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Exciton spectra and energy band structure of $CuAlS_2$ crystals

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ABSTRACT

Three exciton series are investigated in the reflectivity spectra of $CuAlS_2$ crystals at the temperature of 10 K. The $n^A=1$ ($\omega_T=3.543$ eV, $\omega_L=3.546$ eV) and $n^A=2$ (3.565 eV) lines of the Γ_4 (A-series) excitons are observed in the $E\|c$ polarization. In the $E\perp c$ polarization, the Γ_5 excitons ($n^B=1$ at 3.668 eV and $n^B=2$ at 3.686 eV) of the B-series, and $n^C=1$ at 3.813 eV of the C-series are observed. The parameters of the excitons and the more exact values of the $\Gamma_7-\Gamma_6$, $\Gamma_6-\Gamma_6$, and $\Gamma_7-\Gamma_6$ energy gaps are determined. The crystal field and spin–orbit splitting of the valence band is calculated. The electron (m^*_{c1}) and hole (m^*_{V1}, m^*_{V2}, and m^*_{V3}) effective masses have been estimated.

1. Introduction

The $CuAlS_2$ compound belonging to the I–III–VI_2 materials crystallizes in the chalcopyrite structure with the $I\bar{4}2d-D^{12}_{2d}$ space group and it is the most wide bandgap material from this group. The I–III–VI_2 crystals are of interest from the point of view of their implementation in optoelectronic devices [1,2]. Solar cells are successfully developed on the basis of materials from this group [3–9]. Thin film device structures were obtained on some of these materials. The photoelectrical properties of surface barrier structures have been investigated [4,5]. The energy band structure of I–III–VI_2 chalcopyrites is calculated as for nearest analogs of binary compounds with zincblende structure (ZnSe, ZnS) [10–12]. All the crystals from the I–III–VI_2 group are characterized by strong anisotropy of optical properties in the region of fundamental absorption [13–29]. Many of chalcopyrite compounds are obtained by molecular beam epitaxy in the form of epitaxial layers, including the $CuAlS_2$ compound [13]. The $CuGaS_2$–$CuAlS_2$ structures are interesting for the development of new optical devices for the green and blue spectral ranges. There is a relatively small mismatch of crystal lattices (0.4%) and a relatively big difference in the bandgaps of $CuGaS_2$ and $CuAlS_2$ crystals in this system.

In this paper we investigate the optical spectra of $CuAlS_2$ crystals in the exciton region. The energy positions of $n=1$ and $n=2$ lines of the three A-, B-, and C-exciton series are determined. The exciton binding energy and the more precise values of the $\Gamma_7-\Gamma_6$, $\Gamma_6-\Gamma_6$, and $\Gamma_7-\Gamma_6$ energy gaps are determined. The crystal field and spin–orbit splitting of the valence band are calculated. The electron (m^*_{c1}) and hole (m^*_{V1}, m^*_{V2} and m^*_{V3}) effective masses are estimated. The contours of the exciton reflectivity spectra are calculated according to the one-oscillator model of the dispersion relations.

2. Experimental

$CuAlS_2$ crystals in the form of plates with 2.5×8 mm^2 mirror-like surfaces and thickness of 1–2 mm were grown by chemical vapor transport. The surfaces of some plates are parallel to the C-axis. The orientation of crystals was determined according to X-ray diffraction data. The optical reflectivity and luminescence spectra were measured with a double SDL-1 spectrometer. For the low temperature measurements the samples were mounted on the cold station of an LTS-22 C330 optical cryogenic system. The luminescence spectra were excited by the 325 nm line of a Melles Griot He–Cd laser.

3. Results and discussions

According to theoretical calculations of energy band structure [10–12], the minimum inter-band gap is formed by direct electron transition in the center of the Brillouin zone. The lower conduction band is of Γ_6 symmetry, while the upper V_1, V_2, and V_3 valence bands are of Γ_7, Γ_6, and Γ_7 symmetries, respectively.

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From group theoretical arguments and direct product of the group representations, the interaction of a hole from the Γ_7 band with an electron from the Γ_6 band leads to the formation of intrinsic excitons with ground states of Γ_3, Γ_4, and Γ_5 symmetries ($\Gamma_6\times\Gamma_7=\Gamma_3+\Gamma_4+\Gamma_5$). The Γ_4 exciton transition is allowed in $E\|c$ polarization, the Γ_5 exciton transition is allowed in $E\perp c$ polarization, whereas the Γ_3 exciton transition is forbidden in both polarizations. The interaction of a hole from the Γ_6 band with an electron from the Γ_6 band leads to the formation of three exciton series with Γ_1, Γ_2 and Γ_5 symmetries. The Γ_5 excitons are allowed, while Γ_1 and Γ_2 excitons are forbidden in $E\perp c$ polarization according to the selection rules.

The $n^A=1$ ($\omega_T=3.543$ eV, $\omega_L=3.546$ eV) and $n^A=2$ (3.565 eV) lines of the Γ_4 exciton hydrogen-like series are observed in the reflectivity spectra of $CuAlS_2$ crystals measured at 10 K in the $E\|c$ polarization (Fig. 1). The reflectivity spectra in the region of the $n^A=1$ line are of a usual excitonic shape with a maximum at 3.543 eV and a minimum at 3.546 eV. These peculiarities are due to the presence of the transversal and longitudinal excitons. A longitudinal-transversal exciton splitting of 3 meV is estimated for the Γ_4 excitons from these data. A Rydberg constant of 32 meV is determined for the Γ_4 exciton series from the position of $n^A=1$ and $n^A=2$ lines (Fig. 1). The energy of the continuum (E_g, $n=\infty$) is equal to 3.575 eV. These energy values of the ground ($n^A=1$) and excited ($n^A=2$) states of excitons are in accordance with previously reported values of 3.534 and 3.665 eV, measured at 77 K [14–16].

The background dielectric constant has been estimated from the measurements reflectivity in the IR (400 cm^{-1}) and near-IR (12,000 cm^{-1}) regions.

$$\varepsilon_b=\left|\frac{1+\sqrt{R}}{1-\sqrt{R}}\right|^2$$

The reported value of ε_b in $CuAlS_2$ crystals equals 7.05 in the ($E\|c$) polarization and 8.14 in the ($E\perp c$) polarization far from the exciton resonances ($\nu=3000$–4000 cm^{-1}) [26]. According to our data, the reflection coefficient at quantum energies lower than the energy of exciton resonances is $R=0.21$ for ($E\|c$) polarization. The calculated value of $\varepsilon_b(E\|c)$ is 7.26. With this value of ε_b and Rydberg constant $R=0.032$ eV, the Γ_4-excitons reduced mass equals to $\mu=(\varepsilon_b^2)R/R_H=0.11m_0$, where R_{H_2} is the Rydberg energy of the hydrogen atom (13.6 eV). The Bohr radius (a_B) of the S-state of the Γ_4-exciton equals 0.3×10^{-6} cm.

A maximum at 3.668 eV (transversal exciton) and a minimum at 3.670 eV (longitudinal exciton) are observed in the $E\perp c$ polarization for the $n^B=1$ Γ_5 exciton series (Fig. 1). The longitudinal–transversal splitting of the Γ_5 exciton equals 2.0 meV. The $n^B=2$ excited exciton state is observed at 3.687 eV. The binding energy of the Γ_5 exciton equals 25 meV, and the energy of the continuum equals 3.693 eV. The C-exciton is observed at 3.813 eV($n^C=1$) in the same polarization. A band at 4.39 eV was observed at 77 K in the energy interval of 3.6–4.98 eV. Since no other lines were observed between the 3.665 and 4.39 eV at 77 K, the 4.39 eV band has been associated with C-exciton series [16]. As mentioned above, a line at 3.813 eV is observed in the reflectivity spectrum (Fig. 1). Taking into account these data and the exciton spectra of $CuGaS_2$ crystals [23–29], we assume that the 3.813 eV line is related to the ground state of the C-exciton.

For the B-exciton series, the reflection coefficient measured in the ($E\perp c$) polarization equals 21% at 3.6 eV, and the dielectric constant $\varepsilon_b(E\perp c)=7.2$. The calculated Γ_5-exciton reduced mass equals $0.09m_0$ with the exciton binding energy of 25 meV. One should note that the values of $\varepsilon_b(E\|c)$ and $\varepsilon_b(E\perp c)$ are very close to each other in the region of exciton resonances, in contrast to a bigger difference observed far from the exciton resonances ($\nu=3000$–4000 cm^{-1}) [26]. This is because the exciton resonances are close to the optical isotropic wavelength [30].

A weak luminescence is observed at 200 K in $CuAlS_2$ crystals under the excitation by the 325 nm line of a He–Cd laser. The luminescence intensifies with decreasing temperature to 100 K, and further to 10 K (Fig. 2). A broad photoluminescence band is observed at 10 K around 3 eV, along with two narrow bands around 3.3 eV and a band at 3.54 eV. The band at 3.54 eV is assumed to be related to the recombination of Γ_4 exciton polaritons, while the narrow lines are due to the recombination of donor–acceptor pairs (DAP) (Fig. 2).

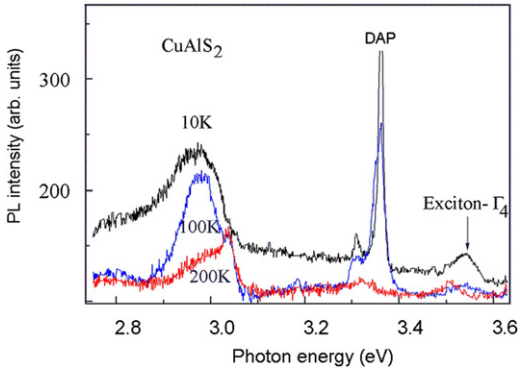

Fig. 2. The luminescence spectra of $CuAlS_2$ crystals excited by the 325 nm line of a He–Cd laser measured at different temperatures.

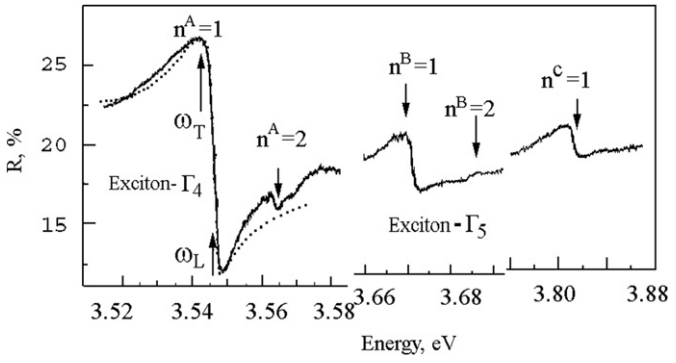

Fig. 1. Optical reflectivity spectra of $CuAlS_2$ crystals. The dot-line is the result of calculation of the reflectivity contour of the $n=1$ line of the Γ_4 exciton taking into account the spatial dispersion, i.e. limited value of the exciton mass M, and the boundary conditions.

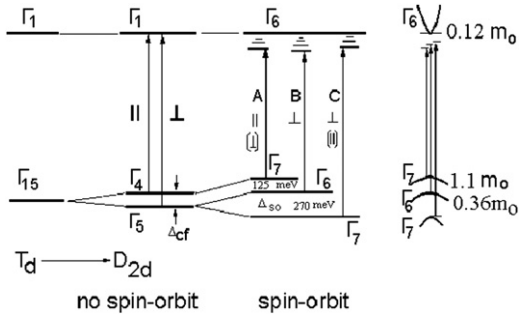

Fig. 3. Band structure at the Γ point showing the transition from zincblende (T_d) to chalcopyrite (D_{2d}) structure for the $CuAlS_2$.