J. Phys. D: Appl. Phys. **2020** https://doi.org/10.1088/1361-6463/ab6f1a IF= 2.829

The *g*-factor of $CuGaSe_2$ studied by circularly polarised magneto-reflectance

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Abstract

High structural quality single crystals of $CuGaSe_2$ were studied using photoluminescence (PL), optical reflectivity (OR) and circularly polarised magneto-reflectance (MR) at 4.2 K in magnetic fields B up to 14 T. At B = 0 T both the PL and OR spectra exhibited the A free exciton, associated with the uppermost sub-band of the valence band of $CuGaSe_2$ split by the tetragonal distortion in the lattice. The magnetic field induced a blue shift of the exciton in the MR spectra. Analysis of the dependence of the spectral position of the A exciton on B in the MR spectra, measured for both right and left circular polarisations of light, enabled the magnitude of its effective g-factor to be determined $|g| = 0.46$.

Introduction

$CuGaSe_2$ is a semiconductor with chalcopyrite lattice structure [1]. Changing the [Ga]/[Ga+In] ratio in $Cu(In,Ga)Se_2$ (CIGS), the alloy of $CuGaSe_2$ with $CuInSe_2$, provides the opportunity to tune the bandgap (E_g) from 1.7 eV (E_g for $CuGaSe_2$ [2]) to 1 eV (E_g for $CuInSe_2$ [3]). As a result, solar cells with the structure ZnO/CdS/CIGS/Mo/glass, where the E_g of the CIGS absorber layer is optimised to match the solar spectrum, have taken the lead in terms of conversion efficiency for single junction thin film solar cells [4]. Despite this significant achievement, many basic parameters of the electronic structure of $CuGaSe_2$ are only known from theoretical studies [5] or not known at all. One of these parameters is the Lande g-factor, which quantifies the Zeeman splitting of lines in the optical spectra under the influence of magnetic fields B. The value of g is important for understanding the electronic properties of a semiconductor. It is also important for the development of the kp theory for the chalcopyrites in general and $CuGaSe_2$ in particular.

Optical spectroscopy is one of the most efficient techniques to determine the parameters controlling electronic structure in semiconductors [6]. This technique becomes much more accurate and informative where there are low concentrations of defects in the examined materials [7]. Low defect concentration is manifested by the appearance of sharp excitonic features in the optical spectra. Due to their small spectral width such excitonic features significantly improve the accuracy of optical measurements and allow analysis of fine changes in the optical spectra under the influence of magnetic fields [8]. In the weak magnetic field regimes, when the field is not strong enough to break the Coulomb forces between the electron and hole in the exciton, excitonic features in the optical spectra undergo a diamagnetic blue shift and are split paramagnetically by the Zeeman effect.

Recent improvements in the structural quality of the ternary chalcopyrites and their solid solutions resulted in a significant reduction of the width of the excitonic features in the optical spectra facilitating examination of the electronic properties in these materials using the optical spectroscopy of their excitons [9-12]. Measurements of the diamagnetic shifts and paramagnetic splitting were reported for the A and B free excitonic lines in magneto-photoluminescence (MPL) spectra of $CuInSe_2$ enabling the determination of the rate of diamagnetic shifts and g-factors in this material [13]. MPL and magneto-reflectance (MR) helped to determine the rate of diamagnetic shifts of the A [14] and B [15] free excitons, respectively, in the optical spectra of high structural quality single crystals of $CuGaSe_2$. However, the application of magnetic fields did not result in a splitting of the free exciton features in such spectra suggesting that g-factors in $CuGaSe_2$ are much smaller than the spectral width of the A and B exciton lines. Circularly polarised magneto-optical spectroscopy can solve this problem by making possible a separate analysis of the optical spectra for the right RCP (σ^-) and left LCP (σ^+) circular polarisations of light [16].

In this study we examine high structural quality $CuGaSe_2$ single crystals using PL and circularly polarised MR at 4.2 K for magnetic fields up to 14 T.

Analysis of the dependence of the spectral position of the A free exciton on the magnetic field in the MR spectra for the RCP and left LCP enables us to determine the rate of the diamagnetic shift and the magnitude of the effective *g*-factor for $CuGaSe_2$.

Experimental details

Single crystals of $CuGaSe_2$ were grown from the melt of a near stoichiometric mix of high purity Cu, Ga, and Se by the vertical Bridgman technique following the procedure often used to grow $CuInSe_2$ [17] but assuming a melting point of 1050° C [18]. The structural properties and the presence of secondary phases in the crystals were studied by x-ray diffraction (XRD) using a Brucker D8 ADVANCE diffractometer.

Freshly cleaved surfaces of the grown crystals were used for the optical studies. Magneto-optical properties of the crystals were examined in a 14 T superconducting magnet at the Laboratoire National des Champs Magnétiques Intenses (Grenoble, France) in the Faraday configuration (the sample surface is perpendicular to the magnetic field direction and to the direction of the excitation light). The MR measurements were carried out using a 100 W halogen tungsten lamp. The 515 nm line of a diode laser was used to excite PL emission. Optical fibres were employed to transmit the laser (for the PL measurements) or lamp (for the RF measurements) beams to a linear polariser mounted with a quarter-wave plate to circularly polarise the light. The polarisation character with respect to the magnetic field was alternated by changing the magnetic field direction to an opposite and was not calibrated. A lens was used to focus the beam to a 50 μm spot on the sample surface and collect the MR or PL signals. Optical fibres were then used to deliver the signal to the slits of a 0.3 m spectrometer with a 600 grooves per mm grating for the MR or 1800 grooves per mm grating for the PL measurements. The dispersed signal was detected by a liquid nitrogen cooled silicon CCD. The measurements were carried out with a spectral resolution of 0.2 meV. The orientation of the lattice structure of the measured crystals with respect to the magnetic field direction was not examined. More details on the experimental set up can be found elsewhere [16].

Results and discussion

According to the pseudo-binary diagram, reported in ref. [18] the solidification of $CuGaSe_2$, is peritectic. However high quality single crystals can be grown from the melt of a near stoichiometric mix of high purity Cu, Ga, and Se at slow cooling rates [14,15,19]. An X-ray powder diffraction pattern measured for the grown crystals, presented in Fig.1, shows chalcopyrite structure reflexes of $CuGaSe_2$ and does not exhibit any significant signs of secondary phases in the material. A Rietveld refinement curve and the difference curve between the experimental and theoretical patterns, also shown in Fig.1, demonstrate a good fit to the experimental data. According to the fit $CuGaSe_2$ crystallised in the *I*-42d chalcopyrite phase with unit cell parameters $a = 0.5613$ nm and $c = 1.1022$ nm. A 4.2 K PL spectrum of the $CuGaSe_2$ crystals, measured at zero field, is shown in Fig.2(a). The spectrum exhibits two sharp lines (A and BX) near 1.72 eV and two broader peaks DA1 and DA2 at 1.67 eV and 1.632 eV, respectively. The A and BX lines were earlier assigned to the A free and BX bound excitons [2,14].

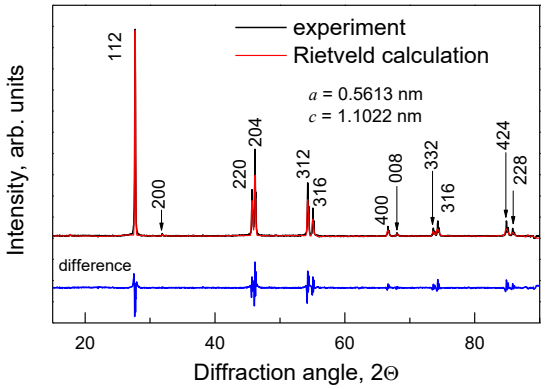

Fig.1. XRD pattern of the $CuGaSe_2$ crystals used for the PL and MR measurements.

Similar to other ternary compounds with the chalcopyrite structure the electronic energy band structure of $CuGaSe_2$ is strongly influenced by the hybridisation of the Cu *d*- and Se *p*-states [1,20]. The difference in the Cu-Se and Ga-Se bonding generates a tetragonal distortion τ, defined as $\tau = 1 - c/2a$, where c and a are the lattice constants. This distortion splits the valence band in the A, B and C sub-bands. The A free exciton represents the uppermost valence sub-band. The presence of the excitonic lines in the spectra confirms the high structural quality of the material and low concentration of defects in it. A positive tetragonal distortion of $\tau = 1.82\%$ in the studied crystals is very close to that reported in ref. [21].

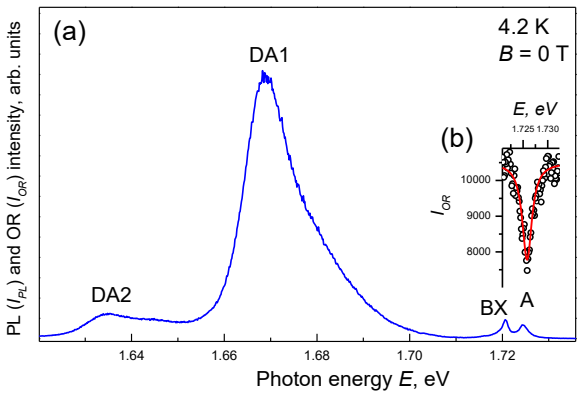

Fig.2. PL (a) and OR (b) spectra of the $CuGaSe_2$ crystals measured at zero field and 4.2 K (○ –experimental data, solid line – best fit).

The DA1 and DA2 peaks were also reported earlier and assigned to donor-acceptor pair recombination [22]. In this paper we focus on the A free exciton. The assignment of the free exciton recombination

mechanism of this line is supported by a free exciton resonance in the optical reflection spectrum shown in Fig.2(b).

Fig.3 exhibits the effect of magnetic fields on the MR spectra for magnetic fields at LCP (σ^+), in Fig.3(a) and RCP (σ^-), in Fig.3(b). For both polarisations the excitonic features are observed to blue shift with increasing fields.

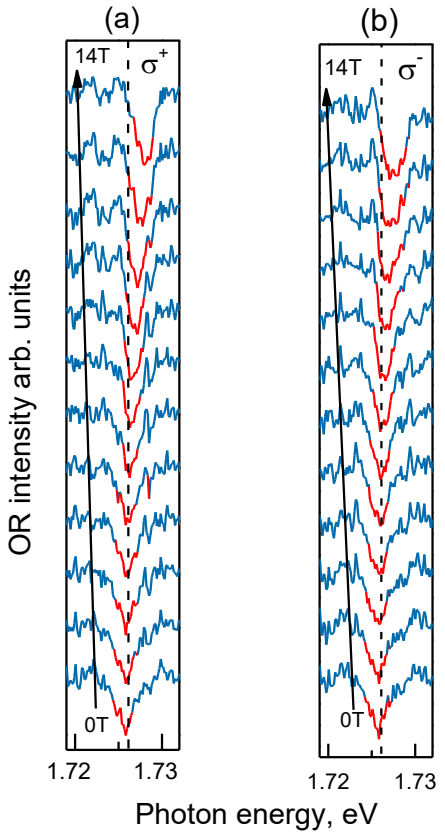

Fig.3. The effect of magnetic fields on the spectral energy of the A free exciton in MR spectra with σ^+ (a) and σ^- (b).

For the spectral energy of the A exciton we took the minimum of the MR signal. This assumption introduces a systematic error to the spectral energy values. Such an error can be seen in Fig.2 where a comparison of the PL and OR spectra at 0 T is shown. However in this paper we use only values of relative shifts of the minimum under the influence of magnetic fields. To improve the accuracy of our analysis we (purely empirically) fitted the OR dips with Lorentzian shapes. An example of such fitting is shown in Fig.2(b).

The dependence of the spectral position of the A exciton for both polarisations is shown in Fig. 4(a). It can be seen that the rates of the blue shift for different circular polarisations of light are not the same. Optical excitation of $CuGaSe_2$ by circularly polarised light generated spin polarised charge carries forming excitons with spin projections corresponding to that of the light. It can be seen in Fig.4(a) that at zero field excitons with opposite spin projections are energetically degenerate whereas the application of magnetic fields induces energy differences in these excitonic resonances. In the weak magnetic field regime, the Coulomb forces between the electron and hole in the exciton are stronger than the tendency of the field to break them apart, so the Lorentz forces only deform the relative motion of the electron and hole in the exciton [23]. Such a deformation admixes *p*-type envelope functions (with the angular momentum $l = 1$) to an *s*-type wave-function (with $l = 0$) of the exciton so its angular momentum becomes proportional to B. Also the energy of a magnetic dipole in the field is proportional to B. Thus the energy of the exciton becomes quadratically dependent on B. It was shown in ref. [14] that for $CuGaSe_2$ a magnetic field can be considered as weak up to 14 T. Therefore the dependence of the A free exciton energy $E_{ex}(B)$ on the magnetic fields up to 14 T can be described by the combination of linear Zeeman and quadratic diamagnetic terms [13,23]:

$$E_{ex}(B) = E_{ex}(0\mathrm{T}) \pm g\mu_B B/2 + s_d B^2, \qquad (1)$$

where $E_{ex}(0\mathrm{T})$ is the spectral energy of the exciton at zero field, μ_B the Bohr magneton, s_d the rate of diamagnetic shift and g is the effective Lande factor. For a free exciton the magnitude of such a factor includes *g*-factors for the electron g_e and hole g_h as $|g| = |g_e + g_h|$.

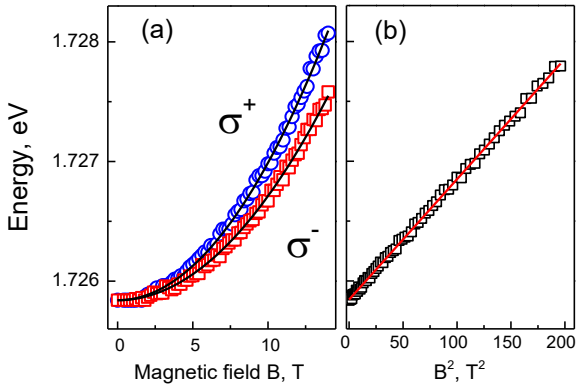

Fig.4. The experimental dependence of the spectral energy of the A free exciton on the magnetic field for LCP (σ^+) - ○ and RCP (σ^-) - □ (a). The dependence of the midpoint between the spectral energy of the A exciton for LCP and RCP (b). The solid lines are best fits.

The dependence of the midpoint between the spectral energies of the A exciton in the left and right circularly polarised spectra, plotted on a B^2 scale, is shown in Fig.4(b). A linear character of the dependence can be clearly seen. These experimental points were fitted with the quadratic term of the function in eq. (1) as shown in Fig.4(b). Such a fitting allowed determination of the value of s_d as (10.01 ± 0.03) μeV/T^2. The experimental points in Fig.4(a) for both polarisations were then fitted with the function in eq.(1), using the determined value of s_d. The fitting resulted in a magnitude of g, $|g| = 0.46 \pm 0.02$. The sign of g could not be determined because the probe was not calibrated.

The determined value of s_d is very close to that of 9.82 μeV/T^2, determined for the A exciton in MPL measurements [9], and to 9.85 μeV/T^2, determined for

the same exciton in MR experiments [15]. The difference can be attributed to variations in the orientation of the examined crystals.

The magnitude of g for $CuGaSe_2$ estimated here is significantly smaller than the average value of g =1.36 for the A free exciton in $CuInSe_2$, determined as $g = (g^{||} \cdot g^{\perp 2})^{1/3}$, where $g^{||}$ and $g^{\perp}$ are anisotropic values of g reported in ref. [13] for the direction of magnetic fields parallel and perpendicular to the tetragonal axis in $CuInSe_2$, respectively.

Conclusion

The effect of magnetic fields up to 14 T on the spectral position of the A free exciton (observed in MR spectra of non-oriented $CuGaSe_2$ single crystals for the right and left circular polarisations of light) was studied. The rate of diamagnetic shift for the A free exciton in $CuInSe_2$ single crystals was determined as 1.01 μeV/T^2 and the magnitude of the g-factor was estimated as $|g| = 0.46$.

Acknowledgement

The study was supported by the Russian Science Foundation (grant 17-12-01500) and LNCMI-CNRS (EMFL).

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