Diamagnetic shift of the A free exciton in $CuGaSe_2$ single crystals

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Single crystals of $CuGaSe_2$ were studied using magnetophotoluminescence in magnetic fields up to 20 T at 4.2 K. The rate of the diamagnetic shift in the A free exciton peak was determined to be 9.82×10^{-6} eV/T^2. This rate was used to calculate the reduced mass as $0.115m_0$, the binding energy as 12.9 meV, the Bohr radius as 5.1 nm and an effective hole mass of $0.64m_0$ (m_0 is the free electron mass) of the free A exciton using a low-field perturbation approach and the hydrogenic model. © *2010 American Institute of Physics*. [doi:10.1063/1.3502608]

$CuGaSe_2$ is a promising chalcopyrite semiconductor compound for the absorber layer in thin-film solar cells. In order to optimize the band gap of the chalcopyrite compound layer, $CuGaSe_2$ is alloyed with $CuInSe_2$, forming $Cu(In,Ga)Se_2$ (CIGS). This improves the performance of the solar cells since the band gap of the CIGS absorber layer can be well matched to the solar spectrum. The achieved efficiency records for CIGS-based solar cells saturate toward 20%,[1] which is significantly lower than the theoretical limit for one-junction solar cells of 30%.[2] To engineer an efficient photovoltaic device it is important to have knowledge of the fundamental physical constants of the semiconductor absorber material. In particular, it is important to have reliable values of the charge carrier effective masses, which determine the transport properties of the devices. For $CuGaSe_2$ the literature only contains theoretical estimates for the electron effective mass, giving a value of $0.14m_0$,[3] where m_0 is the free electron mass, calculated using the model from Ref. 4. Experimentally determined values of the hole effective mass range widely from $0.35m_0$ (Ref. 5) to $3.1m_0$.[6]

The application of high magnetic fields can provide important information on the electronic properties of semiconductors. These fields cause a nonlinear shift in the energy of the excitonic levels toward higher values. This diamagnetic shift[7] is a measure of the confinement of the exciton and can be used to estimate its Bohr radius and reduced mass.[8] Magneto-optical experiments have been reported for the chalcopyrite materials $CuInSe_2$ (Ref. 9) and $CuInS_2$ (Ref. 10) but not for $CuGaSe_2$. In this letter, we report measurements of the effects of high magnetic fields on the photoluminescence (PL) spectra of $CuGaSe_2$ single crystals. These data are used to determine the reduced mass and the Bohr radius of the A free exciton and to calculate a reliable value for the effective hole mass.

The chalcopyrite structure of $CuGaSe_2$ can be derived from the sphalerite structure of ZnSe by the ordered replacement of Zn with either Cu or Ga. The difference in the Cu–Se and Ga–Se bonding results in a tetragonal distortion of the lattice, which can be treated in terms of the quasicubic model[11] as the simultaneous influence of a noncubic crystal field and spin-orbit interactions. This causes the valence band of $CuGaSe_2$ to split into the three subbands, A, B, and C with the Γ_{7v}, Γ_{6v}, and Γ_{7v} symmetry, respectively.[12] The A, B, and C free exciton resonances, corresponding to the three valence subbands, have been observed in reflectivity spectra at 1.729 eV, 1.813 eV, and 2.016 eV at 77 K, respectively, and selection rules have been established.[12]

$CuGaSe_2$ single crystals were grown from a stoichiometric mixture of Cu, Ga, and Se elements of 99.999% purity using the vertical Bridgman technique.[13] Room temperature Hall effect measurements indicated hole concentrations in the range 0.8 to 2.5×10^{17} cm^{-3}, which are expected to be further reduced on cooling to cryogenic temperatures. The 4.2 K PL spectra reported below showed no clear dependence on the hole concentration. The magnetophotoluminescence (MPL) measurements were carried out at the Grenoble High Magnetic Field Laboratory using a 20 T resistive magnet at 4.2 K. Optical fibers were used to transmit the 514 nm line of an Ar^+ laser to the sample and the MPL signal to the entrance slit of a 0.5 m spectrometer with an 1800 grooves/mm grating blazed at 500 nm. The dispersed light was then detected by a 1340 element silicon charge coupled device. A 100 W tungsten halogen lamp and a 1 m single-grating monochromator with a 1200 grooves/mm grating were used for the reflectance (RF) measurements. The RF signal was detected by a photomultiplier tube (Hamamatsu R636) in a conjunction with standard lock-in techniques.

The near band gap region of the RF and PL spectra taken in $CuGaSe_2$ at 5 K and 4.2 K, respectively, are shown in Fig. 1. The RF spectrum reveals a prominent resonance at 1.727 eV, assigned to the ground state of the A free exciton. Likewise, the peak at similar energy in the PL spectrum is also attributed to the A free exciton. A higher intensity peak at 1.7208 eV is also visible in the PL spectrum, attributed to a bound exciton (BE). Analysis of temperature dependent PL spectra shows that the thermal quenching of this peak is faster than that of the free exciton peak. This BE peak has been reported in the literature and attributed to the radiative recombination of an exciton bound to a neutral acceptor.[14] This letter focuses on the properties of the A free exciton under magnetic fields.

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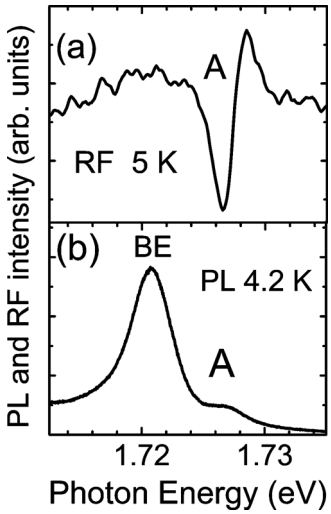

FIG. 1. RF (a) and PL (b) near band gap spectra for $CuGaSe_2$ single crystals, taken at 5 K and 4.2 K, respectively. The A free exciton and a BE peak are labeled.

Increasing the magnetic field strength from 0 to 20 T results in nonlinear blueshifts in both the BE and the A free exciton lines, as shown in Fig. 2. In order to accurately determine the dependence of the spectral position of the A free exciton on the magnetic field strength, the A and BE peaks have been fitted with Gaussians. The total shift in the A free exciton peak from 0 to 20 T, was measured to be 3.4 meV. The full width at half maximum (FWHM) of the A free exciton peak was 4.5 meV and did not change with increasing magnetic field. No field-induced peak splittings are resolved in the spectra, which is probably due to the relatively large FWHM.

The diamagnetic shift in the free A exciton peak under the influence of magnetic field is caused by the deformation of the relative motion of the electron and hole in the exciton caused by Lorentz forces.[7] For weak magnetic fields, the effects of such deformation can be treated as a perturbation. For the ground state, with an *s*-envelope wave-function and angular momentum of $l=0$, this deformation can be described in terms of an admixture of the *p*-envelope functions

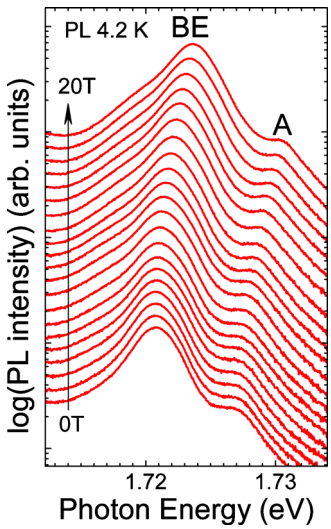

FIG. 2. (Color online) PL spectra of the free A exciton and the BE under magnetic field from 0 to 20 T taken at 4.2 K.

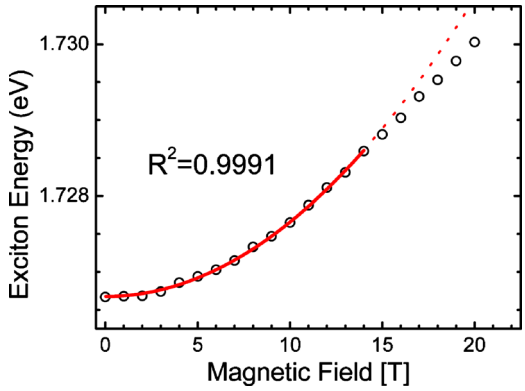

FIG. 3. (Color online) The evolution of the free A exciton PL peak position under the influence of a magnetic field. The solid line represents a quadratic fit up to 14 T.

with $l=1$. As a result, the angular momentum of the exciton becomes proportional to the magnetic field strength B. The energy of a magnetic dipole in a magnetic field is also proportional to B, resulting in an overall quadratic dependence of the excitonic energy with respect to B for the low magnetic field region as follows:[7]

$$E(B) = E_0 + c_d B^2, \tag{1}$$

where E_0 is the zero-field spectral position of the exciton peak and c_d, the rate of the shift, is a material parameter proportional to the square of the size of the exciton wave function in the plane perpendicular to the field.

The strength of the magnetic field can be characterized by the nondimensional parameter $\gamma=\hbar eB/(2Ry^*\mu)$,[15] where $\hbar$ is Planck's constant, e is the electron charge, Ry^* is the excitonic Rydberg energy, and $\mu=m_e m_h/(m_e+m_h)$ is the reduced mass of the exciton, m_e and m_h are the effective electron and hole mass, respectively. The low-field condition assumes $\gamma \ll 1$. To make an estimate of the extent of the low-field region the available values of the effective electron and hole masses in $CuGaSe_2$ are used to estimate the A exciton reduced mass as $\mu=0.125$. A hole effective mass of $m_h=1.2m_0$ has been selected from the wide range.[16] Using the experimental value of the A exciton binding energy (13 meV) (Ref. 13) as Ry^* gives a value of γ of 0.36 at 10 T. This suggests that up to at least about 10 T the Coulomb energy dominates and the external magnetic field can be treated as a perturbation, with Eq. (1) describing the diamagnetic shift.

The evolution of the spectral position of the A exciton peak under increasing magnetic fields from 0 to 20 T is shown in Fig. 3. The quadratic expression in (1) was used to least square fit the experimental data points up to various maximum values of the field. The best fit, corresponding to the maximum value of the square of the correlation coefficient $R^2=0.9991$, was obtained for the data points up to 14 T as shown in Fig. 3. This suggests that the weak field approximation works well up to 14 T.

A first-order perturbation approach has been used in Ref. 8 to evaluate the dependence of diamagnetic energy shifts ΔE_d on the Bohr radius a_B and reduced mass μ for a hydrogenlike exciton in bulk semiconductors,

TABLE I. Effective Rydberg (Ry^*), Bohr radius (a_B), effective hole mass (m_h), and reduced mass μ of the A exciton calculated from the rate of the diamagnetic shift c_d.

c_d (eV/T^2)	μ/m_0	Ry^* (meV)	a_B (nm)	m_h/m_0
9.82×10^{-6}	0.115	12.9	5.1	0.64

$$\Delta E_d = (e^2 a_B^2/4\mu)B^2 = (4\pi^2\hbar^4\varepsilon^2\varepsilon_0^2/e^2\mu^3)B^2, \quad (2)$$

where ε and ε_0 are the static dielectric constants in $CuGaSe_2$ and permittivity of vacuum, respectively. The best fit in Fig. 3 corresponds to a diamagnetic shift rate of $c_d=(9.82\pm0.09)\times10^{-6}$ eV/T^2. A reduced mass of $\mu=0.115m_0$ was then calculated using Eq. (2) and the literature value of the static dielectric constant $\varepsilon=11$.[14]

There is no experimental value for the electron effective mass m_e in the literature. However, Persson[17] recently reported a theoretical dependence of m_e in $CuIn_{1-x}Ga_xSe_2$ on the content of gallium x as $m_e(CuIn_{1-x}Ga_xSe_2)=[m_e(CuInSe_2)+0.05x]m_0$. Using the experimental value of $m_e(CuInSe_2)=0.09m_0$ (Ref. 18) gives a value of $m_e=0.14m_0$ for the effective electron mass in $CuGaSe_2$, which is identical to the value calculated earlier[3] using the theoretical model of Kildal[4] developed without taking in account the hybridization Cu d with Se p states. Such a coincidence suggests that Cu d states do not have much influence on the conduction band near the Γ point. Our reduced exciton mass then leads to an estimate of the hole effective mass as $m_h=0.64m_0$, which falls within the range of experimentally measured values.

The value of the excitonic Rydberg energy, estimated from Eq. (3) using the determined $\mu=0.115m_0$ and $\varepsilon=11$ is $Ry^*=12.9$ meV. This is in excellent agreement with the value $E_b=13\pm2$ meV, determined from the experimentally measured energy of the A exciton first excited state,[14]

$$Ry^* = 13.6eV \times \frac{\mu}{m_0} \times \frac{1}{\varepsilon^2}. \quad (3)$$

The exciton Bohr radius is estimated as $a_B=5.1$ nm. The results of our measurements and calculations are summarized in Table I.

Recently the rates of the diamagnetic shift in excitonic lines under magnetic fields up to 20 T has been measured for the related chalcopyrite compounds $CuInSe_2$ (Ref. 9) and $CuInS_2$.[10] The rate for the A exciton in $CuInSe_2$ was found to be 2.7×10^{-5} eV/T^2, in the low-field region of the magnetic field strength. The rate is larger than for $CuGaSe_2$, which can be attributed to the larger Bohr radius of 7.6 nm for the A exciton. The rates of the diamagnetic shifts for the A free exciton lines, in another chalcopyrite compound $CuInS_2$ were measured to be 4.55×10^{-6} eV T^{-2} and 4.45×10^{-6} eV T^{-2} for the A_{LPB} lower- and A_{UPB} upper-polariton branches, respectively. These rates are significantly smaller than those found in $CuInSe_2$ and $CuGaSe_2$ due to smaller excitonic Bohr radii in $CuInS_2$, ~3.8 nm.

In conclusion, the rate of the diamagnetic shift 9.82×10^{-6} eV/T^2 of the A free exciton states in $CuGaSe_2$ has been measured from MPL spectra assuming a low-field approximation. This rate was used to determine reliable values for the reduced mass $\mu=0.115m_0$, the binding energy 12.9 meV, the Bohr radius 5.1 nm as well as the effective mass of the hole $0.64m_0$.

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