662	
	n = 3	1.0716	
	n = ∞ $\Gamma_7(\Gamma_4)V_1$-$\Gamma_6(\Gamma_1)C_1$	1.0760	
B	n = 1	1.0431	$\varepsilon_{midd}^{\Delta R/\Delta\lambda}=6.6\pm0.1$ $\mu=0.1099m_0$; M = $1m_0$ $m_{C1}^*=0.13m_0$ $m_{V2}^*=0.87m_0$, R =0,0363
	n = 2	1.0703	
	n = 3	1.0754	
	n = ∞ $\Gamma_6(\Gamma_5)V_2$-$\Gamma_6(\Gamma_1)C_1$	1.0794	
C	n = 1	1.2864	$\mu=0.092m_0$ $m_{C1}^*=0.13m_0$ $m_{V3}^*=0.29m_0$, R = 0,0304
	n = 2	1.3092	
	n = ∞ $\Gamma_7(\Gamma_4)V_3$-$\Gamma_6(\Gamma_1)C_1$	1.3168	

Proceeding from the relations provided above, reflectivity exciton spectrum contours are calculated within the framework of the classical optics taking into consideration the SD and the availability of DL (fig.3). The calculation of WDR contours shows that $\gamma > \omega_{LT}$. The data for A excitons are the following γ = 7 meV, ω_{LT} = 1.5 meV, ω_0 = 1.035 eV, M = $1m_0$ and for B exciton are γ = 4 meV, ω_{LT} = 1.6 meV, ω_0 = 1.0420 eV, M = $1m_0$. The dead-layer (DL) depth is equal to 0. Along with that on experimental spectrum contours of WDR, the M value alteration can be revealed within 20% (20% - precision of M determination).
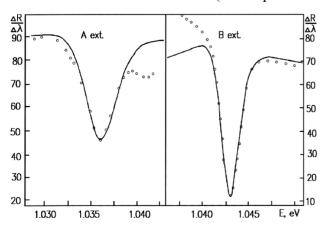

Fig.4. Contour of WDR spectra of n=1 lines for both A (a) and B (b) excitons in CuInSe$_2$ crystals (experimental values – open circles; theory calculation – solid lines).

For A and B series, the exciton translation mass of excitons M is equal to lm_0. Taking into account that Rydberg constant for A and B excitons is respectively equal to 39,1 and 36,3 meV and the background dielectric constants is equal to 6.0 (E II c) and 6.86 (E⊥c), we obtain that $\mu = 0.1183m_0$ (A_{ext}) and $\mu = 0.1099m_0$ (B_{ext}).

For each exciton series the reduced effective masses are determined given the following condition;

$$\mu_j = \varepsilon_{\perp f}\varepsilon_{IIf}R_j / R_{(H)}$$

where j is A, B and C excitons, R_i is the Rydberg constant of j excitons, $R_{(H)}$ is the Rydberg constant of the hydrogen atom, $\varepsilon_{\perp f}$ and ε_{IIf} are the dielectric constants taken from the infrared reflection.

Taking into consideration that the $M = m_V^* + m_C^*$ and $1/\mu = 1/m_V^* + 1/m_C^*$ the electron and hole effective masses are determined. For pair of band responsible for the formation of A excitonic series $mV_1^* = 0.86m_0$ and $mC_1^* = 0.14m_0$. For the pair of bands responsible for the formation of B excitonic series the effective masses are the following: $mV_2^* = 0.87m_0$ and $mC_2^* = 0.13m_0$ (fig.2 b). In this ref. both effective masses of the light holes $mV_2^* = 0.092m_0$ and the effective mass of holes in the spin-orbit split V_3 band $mV_3^* = 0.085m_0$ are provided. As it is seen, according to our data the effective mass mV_2^* is equal to $0.87m_0$, that is it practically corresponds to the mass mV_1^*. In order that the effective mass mV_2^* be equal to $0.092m_0$, it is necessary that the Rydberg constant of B exciton series be 0.017 eV, that is the binding energy of B excitons should be twice lower than energy binding of A excitons, In $CuInSe_2$ upper valence bands $\Gamma_7(V_1)$ and $\Gamma_6(V_2)$ are formed as a result of the Γ_4 state splitting by crystal-field (Fig.2). Since the band genesis is identical, consequently it would be more logical to consider that the effective masses should not differ by dozens of times. At R = 30.4 meV and $mC_1^* = 0.13m_0$, the effective mass mV_3^* is equal to $0.29m_0$ (Fig. 2).

Conclusion

The excitonic reflectivity spectra and the wave-length derivative reflection spectra have been investigated for $CuInSe_2$ crystals. The exciton binding energies and exact values of the band gaps of all three intervals $\Gamma_7 (V_1) - \Gamma_6 (C_1)$, $\Gamma_6 (V_2) - \Gamma_6 (C_1)$, $\Gamma_7 (V_3) - \Gamma_6 (C_1)$ have been also calculated.

References

[1] A. Shaukat, R.D. Sinph, J. Phys. & Chem. Solids 39 N12,1269, (1978).
[2] I.V. Bondar, A.P. Bologa, B.V. Korzun, Phys. St. Sol. B 109, K3L (1982).
[3] I.V. Bondar, A.P. Bologa, Cryst. Research and Technology 17, K109, (1982).
[4] J. E. Jaffe, A. Zunger, Phys.Rev. B 28, 5822, (1983).
[5] J.E. Jaffe, A. Zunger, Phys. Rev. B 29, N4, (1984).
[6] J.L. Shay, B. Tell, H.M. Kasper, L.M. Schiavone, Phys. Rev. B 7, N10, 4485, (1973).