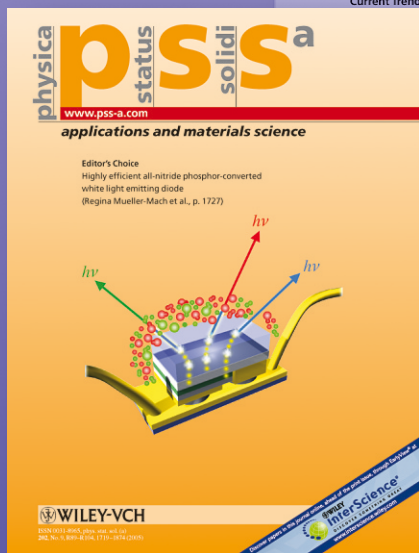


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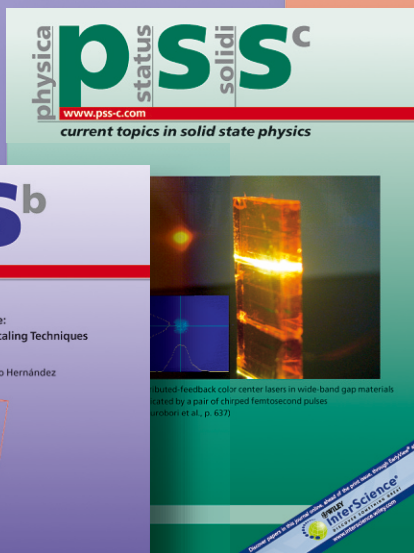
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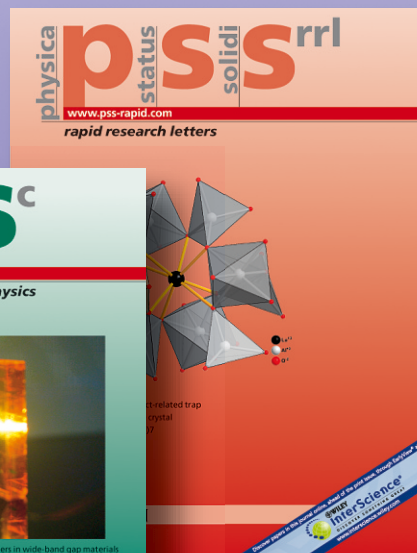
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Effects of magnetic fields on free excitons in CuInSe₂

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The effects of magnetic fields up to 20 T were studied in CuInSe₂ single crystals using photoluminescence (PL) at 4.2 K. Diamagnetic shifts of the free *A* and *B* excitons measured in the PL spectra in CuInSe₂ at 4.2 K under the magnetic fields were used to estimate the reduced masses (0.095*m*₀ for the *A*

and 0.098*m*₀ for the *B* exciton), binding energies (7.0 meV for the *A* and 7.2 meV for the *B* exciton) and Bohr radii (7.6 nm for the *A* and 7.3 nm for the *B* exciton) of the free-excitons in CuInSe₂ assuming that both excitons are isotropic and hydrogen-like.

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1 Introduction CuInSe₂ (CIS) is a promising chalcopyrite compound for the absorber layer of solar cells which are leading in terms of conversion efficiency and stability amongst thin-film photovoltaic devices. Despite a great potential and considerable amount of research carried out on this material the achieved efficiency of CIS-based solar cells, of about 20% [1], is significantly lower than 30%, the theoretical limit for one junction solar cell. This suggests a lack of understanding of the physical properties of this material.

Methods of optical spectroscopy of excitonic states provide rich and reliable information on the electronic structure and nature of defects in semiconductors. However in the case of CIS only a few studies [2–5] on excitonic states, where excitons in the PL spectra are well-resolved, and probably only one attempt to use magnetic fields for studying excitons [6] can be found in the literature to date.

In this study we analyse the effects of magnetic fields of much higher strength (*B*) than those reported in [6]. Also the excitonic features in the photoluminescence (PL) spectra are better resolved. The goal of this study is to measure diamagnetic shifts of free excitonic lines in the PL spectra of CIS and from the rates of these shifts estimate the reduced masses, binding energies and Bohr radii of the excitons. Reliable values of these parameters are important for further progress of the CIS-based solar cell technology.

2 Experimental High quality CuInSe₂ single crystals have been grown by the authors using the vertical Bridgman technique [7]. The elemental compositions of the samples measured by energy dispersive X-ray analysis (EDX) were very close to the ideal stoichiometry. Cleaved surfaces of the crystals were studied by photoluminescence (PL) at 4.2 K in a liquid helium bath cryostat. The 488 nm line of an Ar⁺ ion laser has been used as an excitation source for the PL measurements. Light from the laser was transmitted through a single-mode fiber and focused on the surface of the samples by two lenses. The PL signals from the samples were collected into a 0.6 mm diameter near-infrared optical fiber. The PL transmitted by the fiber was focused on the slits of a 1 m single-grating monochromator. A liquid nitrogen cooled near-infrared photomultiplier tube Hamamatsu R5509/1368 was used as a detector. Magnetic fields up to 20 T were generated by a resistive magnet in Grenoble High Magnetic Field Laboratory. The *K*-vector of the incident light was parallel to the magnetic field (*B*) in all experiments. The spectral resolution of the measurements was about 0.1 meV.

3 Results and discussion The near band-edge PL spectra taken at 4.2 K, at magnetic fields up to 20 T, are shown in Fig. 1(a). These spectra exhibit several sharp and well resolved lines associated earlier with excitons [3, 4].

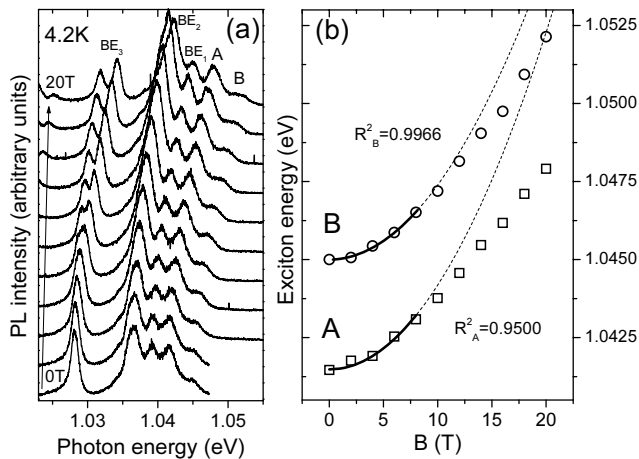


Figure 1 (a) The evolution of the PL spectra of the free A, B and bound BE excitons in CuInSe₂ under magnetic fields from 0 to 20 T; (b) quadratic functions fitted into the spectral positions of the A (□) and B (○) excitons shifting under the magnetic fields up to 8 T (solid lines). The fitting quality is represented by the coefficients of determination R^2_A and R^2_B for the A and B excitons, respectively.

The A and B lines in these spectra were assigned to free excitons comprising electrons from the conduction band and holes from the A and B sub-bands of the valence band, respectively. The chalcopyrite structure of CIS can be derived from the sphalerite structure of ZnSe by the ordered replacement of Zn with either Cu or In. Such a replacement results in a tetragonal distortion in the lattice which lifts the triple degeneracy of the CIS valence band at the Γ point of the Brillouin zone by splitting it into the three sub-bands A, B and C [8]. In this report we are not discussing the C free exciton. The bound exciton (BE) lines were assigned to excitons bound to shallow defects [2, 3, 6].

The magnetic fields shift all the excitonic lines towards higher energies as it can be seen in Fig. 1a. Also one bound exciton line (BE₃) splits under the influence of the magnetic fields into two components.

Application of magnetic fields has two effects on the excitonic energy levels: Zeeman spin-splitting, which is linear with respect to the strength B of the field, and a non-linear increase of their energy or diamagnetic shift [9]. This shift is generated by deformations in the relative motion of the electron and hole in the exciton caused by Lorentz forces. For weak magnetic fields the effects of such deformations can be treated as a perturbation. For the ground-state of the exciton (s -envelope wave-function, when the angular momentum l is zero) this deformation can be considered as an admixture of p -envelope functions (with $l = 1$) making the exciton angular momentum proportional to B . The energy of a magnetic dipole under the influence of a magnetic field is also proportional to B . In total weak magnetic field diamagnetic energy shifts of an ex-

citonic ground state can be estimated by a quadratic function:

$$E(B) = E_0 + c_d B^2, \quad (1)$$

where E_0 is the zero-field ($B = 0$) spectral position of the exciton and c_d is a material's parameter proportional to the square of the exciton size in the plane perpendicular to the direction of the field \mathbf{B} and is a measure of the confinement of the exciton. In this paper we are going to discuss only diamagnetic shifts of the A and B free excitons. Effects of splitting of the peaks associated with bound excitons will be discussed elsewhere.

The experimental values of the diamagnetic shifts of the A and B excitonic lines are shown in Fig. 1b by box- and circle-symbols, respectively. The strength of a magnetic field can be represented [10] by the non-dimensional parameter $\gamma = \hbar e B / (2 R y^* \mu)$, where \hbar is the Planck's constant, e is the electron charge, $R y^*$ is the excitonic Rydberg energy and $\mu = m_e m_h / (m_e + m_h)$ is the reduced mass of exciton, m_0 is the free electron mass, m_e is an effective electron mass, m_h is an effective hole mass. The excitonic Rydberg energy is the binding energy of the exciton. For the A free exciton $R y^*$ was experimentally measured as 7.0 meV [11] and 7.5 meV [12]. Taking the effective masses of the electron $m_e = 0.09 m_0$ and hole $m_h = 0.71 m_0$ [13] we can find that at the highest strength of the magnetic field γ does not satisfy the weak field condition ($\gamma \ll 1$). However analysing the diamagnetic shifts of the A and B excitonic lines in our PL spectra we have found that the quadratic function (1) can be least square fitted quite well into the experimental values of the shifts of both the A and B excitons up to $B = 8$ T, as it can be seen in Fig. 1b. The square of the correlation coefficients of $R^2_A = 0.9500$ and $R^2_B = 0.9966$ describing the accuracy of the fitting into the A and B exciton shifts suggest that the low-field perturbation approach can be used for the fields up to 8 T. The material parameters c_d , the rate of the shift, found from these fits for the A and B excitons are shown in Table 1.

The binding energy, Bohr radius and reduced mass μ of a free exciton can be calculated from c_d using the following expression [14]:

$$\Delta E_d = (e^2 a_B^2 / 4 \mu) B^2 = (4 \pi^2 \hbar^4 \varepsilon^2 / e^2 \mu^3) B^2, \quad (2)$$

where ε is the static dielectric constant of the material. This expression has been obtained by using the first-order perturbation approach to describe diamagnetic energy shifts of an isotropic hydrogen-like exciton in bulk semiconductor.

The reduced masses μ , binding energy $R y^*$ and Bohr radius a_B for both the A and B excitons, calculated assuming that both excitons are isotropic and hydrogen-like, are shown in Table 1. The calculations were carried out for the dielectric constant in CuInSe₂ $\varepsilon = 13.6$ [15].

The reduced mass of the A exciton $\mu = 0.08 m_0$, calculated using the literature effective masses of the electron $m_e = 0.09 m_0$ and hole $m_h = 0.71 m_0$ [13], is smaller than $0.0946 m_0$, obtained in our experiment. However our value

Table 1 The binding energies (Ry^*) and Bohr radius (a_B) of the A and B excitons as well as their reduced masses μ calculated from the rates of the diamagnetic shifts c_d using expression (2).

Exciton	c_d (eV·T ⁻²)	Ry^* (meV)	a_B (nm)	μ/m_0
A	$2.7 \cdot 10^{-5}$	7.0	7.6	0.095
B	$2.4 \cdot 10^{-5}$	7.2	7.3	0.098

of the A exciton binding energy $Ry^* = 7.0$ meV, seems to be in a better agreement with the experimental values of 7.0 meV [11] and 7.5 meV [12] than the binding energy of 5.9 meV, which can be calculated using the hydrogenic model from the reduced mass $\mu = 0.08m_0$ and $\epsilon = 13.6$. Comparisons of the binding energy for the B exciton are not possible because to the best of our knowledge there are no other experimental values of Ry^* for the B exciton have been reported to date. The reduced mass of the B exciton $\mu = m_e m_h / (m_e + m_h) = 0.045m_0$, estimated from the effective mass of the electron $m_e = 0.09m_0$ and hole $m_h = 0.092m_0$ [16], is considerably smaller than our value of $0.098m_0$.

Similar analysis of diamagnetic shifts has been reported for free excitons in ZnS [17]. Recently diamagnetic shifts under magnetic fields up to 10 T have been measured in CuInS₂ [18]. The rates of these shifts c_d for the non-degenerated A (A_{LPB} lower- and A_{UPB} upper-polariton branches) and doubly degenerated BC free excitons, assuming the low field model, was measured to be $4.55 \cdot 10^{-6}$, $4.45 \cdot 10^{-6}$ and $8.68 \cdot 10^{-6}$ eV·T⁻², respectively. These rates are significantly smaller than those found in CuInSe₂ which is probably due to smaller excitonic Bohr radii in CuInS₂, 3.8 and 4.7 nm for the A and BC excitons, respectively.

4 Conclusion Diamagnetic shifts of the free A and B excitons measured in the PL spectra in CuInSe₂ at 4.2 K under magnetic fields up to 20 T were used to estimate the reduced masses ($0.095m_0$ for the A and $0.098m_0$ for the B exciton), binding energies (7.0 meV for the A and 7.2 meV for the B exciton) and Bohr radii (7.6 nm for the A and 7.3 nm for the B exciton) of the free-excitons in CuInSe₂ assuming that both excitons are isotropic and hydrogen-like.

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