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# Landau levels of the C-exciton in $CuInSe_2$ studied by magneto-transmission

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The electronic structure of the solar cell absorber $CuInSe_2$ is studied using magneto-transmission in thin polycrystalline films at magnetic fields up to 29 T. A, B, and C free excitons are resolved in absorption spectra at zero field and a Landau level fan generated by diamagnetic exciton recombination is observed for fields above 7 T. The dependence of the C band exciton binding energy on magnetic fields, calculated using a hydrogenic approximation, is used to determine the C exciton Rydberg at 0 T (8.5 meV), band gap (1.2828 eV), and hole effective mass $m_{so} = (0.31 \pm 0.12)m_0$ for the C valence sub-band. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4897995]

$CuInSe_2$ is a direct band gap semiconductor compound with chalcopyrite structure, which is used in solar cell absorber layers. The $CuInSe_2$-based technologies are amongst the leaders for thin film photovoltaics (PV) in terms of conversion efficiency and stability. The very high absorption coefficient of $CuInSe_2$, one of the highest in the region from 0.9 to 2.5 eV (greater than $10^5\,cm^{-1}$ from 1.04 eV)[1] amongst semiconductors used for solar cell absorbers,[2] provides an opportunity to reduce the absorber layer thickness down to submicron values. This lowers the cost of solar cells making them competitive against conventional sources of electricity. The 20.8% laboratory scale record for the conversion efficiency in $CuInSe_2$-based solar cells[3] is, however, well below the theoretical limit of 30% for a single junction PV device[4] suggesting a lack of knowledge on the electronic properties of $CuInSe_2$-based solar cells in general and of $CuInSe_2$ in particular.

Improvements in the structural quality of $CuInSe_2$ by reducing the defect concentrations below a level where sharp excitonic features appear in the optical spectra make the methods of optical spectroscopy significantly more efficient and broaden the range of techniques available for analysis. Early optical spectroscopy studies of the excitonic properties of $CuInSe_2$ revealed the complexity of the valence band, which is split into A, B, and C sub-bands by the simultaneous influence of the non-cubic crystal field and spin-orbit coupling.[5] Recently, the excitonic studies were extended by works based on new advances in the material structural quality[6–9] determining accurate values of the A and B exciton binding energies $E_b$[7] and hole effective masses.[9] Significantly fewer papers however are concerned with the C exciton, although the C-band parameters are necessary for the development of *kp* theory in the chalcopyrites. Only its spectral position[7,10,11] can be found in the literature whereas neither $E_b$ nor experimentally determined effective masses have been reported so far.

Strong magnetic fields quantize the energy of electrons and holes, excited by absorption to the conduction and valence bands, respectively. The recombination of diamagnetic excitons (DX)[12] formed by the Coulomb interaction of these electrons and holes can be observed in magneto-transmission (MT) spectra of high structural quality thin films as Landau level (LL) fans. Analysis of such fans can provide accurate spectral positions of the bands, $E_b$ of free excitons and their reduced masses.

In this paper, the electronic structure of $CuInSe_2$ is examined using MT in thin excitonic quality polycrystalline films. Clear LL fans associated with recombination of DX are observed in the spectra. Binding energies for the C valence band DX are theoretically calculated as a function of field ($B$) and then added to the experimentally observed DX spectral positions to determine the C-band LL energies. The band gap and hole effective masses for the C valence sub-band are then determined.

High structural quality 1.2 $\mu$m thick $CuInSe_2$ thin films are grown by a two stage process: Cu and In precursors thermally evaporated on glass were first annealed in Se vapour at 270–310 °C for 60 min and then at 520 °C for 20 min.[1,13] The elemental composition of the resulting *p*-type conductivity films, measured by energy dispersive x-ray analysis, was found to be close to the ideal stoichiometry [Cu]/[In] = 1.01, [Cu + In]/[Se] = 1.00.

The MT measurements were carried out at magnetic fields up to 29 T at the Laboratoire National des Champs Magnétiques Intenses in Grenoble (France) in a 4.2 K helium vapour cryostat combined with a 20 MW resistive magnet. Optical fibres deliver the light from a 100 W tungsten halogen lamp to the sample as well as transmitted signal to the

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slits of a 0.3 m spectrograph with an InGaAs array detector. The spectral resolution and accuracy of the spectral line positions were of 0.1 meV and 0.2 meV, respectively. The samples were mounted in the magnet bore in the Faraday configuration: film surfaces being perpendicular to the magnetic field direction and the direction of the light. In order to facilitate the analysis the MT spectra $I(B)$ at magnetic fields $B$ were normalised dividing by zero field spectra $I(0\,\mathrm{T})$.

An example of the zero magnetic field absorption spectra of the films is shown in Fig. 1(a). The steep increase in the absorption near 1.04 eV is due to the A and B excitons, which can be resolved on a finer scale, as reported earlier.[1] Beyond the A and B excitons, a gradual rise of absorption can be seen towards a feature at 1.2750 eV, also shown in Fig. 1(b) on a linear scale. This peak can be assigned to the C free exciton because its spectral position is close to the C exciton in the wavelength derivative reflectivity spectra of $CuInSe_2$ single crystals.[7]

The evolution of the normalised MT spectra $I(B)/I(0\,\mathrm{T})$ in the region of the C exciton with increasing magnetic field is shown in Fig. 2(a). The intensity is presented on a grey scale from low (white) to high (black). The dominant feature 0, sloping across the figure at energies around 1.27 eV, represents the C exciton ground state. The normalised MT spectrum at 29 T is shown in Fig. 1(b). The C exciton spectral position corresponds to the minimum of the $I(B)/I(0\,\mathrm{T})$ oscillation. Increasing magnetic fields enhances the C oscillator amplitude. At fields above 7 T, the features 1, 2, and 3 are seen crossing the plot at gradually decreasing gradients. At fields over 12 T, several new features labelled as AB appear in Fig. 2(a).

At weak magnetic fields, the spectral positions of the excitons shift towards high energies following a quadratic dependence on $B$ whereas for strong fields quantization of the charge carrier motion in the plane perpendicular to $\boldsymbol{B}$, should be considered.[12]

The strong magnetic field limit can be evaluated by $\beta = \hbar\Omega/(2Ry^*)$,[12] where $\Omega = eB/(\mu c)$ is the exciton cyclotron frequency, $\varepsilon$ the static dielectric constant, $\mu$ the exciton reduced mass, $m_0$ the free electron mass, $Ry^*$ excitonic

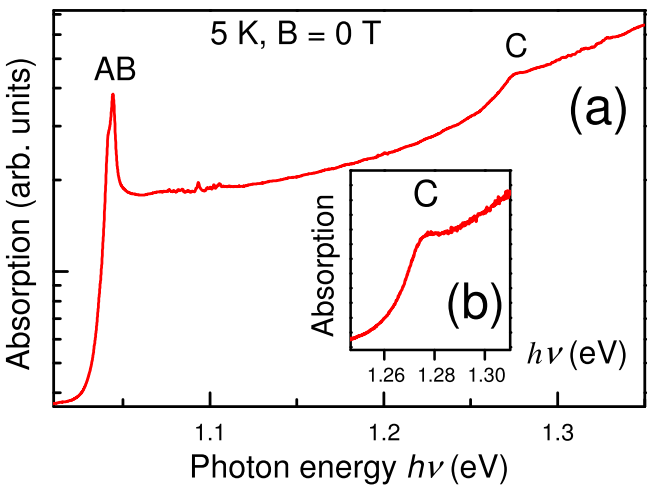


FIG. 1. Zero field absorption spectrum of $CuInSe_2$ thin film demonstrating A, B, and C free excitons (a), the C exciton region absorption spectrum plotted on a linear scale (b).

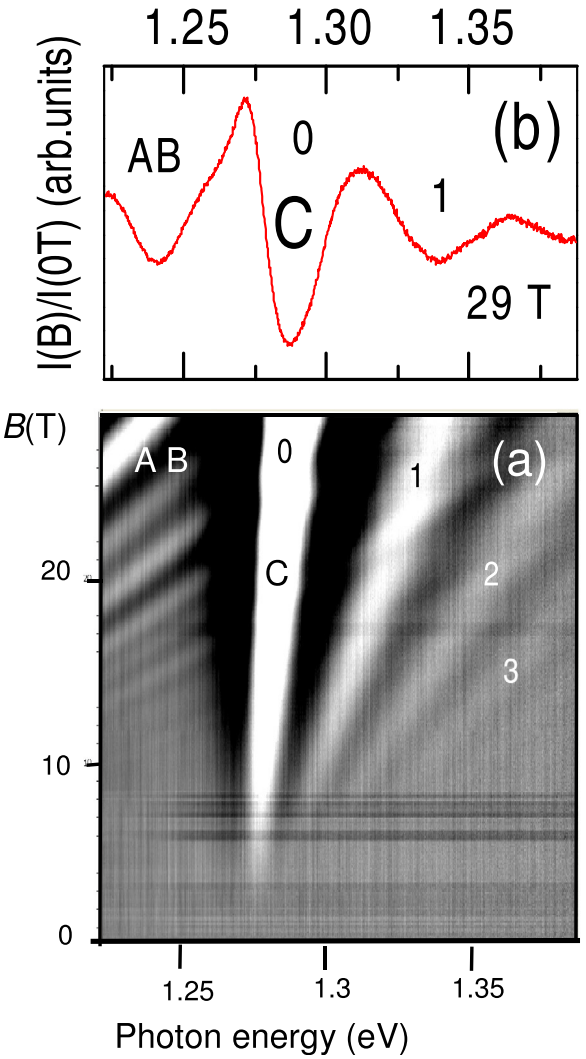


FIG. 2. Evolution of normalised MT spectra $I(B)/I(0\,\mathrm{T})$ for the C exciton (0) and diamagnetic excitons (1, 2, and 3) (a), normalised MT spectrum at 29 T (b). AB lines are the Landau fan for the A and B band diamagnetic excitons.

effective Rydberg energy $Ry^* = Ry\mu/(m_0\varepsilon^2)$ and $Ry = 13.6$ eV. For $\beta \ll 1$, the fields are below the weak field limit, Coulomb forces dominate and the magnetic field can be treated as perturbation. For $\beta \gg 1$ (Elliott-Loudon criterion), the magnetic field forces exceed significantly the Coulomb forces and LL effects are observed. The strong field limit for the A exciton, whose parameters are better reported than those for the C exciton, is met at fields above 30 T (assuming $Ry^* = 8.5$ meV (Ref. 8) and $\mu = 0.081 m_0$ (Ref. 9)). However, for excited states with $n > 1$ (n is the exciton principal quantum number), we can apply the modified criterion $\beta n^2 \gg 1$.[15] A similar high field limit is expected for the C exciton. Its validity can be seen in Fig. 1(a), where the features 1, 2, and 3 appear in the spectra at fields just above 7 T. These features are DX excitons for the C band whereas AB features can be assigned to the A and B DX associated with the A and B bands.

The DX binding energies $Ry^*(l,B)$, labelled using the LL number $l$ and magnetic field $B$, can be found by solving a Schrodinger equation for excitons in a one dimensional potential determined by averaging the Coulomb potential in the plane perpendicular to $\boldsymbol{B}$.[12,15] A full set of band parameters for the quasi-cubic approximation is required to

determine such $Ry^*(l,B)$.[12] However, in the case of LLs associated with the C band hole, a simplified method for the calculation of $Ry_{so}^*(l,B)$ using accurate solutions for hydrogen atom[16] determined assuming the parabolicity of both the conduction and valence C bands can be applied. We also assume the C band hole mass to be isotropic following the theoretical prediction in Ref. 17.

The zero field binding energy of the C exciton ground state can be then found as the effective Rydberg $Ry_{so}^*(0,0) = \mu_{so}^p Ry/(m_0\varepsilon^2)$, where $\mu_{so}^p$ is the reduced mass of the C exciton polaron ($1/\mu_{so}^p = 1/m^p{}_e + 1/m^p{}_{so}$), $\varepsilon$ is the theoretically calculated static dielectric constant $\varepsilon = (\varepsilon_{\parallel}\varepsilon_{\perp}^2)^{1/3} = 10.76$ (Ref. 17) (used in this paper following Ref. 9), and $m^p{}_e$ and $m^p{}_{so}$ are the polaron effective masses of electron and hole, respectively. Polaron masses $m^p$ are slightly heavier than the bare masses $m^b$ due to charge carrier interactions with optical mode phonons. $m^p = m^b(1+\alpha_F/6)$, where $\alpha_F$ is the Fröhlich carrier coupling constant. In this paper, we use the bare electron mass $m_e{}^b = 0.09m_0$ (Refs. 14 and 9) and assume the Fröhlich carrier coupling constant for electrons $\alpha_{Fe} = 0.202$ to be isotropic.[9] The hole Fröhlich constant $\alpha_{Fso}$ can be calculated using standard expressions:[18]

$$\alpha_{Fso} = \alpha_{Fe}\sqrt{m_{so}{}^b/m_e{}^b}, \quad (1)$$

where $m_{so}{}^b$ is the bare C hole effective mass. To calculate $Ry_{so}^*(l,B)$ for states with $l \geq 1$, the normalised scale $\theta = B/(2l+1)$ for $B$ has been introduced.[19] Such a scale makes possible approximations of Rydbergs for $l \geq 1$ using those at $l = 0$. This method was earlier used to determine the GaAs split off band parameters from strong field MT measurements.[20] An attempt to determine $Ry_{so}^*(l,B)$ in GaAs using more accurate techniques[21] demonstrated no considerable difference in the resulting binding energies suggesting a good accuracy of the scale normalisation method in Ref. 19.

The first iteration of $Ry_{so}^*(l,B)$ is calculated assuming the A exciton polaron reduced mass of $0.081m_0$.[9] The values of $Ry_{so}^*(l,B)$ are then added to the DX experimental spectral energies 0, 1, 2, 3 shown in Fig. 2(a). The spectral energies of the resulting C band LL can be described by the linear dependence of $E_{LL} = E_g(\mathrm{C}) + \hbar\Omega(m_0/\mu_{so}{}^b)(l+1/2)$ on $B$. The slopes of these lines are inversely proportional to the bare reduced mass $\mu_{so}{}^b$. In order to improve the accuracy of the calculations, all the LL corresponding to 0, 1, 2, and 3 are combined on a $\hbar\Omega$ $(l+1/2)$ scale in one plot, shown in Fig. 3, and fitted with a straight line. From the slope of this line, we can find $\mu_{so}{}^b$ and then calculate $m_{so}{}^b$, $\alpha_{Fso}$ using Eq. (1), $m^p{}_{so}$, and $Ry_{so}^*$ and iterate until the value of $\mu_{so}{}^b$ converges to within 0.1%.

Fig. 3 shows the resulting line fit. A value of $(1.2828 \pm 0.0003)$ eV for $E_g(\mathrm{C})$ is determined at $\hbar\Omega$ $(l+1/2) = 0$ whereas $\mu_{so}{}^b = (0.0696 \pm 0.0004)m_0$ is found from the slope of this line. Naturally, the straight line fit is not the only source of uncertainties. Then, the C band bare hole effective mass $m_{so}{}^b = (0.31 \pm 0.12)m_0$ is calculated and rounded taking into account the uncertainties in $\mu_{so}{}^b$ and $m_e = (0.09 \pm 0.01)m_0$.[14] The large uncertainty in $m_{so}{}^b$ is a result of the high value of $m_{so}{}^b/m_e$. The bare hole effective mass value corresponds to $\alpha_{Fso} = 0.374$ and the polaron effective mass $m_{so}{}^p = 0.31m_0$ are calculated. Using the electron polaron effective mass $m_e{}^p = 0.093m_0$,[9] the exciton-

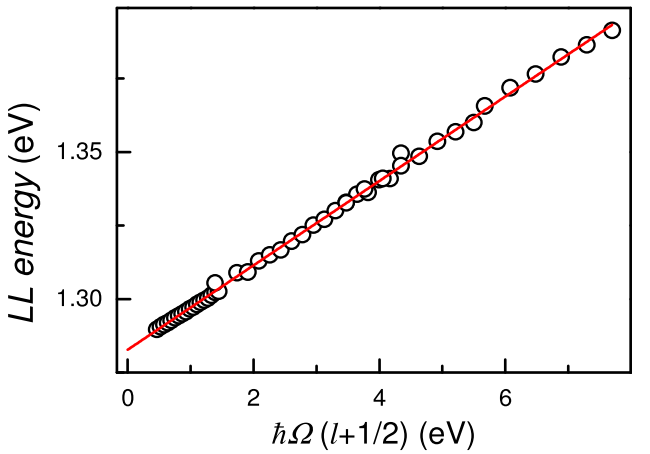


FIG. 3. Combined Landau levels (experimental data of the C(0) and diamagnetic 1, 2, and 3 excitons with added $Ry_{so}^*(l,B)$) plotted on a $\hbar\Omega$ $(l+1/2)$ scale.

polaron reduced mass $\mu_{so}{}^p = 0.0724m_0$ is also determined leading to $Ry_{so}^*(0,0) = 8.5$ meV. Fig. 4(a) shows the resulting magnetic field dependencies of the DX binding energies $Ry_{so}^*(l,B)$.

The calculated hole masses are significantly greater than $0.085m_0$, which was estimated by Neumann *et al.*[22] from the density of state effective mass of the A and B valence subband holes using a theoretical approach.[23] Closer values of $0.28m_0$ for the parallel and $0.27m_0$ for the perpendicular to the $z$ direction components in the tetragonal lattice structure are predicted by first principle calculations.[18]

The determined C exciton ground state ($l = 0$) binding energy at zero field $E_b(\mathrm{C}) = Ry_{so}^*(0,0) = 8.5$ meV is very close to $E_b$ for A and B of 8.5 and 8.4 meV, respectively.[8] Subtracting 8.5 meV from $E_g(\mathrm{C})$ the spectral position of the C exciton can be calculated as 1.2743 eV which is close to the experimentally observed value of 1.2750 eV in the zero field absorption spectrum in Fig. 1.

Fig. 4(b) shows the C band LL energies (with $Ry_{so}^*(l,B)$ added to the experimental data). The straight lines LL0, LL1, LL2, and LL3, corresponding to LL with $l = 0$, 1, 2, and 3, are fitted in Fig. 4(b) assuming zero field $E_g(\mathrm{C}) = 1.2828$ eV. The lines LL0 and LL1 are seen to fit well to the experimental

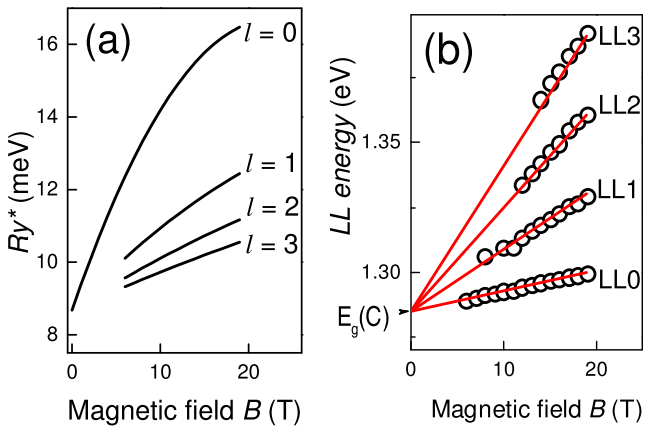


FIG. 4. Dependencies of the C band DX binding energies $Ry^*(C)$ on magnetic fields $B$ (a), spectral energies of the LL determined by adding the binding energies to DX (b).

points whereas those for LL2 and LL3 demonstrate some mismatch which can be explained by increasing uncertainties in their spectral position due to a reduction of the signal to noise ratio in the experimental spectra.

In conclusion, the electronic structure of $CuInSe_2$ has been studied in thin polycrystalline films using Landau level spectroscopy at magnetic fields up to 29 T. A Landau level fan generated by diamagnetic exciton recombination is observed at magnetic fields above 7 T. The C band exciton binding energy dependencies on magnetic fields, calculated using a hydrogenic approximation, were used to determine the C exciton Rydberg (8.5 meV at 0 T), band gap (1.2828 eV), and hole effective mass $m_{so} = (0.31 \pm 0.12)m_0$ for the C valence sub-band.

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