

EXCITON-PHONON SPECTRA IN $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ CRYSTALS

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Abstract

In this work, the wave-length derivative reflection (WDR) spectra of $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ crystals have been investigated in the region of A, B and C series. The $n = 1$, $n = 2$ and $n = 3$ states are determined and centers of exciton lines ($n = 1$) are calculated. The parameters of excitons and bands have been determined for the region of band gap minimum.

Key words: excitons; reflection spectra; exciton-phonon spectra; band gap

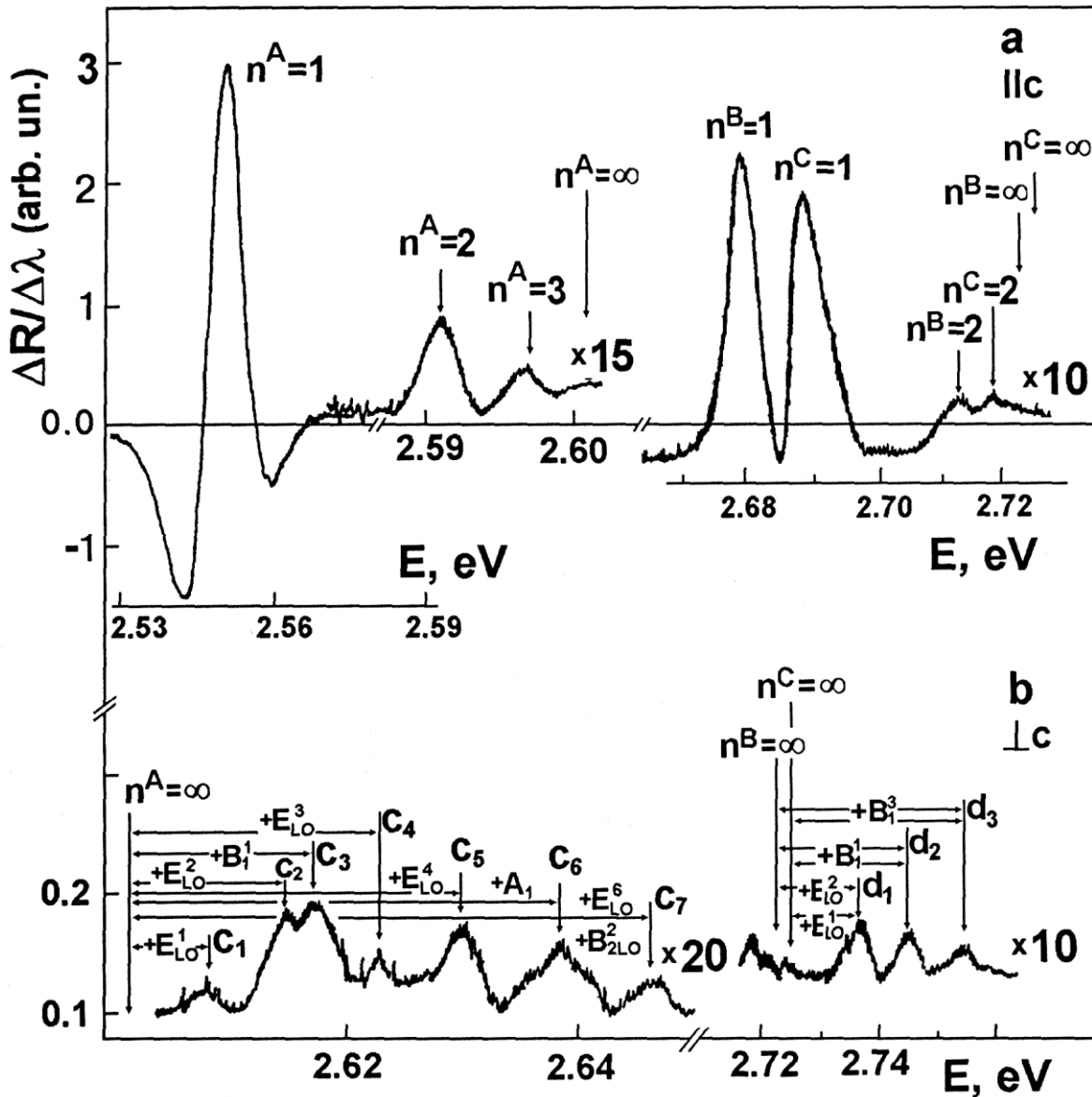
1. EXPERIMENTAL

The crystals under study were grown by the chemical transport method. The specimens had the shape of $\sim 5 \times 10 \text{ mm}^2$ plates with mirror surface and a thickness of 300 - 400 μm . WDR spectra were measured by using MDR-2 spectrometer. MDR-2 has a strength light 1:2,5. The size of diffraction gratings of 600 rulings per mm is $140 \times 140 \text{ mm}$, focal distance - 400 mm and provided resolution - 40 $\text{\AA}/\text{mm}$. The mirror vibrated at $\sim 73 \text{ Hz}$ near the exit slit and produced a $\sim 6 - 8 \text{ \AA}$ wavelength modulation. A modulated signal was registered by photomultiplier FEU-62 with a phase-sensitive detector Unipan-233. During the WDR measure, the samples were immersed in liquid nitrogen. An orientation error of the polarization vector of a light wave and of crystal axes did not exceed 5° .

2. RESULTS AND DISCUSSION

The materials $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ belong to group I-III-VI₂, crystallize in structure with spatial group $I4_2d - D_{2d}^{12}$. There is a great of research interest to materials of this group, as a result of this, an expected application in optoelectronic devices [1-3]. On the basis of these materials, converters of the solar energy are being developed. In λ -modulated reflection spectra of CuGaS_2 crystals (fig.1) the lines of $n = 1$ A, B and C excitons are found out at 2.5554 eV, 2.6819 eV and 2.6915 eV, respectively. The A excitonic series is permitted in $E \perp c$ polarization, and the B and C series are observed in both polarizations ($E \perp c$, $E \parallel c$). These lines have more large intensity in the $E \parallel c$ polarization. The energy positions of $n = 1$ lines for all three series are in good agreement with reference data [4-6]. In the short-wave region of the $n = 1$ line of A excitons there are two additional lines at the 2.5925 and 2.5983 eV (fig.1). These lines are caused by the excited condition ($n = 2$ and $n = 3$) of the A excitonic series. Based on the energy position of these lines the binding energy of A excitons and minimum energy interval responsible for the A exciton series are determined. For this series the Rydberg constant is equal to 41.8 meV and the energy of interband transition (continuum energy) equals to 2.6029 eV. From fig.1 it is seen, that for B and C exciton series the $n = 2$ and $n = 3$ lines are distinguished with the good resolution. Proceeding from these data the Rydberg constants of B and C excitons are determined, which are equal to 44.8 and 36.8 meV. The band gaps for B and C series are equal to 2.7267 and 2.7283 eV.

In λ -modulated reflection spectra of CuGaS_2 crystals the structure of weak bands $C_1 - C_7$ is observed in the shortwave side of A exciton series. These bands are caused by direct transitions into the 1S states of


 Fig.1. WDR spectra of CuGaS₂ crystals

of excitons with the simultaneous emission or absorption of optical phonons. Found out C₁, C₂ and C₃ bands are distanced from transition $\Gamma_7(V_1) - \Gamma_6(C_1)$ on 8.6, 11.3 and 17.1 meV, respectively and are caused by the $\Gamma_7(V_1) - \Gamma_6(C_1)$ transitions with emission of the E_{LO}^1 , E_{LO}^2 and B_1^1 phonons, respectively (fig.1). The bands C₄ - C₇ are shifted from the $\Gamma_7(V_1) - \Gamma_6(C_1)$ transitions on the energy values of E_{LO}^3 , E_{LO}^4 , A_1 and E_{LO}^6 (B_{2LO}^2) phonons, respectively.

In area of energies $E > E_g^B$ and $E > E_g^C$ the bands d₁ - d₃ are revealed, which are caused by transitions $\Gamma_6(V_2) - \Gamma_6(C_1)$ and $\Gamma_7(V_3) - \Gamma_6(C_1)$ with emission of E_{LO}^1 (E_{LO}^2), B_1^1 and B_1^3 phonons, respectively. Also, the same exciton-phonon bands are observed in solid solutions CuIn_{1-x}Ga_xS₂.

In solid solution CuIn_{1-x}Ga_xS₂ the energy location of $n = 1$ lines for A, B and excitons change nonlinear at composition (X) changing (fig.2, dashed curves). The deviation from linearity is observed also for band gaps $\Gamma_7(V_1) - \Gamma_6(C_1)$, $\Gamma_6(V_2) - \Gamma_6(C_1)$ and $\Gamma_7(V_3) - \Gamma_6(C_1)$. The binding energies of all three series changes linearly. The dependence of both energy intervals $V_1 - C_1$, $V_2 - C_1$, $V_3 - C_1$ and energy of a $n = 1$ exciton line from composition X is described by expression:

$$E_g(X) = E_g^1 X + E_g^2(1 - X) - cX(X - 1)$$

where E_g^1 and E_g^2 is the band gap of CuGaS_2 and CuInS_2 , respectively, c - factor of nonlinearity. For considered solid solutions this factor equals to 0.462. The deviation from linearity for excitonic lines also is determined by this expression. Thus, to E_g^1 there corresponds the $n = 1$ line energy of the A exciton for CuGaS_2 , and to E_g^2 - the $n = 1$ line energy of the A exciton for CuInS_2 . The similar account was carried out for B and C excitons.

In crystals CuInS_2 the value of binding energy (R) for A excitons is more than for B (C) excitons. In CuGaS_2 crystals the binding energies of A, B and C series differ insignificantly. The dependence of binding energies of excitonic series from composition of solid solutions X is presented in fig.2.

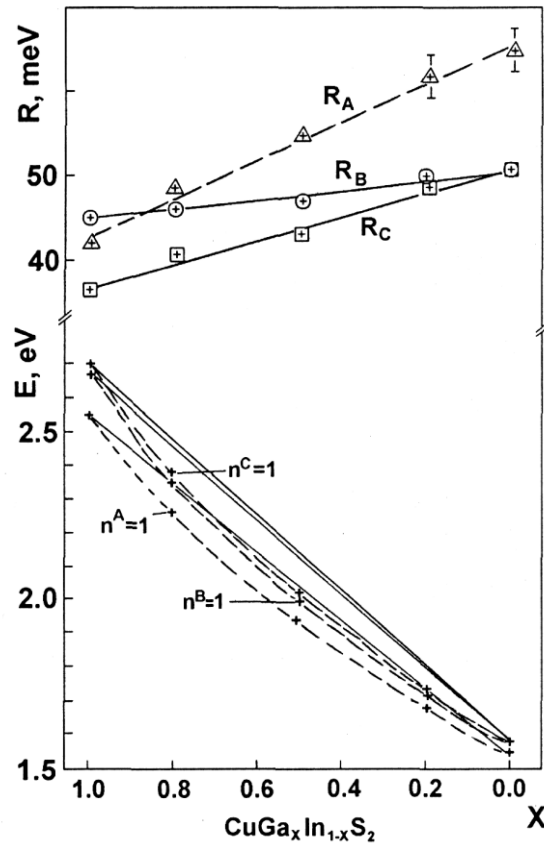


Fig.2. Compositional dependences of Rydberg constants and exciton lines $n = 1$

In λ -modulated reflection spectra (WDR) of $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ solid solutions the features $n = 1$, 2 and 3 for A, B and C excitonic series are revealed. The energy positions of $n = 1$ lines and calculated values of the splitting due to the crystal-field (Δ_{CF}) and spin-orbit interaction (Δ_{SO}) change nonlinear with the changing of composition X . The WDR spectra contours for lines $n = 1$ of the A, B and C excitons have been calculated taking in consideration spatial dispersion and dead-layer (t) (table 1). These calculations have shown, that the exciton translational mass ($M(m_0)$) is increased from 0.9M (CuGaS_2) up to 3.0M (CuInS_2) and the damping factor γ has higher values in the solid solutions, than in the end-member compounds (i.e. CuGaS_2 and CuInS_2). On the basis of obtained values of both translational masses $M(m_0)$ and Rydberg constants the effective masses of electrons m_{c1}^* and holes m_{v1}^* , m_{v2}^* and m_{v3}^* (fig.3) are determined for A, B and C excitonic series.

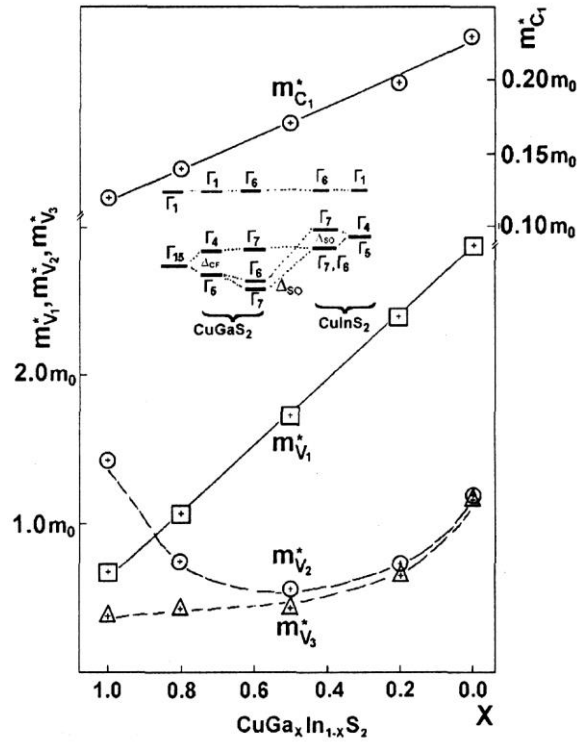


Fig. 3 Compositional dependences of the effective masses

Table 1

Results obtained from calculations of WDR spectra of solid solutions $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ in frames of classical model in view of spatial dispersion and dead-layer.

	Parameters	Composition				
		X = 1.0	X = 0.8	X = 0.5	X = 0.2	X = 0.0
A exci- ton	ω_0, eV	2.550	2.252	1.941	1.700	1.554
	ω_{LT}, meV	6.0	4.2	5.0	6.0	0.5
	γ, meV	10.0	23.0	12.0	13.0	9.6
	$\varepsilon'', \varepsilon^\perp$	6.0	6.1	6.4	6.65	6.93
	t, Å	2.0	3.0	100	110	60
	M	0.9	1.3	2.0	2.8	3.0
	μ^A	0.105	0.124	0.153	0.181	0.230
	μ^B	0.111	0.118	0.132	0.154	0.182
	μ^C	0.091	0.106	0.122	0.152	0.182
	M(m_0)	0.8	1.2	1.9	2.6	3
	$m_{c1}^* (m_0)$	0.12	0.14	0.17	0.196	0.23
	$m_{v1}^* (m_0)$	0.68	1.06	1.73	2.40	2.87
	$m_{v2}^* (m_0)$	1.44	0.75	0.59	0.72	1.2
	$m_{v3}^* (m_0)$	0.39	0.44	0.43	0.68	1.1

The electron mass m_{c1}^* changes linearly from 0.12 m_0 (CuGaS₂) up to 0.23 m_0 (CuInS₂). In a wider interval changes the hole mass m_{v1}^* being increased from 0.68 m_0 (CuGaS₂) up to 2.87 m_0 (CuInS₂). The original nonlinear charge is observed for masses m_{v2}^* and m_{v3}^* .

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