Exciton Spectra of $AgAsS_2$ Crystals

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***Abstract* – Reflectivity and wavelength modulated reflectivity spectra of $AgAsS_2$ crystals are investigated in the region of exciton resonances. The exciton and energy band structure parameters were determined.**

***Index Terms* – Reflectivity, modulated reflectivity spectra, energy band structure, exciton spectra**

I. INTRIDUCTION

$AgAsS_2$ crystals belong to layered materials with different anisotropy degree of interatomic interaction forces. $AgAsS_2$ compound crystallizes in a monoclinic lattice with $C_{2/c} - C_{2h}^6$ spatial group. The lattice parameters are as following: a - 17.23, b = 7.78, c= 15.19Å, β- 101°12'. Unit cell contains 24 formula units (Z=24), while the primitive Bravias lattice contains 12 units (Z=12). Smithite crystal structure belongs to the C_c — C_s^4 spatial group. In $AgAsS_2$ crystals interatomic interaction forces are divided into strong intramolecular (intralayer) forces and weak intermolecular (interlayer) forces. In these crystals, it was possible to distinguish the splitting of vibrational modes caused by intralayer and interlayer interaction and to define the splitting of vibrational modes by the double Davydov resonance. Effective Szigeti charge, dynamic effective Born charge, cation and anion relative ionic charges were defined. $AgAsS_2$ crystals grown in ampoules by chemical vapor transport method represent plates with mirror surface 2.5x1.0 cm^2 with thickness of 300-400 μm. The surfaces of some plates were parallel to the C axis. Reflection spectra and wavelength modulated reflection spectra were measured by the MDP-2 spectrometer. For low-temperature measurements the samples were mounted on the cold station of a LTS-22 C 330 optical cryogenic system.

II. EXPERIMENTAL TECHNIQUE AND RESULTS

The edge absorption edge of $AgAsS_2$ crystals at room temperature for E||c and E⊥c polarization is different. The absorption edge for E||c and E⊥c polarization at photon energies energy E ≥ 2,3eV increases rapidly and crystals with thickness of few microns become opaque (fig. 1). $AgAsS_2$ absorption edges are shifted to higher energies with decreasing temperature. The temperature shift coefficient $\beta=\Delta E/\Delta T$ for E||c and E⊥c polarization is equal to $3{,}1\times10^{-4}$ eV/K. The E_g^A and E_g^B absorption bands are observed at energies of 2,358eV and 2,402eV in the transmittance spectra of crystals with thickness d = 5,7 μm measured in E||c polarization (fig. 1). For E⊥c polarization, the E_g^C and E_g^D absorption bands are observed at energies of 2,445eV and 2,510eV, respectively. The character of changes in the spectra of edge transmittance (absorption) gives evidence that the absorption edge is formed by direct allowed transitions. The anisotropy of edge absorption is due to direct polarized electronic transitions which take place in accordance with the selection rules for electronic transitions of C_{2h}^6 symmetry group crystals. The four observed maximums of transmittance (absorption) spectra in the region of the intrinsic absorption for E||c and E⊥c polarization are due to electronic transitions from the V1 and V2 valence bands to the C1 and C2 conduction bands in the center of the Brillouin zone. The energy values of 2,358 eV, 2,402 eV, 2,358 eV and 2,402 eV define the minimal energy intervals between V1-C1, V2-C1, V1-C2 and V2-C2 bands, respectively.

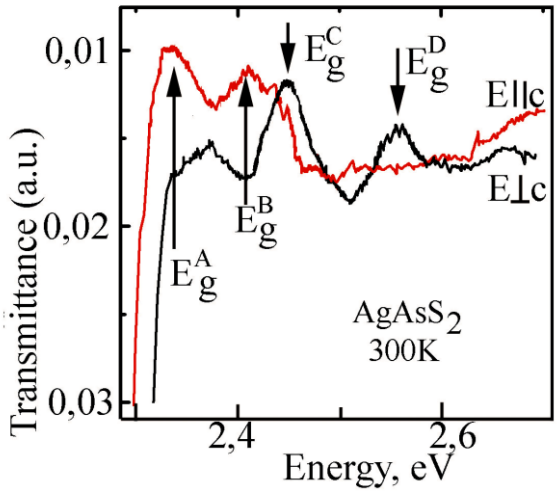

Fig.1. Transmittance spectra of $AgAsS_2$ crystals at 300K with E||c and E⊥c polarization (crystal thickness of 78μm - curves p1,p2,p3; crystal thickness of 54μm -curve p4; crystal thickness of 4,5μm - curve p5).

Absorption spectra at 300K and 10K (spectra are discussed below) give evidence that the fundamental bandgap is formed by direct allowed transitions. The exciton binding energy is small (12,3meV) and the excitons are dissociated at room temperature. The anisotropy of the absorption edge at 2.3 eV is due to the presence of polarized electronic transitions which take place in accordance with the selection rules for electronic transitions of C_{2h}^5 symmetry group crystals [1-2]. The transitions are split due to crystal field. At the same time, there is a splitting due to the spin-orbit interaction.

Low-temperature measurements showed that the fundamental bandgap is formed by direct allowed transitions. The fine structure of the wavelength modulated optical reflection spectra was investigated in the fundamental absorption edge region at the temperature of 10K. For the first time, the ground and excited states of four exciton series A, B, C and D were observed. Series A were observed for E||c polarization with the ground state n=1 at 10K at the energy of 2,3975eV and with the excited state n=2 at the energy of 2,4075eV. The Rydberg constant is equal to 13,3meV and the minimum bandgap is equal to

2,4108eV. Exciton series B, C and D are situated in the short-wavelength interval. For exciton series D the minimum bandgap is equal to 2,5792eV. The Rydberg constant is equal to 24,4meV. Therefore, the exciton binding energy is small (13,3meV and 24,4meV), and they are dissociated at room temperature. Consequently, the structure of the polarized electronic transitions can be discussed within the framework of the selection rules for electronic transitions without taking into account the symmetry of exciton states.

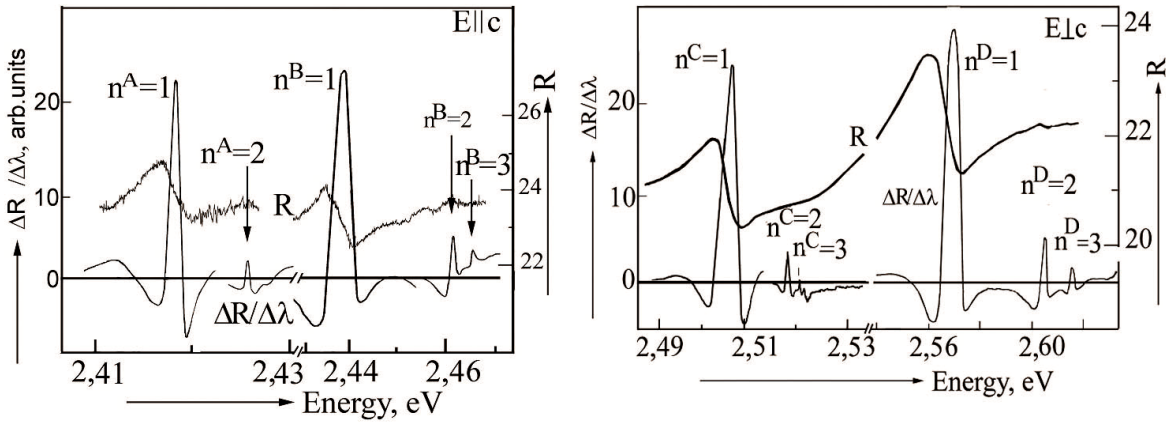

Fig.2 Reflection spectra and wavelength modulated reflection spectra of $AgAsS_2$ crystals in E||c and E⊥c polarization at 10K.

The lines n=1 were observed in the reflection spectra of $AgAsS_2$ crystals at the temperature of 10K and E||c polarization (ω_t = 2.417eV, ω_L = 2.418eV, see Fig.1). For this polarization type, the excitons of $\Gamma_2^-(z)$ symmetry are active for crystals of C_{2h} symmetry. The reflection spectra in the region of the line n=1 has a usual exciton form with a maximum and a minimum. These features are due to the presence of transverse and longitudinal excitons. Based on these data the energy of longitudinal-transverse splitting of $\Gamma_2^-(z)$ excitons was estimated to be equal to 1meV. In the spectral dependence of the wavelength modulated reflection (fig.2), the intensive lines were defined at the energy levels of 2,4175eV and 2,4275eV which are due to the states n=1 and n=2 of the hydrogen-like $\Gamma_2^-(z)$ exciton series. The Rydberg constant determined from the energy position of the lines n=1 and n=2 (fig.1) for these exciton series is equal to 13,3meV. The energy continuum (E_g, $n = \infty$) is equal to 2.4108 eV. A maximum and minimum of reflection with a weak change in the intensity of the reflection (2%) are detected for E⊥c polarization in the reflection spectra at the energies 2,439 – 2,440eV. Intensive features are revealed in the wavelength modulated reflection spectra at the energies 2,4396eV, 2,4642eV and 2,4682eV which are due to the states n=1, n=2 and n=3 of excitons with $\Gamma_2^-(z)$ symmetry. The Rydberg constant for these exciton series obtained from the calculation according to the energy position of the ground and excited states is equal to 32,8meV. The energy continuum (E_g, $n = \infty$) is equal to 2.4724 eV (fig.2).

TABLE 1. EXCITON PARAMETERS OF $AGASS_2$ CRYSTALS

		A(eV)	B(eV)	C(eV)	D(eV)	Δ_{cf}(meV)	Δ_{so}(meV)
Exciton	n=1	2.418	2.440	2.509	2,575	-0.002	151
state	n=2	2.428	2.464	2.520	2,593		
	n=3		2,468	2,522	2,597		
	R	0.013	0.032	0.015	0,024		
E_g 10K	(n=∞)	2.431	2.472	2.450	2,529	-49.6	149
E(min.T) 300K		2,358	2,402	2,445	2,510		

A maximum at 2,505eV (transverse exciton) and a minimum at 2,508eV (longitudinal exciton, fig.3) are observed in E⊥c polarization. Longitudinal-transverse splitting of Γ_5 exciton is equal to 2,0meV. This hydrogen-like series detected in the E⊥c polarization (conventionally named C- Series), in accordance with the selection rules [1-3], can be formed by the states of orthoexciton with $2\Gamma_1^- + \Gamma_2^-$ symmetry. These states are forbidden in the electric quadrupole approximation. The lines n=1, n=2 and n=3 at the energies 2,5089eV, 2,5199eV, 2,5201eV, respectively, are observed in the wavelength modulated reflection spectra. Taking into account the energy position of the ground state n=1 and excited state n=2, the exciton series C binding energy is equal to 14,6meV and the continuum (E_g, $n = \infty$) is equal to 2,5235eV. A maximum and a minimum of the reflection spectra are found at the energies of 2,566eV and 2,572eV in the short-wavelength region of the C-series for E⊥c polarization. In the wavelength modulated reflection spectra, the features are observed at the energies of 2,5752eV, 2,5932eV and 2,5970eV, which are due to the states n=1, n=2 and n=3 of excitons series D with $2\Gamma_1^- + \Gamma_2^-$ symmetry, respectively. The Rydberg constant of these exciton series is equal to 24,4meV from the calculation of the lines n=1 and n=2 energy position. The continuum (E_g, $n = \infty$) of these series is equal to 2,5992eV.

TABLE 2. EXCITON PARAMETERS AND ENERGY BAND PARAMETERS OBTAINED FROM THE CALCULATIONS OF THE OPTICAL REFLECTION SPECTRA AND WAVELENGTH MODULATED REFLECTION SPECTRA OF $AGASS_2$ CRYSTALS

E‖c, 10K, $\varepsilon_\infty = 7.4$			E⊥c, 10K, $\varepsilon_\infty = 7.26$	
Parameters	A	B	C	D
ω_0, eV	2.411	2.439	2.506	2.566
ω_{LT}, meV	1	1	2	4
γ, meV	0.2	0,2	0.16	0,5
M, m_0				1,5
R, eV	0.013	0.032	0.015	0.024
μ, m_0	0.054	0,129	0.06	0,093
m_C^*, m_0	0.1	0.1	0.1	0,1
m_V^*, m_0	0,12	0.44	0.14	1,4

In the region of exciton resonance, the reflection coefficient is equal to 0,22-0,23 and ε_d changes in the interval 7,26-7,4. The value of the background dielectric constant near the exciton resonance was used in calculations. With ε_d = 7.4, the effective mass $\mu = \varepsilon_b^2 R/R_H$ equal to $0.054m_0$ was obtained for the most long-wavelength exciton, where R (0,013eV) is the Rydberg constant for Γ_2^-(z)-exciton and R_{H_2} is the Rydberg energy of hydrogen atom (13,6eV). The Bohr radius (a_B) of the S-State for Γ_2^-(z)-exciton is equal to 0.3×10^{-6} cm^{-1}. With ε_d = 7.4, the effective mass $\mu = \varepsilon_b^2 R/R_H$ of B-excitons with Γ_2^-(z)-symmetry is equal to $0.129m_0$, the exciton binding energy being equal to R =0.032eV. The Bohr radius (a_B) of the S-State for Γ_4-exciton is equal to $0,21\times10^{-6}$ cm^{-1} (table 2).

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