

A Magneto-Reflectivity Study of CuInTe₂ Single Crystals

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CuInTe₂ single crystals are studied using optical magneto-reflectance (MR) in magnetic fields B up to 20 T at 4.2 K. The spectra exhibit the A and B free excitons' blue shifting at increasing magnetic fields. Fitting quadratic functions to the experimental dependencies of the exciton spectral energy on B assuming a low field limit allow the determination of diamagnetic shift rates of 8.2×10^{-5} and 8.5×10^{-5} eV T⁻² for the A and B free excitons, respectively. The excitons' reduced masses of $0.0575m_0$ and $0.0568m_0$ (m_0 is the free electron mass), Rydbergs of 6.2 and 6.1 meV, and Bohr radii of 10.4 and 10.5 nm are then estimated. An electron effective mass of $0.062m_0$ and B sub-band effective hole mass of $0.70m_0$ are determined using a literature value of the A valence sub-band hole of $0.78m_0$.

1. Introduction

CuInTe₂ belongs to a family of ternary semiconductors with chalcopyrite lattice structures.^[1] Similar to other chalcopyrite compounds, the alternation of two different cation atoms (Cu and In in the case of CuInTe₂) on the cation lattice induces a tetragonal distortion which splits the valence band of CuInTe₂ in A, B, and C sub-bands. For some chalcopyrites (CuInSe₂ and CuGaSe₂), an application in the absorber layer of thin-film solar cells has been already found.^[2] Their direct bandgaps (E_g)

of 1^[3] and 1.7 eV,^[4] respectively, allow the bandgaps of their alloy Cu(In,Ga)Se₂ (CIGS) to be tuned to match the solar spectrum by changing the [Ga]/[Ga + In] ratio. An increase in the [Ga]/[Ga + In] ratio at first results in the rise of the open circuit voltage (V_{oc}) of CIGS-based solar cells. However, at [Ga]/[Ga + In] in excess of 0.3, the V_{oc} saturates, developing a deficit which increases with rising gallium content.^[5] This problem has not been solved as yet. The bandgap of CuInTe₂ of 1 eV is close to that of CuInSe₂, suggesting that CuInTe₂ can also be used in the absorber layer of thin-film solar cells. Indeed, the conversion efficiency (η) of solar cells with

Cu(In,Ga)Te₂ absorbers has already exceeded 4%.^[6] However, this value is still below 22.9%,^[7] the current η of Cu(In,Ga)Se₂-based photovoltaic (PV) devices. The electronic properties of CuInTe₂ are significantly less studied than those in CuInSe₂ and CuGaSe₂. A further progress in the development of CuInTe₂-based devices can be expected once the understanding of the electronic properties of this material is better.

Charge carrier effective masses are very important parameters of the electronic structure of semiconductors because such masses define the mobility of the carriers which, in turn, strongly influences the performance of electronic devices fabricated using these semiconductors.^[8] A recent study of the electronic structure of CuInTe₂ carried out using angular-resolved photoelectron spectroscopy demonstrated a remarkable steepness of the energy–momentum (E – k) dispersion relations of the valence band in this compound.^[9] This can be very beneficial for solar cells based on this material.

Charge carrier masses reported for CuInTe₂ in the literature reveal a significant scatter. The hole effective mass varies from $2.2m_0$ ^[10] to $0.11m_0$,^[11] where m_0 is the free electron mass, whereas that of the electron ranges from $0.058m_0$ ^[10] to $0.14m_0$ ^[12] or $0.155m_0$.^[13]

The dispersion relations of the conduction and valence bands of semiconductors can also be examined by magneto-optical spectroscopy.^[14] Such methods have been used to estimate the reduced masses of free excitons in CuInSe₂^[15] and CuGaSe₂.^[4] A key requirement for the use of such techniques is the high structural quality of the examined materials. Such materials should exhibit sharp excitonic features in their optical spectra which is possible at low defect concentrations.^[16]

In this report, excitonic grade single crystals of CuInTe₂ (exhibiting excitons in their optical spectra) were examined by magneto-reflectance (MR) in magnetic fields B up to 20 T at 4.2 K.

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2. Results and Discussions

Optical reflectance (OR) spectra of CuInTe₂, measured at zero magnetic field and 4.2 K, exhibit two excitonic oscillations earlier assigned to the A and B free excitons at 1.053 and 1.072 eV, respectively.^[17] These excitons are shown in Figure 1a.

The application of magnetic fields shifts both excitons toward higher energies. This shift is shown in Figure 1b. It is also shown that rising magnetic fields increase the magnitude of the oscillations of the A exciton. Each spectrum was fitted with the following function^[18]

$$R(E) = R_0 + R_x(\text{Re}\{e^{i\theta}(E_x - E + i\Gamma_x)/[\Gamma_x^2 + (E_x - E)^2]\}) \quad (1)$$

where E_x is the spectral energy of the A or B excitons, Γ_x is the broadening parameter, θ is the phase ($\theta_A = \theta_B$), R_x is the amplitude, and R_0 is the background. An example of the fitting for the zero field spectrum is shown in Figure 1a. Such a fitting improved the accuracy of the determination of the spectral position of the excitons. Changes in the spectral position of the A and B excitons with increasing magnetic fields are shown in Figure 2.

The effect of the magnetic field depends on the balance of the strengths of the Lorentz and Coulomb forces. Weak fields do not break the Coulomb bond between the electron and hole but deform their relative motion, making the originally s-type exciton wave-function slightly p-type.^[8] As a result, this wave-function acquires an angular momentum ($l = 1$) becoming proportional to B . Together with the magnetic dipole energy of the exciton, which is also proportional to B , the spectral energy of the exciton becomes quadratically dependent on B . Once the field becomes strong enough to break the Coulomb forces this quadratic dependence is substituted by a linear one. Thus, within weak magnetic field limits the dependence of the spectral energy $E(B)$ of a free exciton on B can be described as the follows

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

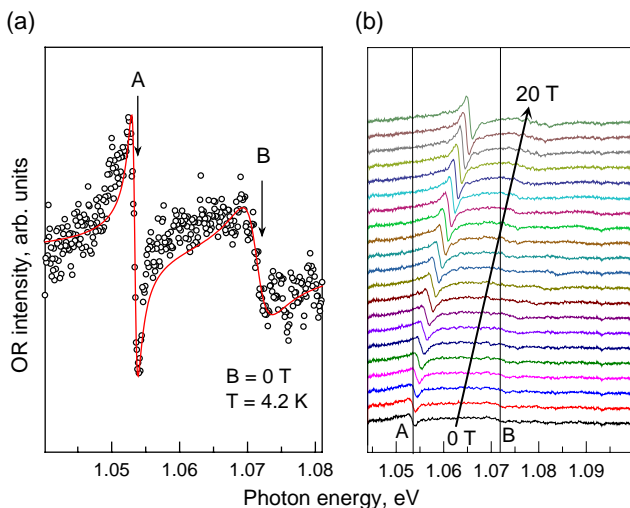


Figure 1. a) Experimental OR spectrum at zero magnetic field (o), red solid line is the best fit; b) MR spectra at magnetic fields B , increasing from 0 to 20 T.

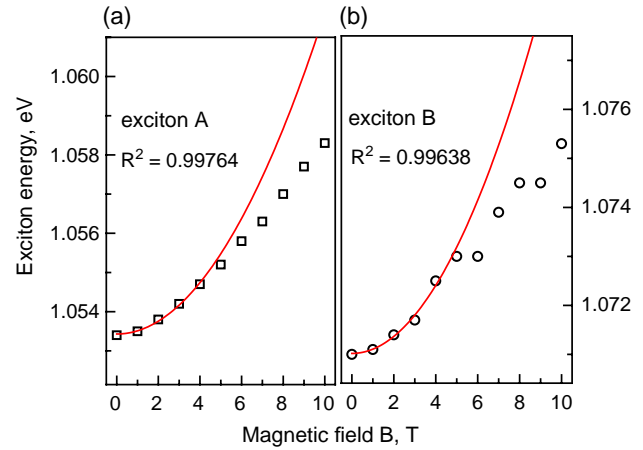


Figure 2. The dependence of the spectral position of the a) A and b) B free excitons on the magnetic field strength B (o). The red solid lines are best fits using quadratic functions.

where E_0 is a zero field spectral energy and c_d is the rate of the shift called diamagnetic coefficient. This coefficient is proportional to the squared exciton wave-function and can be used to estimate the exciton size, the Bohr radius a_B .^[8]

The experimental points of the $E(B)$ dependence of the A and B excitons were fitted with the function in Equation (2), gradually increasing the number of fitted points starting from 3. After each fitting, the correlation coefficient R^2 , reflecting the accuracy of the fit, was examined. Up to the fifth point (4 T) R^2 increased sharply. Further increases in the point number were rather marginal, suggesting that at fields in excess of 4 T, the dependence $E(B)$ admixes a linearity, indicating the approach of the weak field limit when magnetic forces start breaking the coulomb bonds.^[8]

The best fits and corresponding R^2 are shown in Figure 2. The diamagnetic shift rates c_d of $(8.2 \pm 0.3) \times 10^{-5} \text{ eV T}^{-2}$ for A and $(8.5 \pm 0.4) \times 10^{-5} \text{ eV T}^{-2}$ for B excitons were determined. These shift rates are also shown in Table 1.

A hydrogenic model for free Wannier excitons, neglecting the interaction between A and B valence sub-bands, assuming isotropic parabolic valence and conduction bands, relates the diamagnetic spectral energy change ΔE_d induced by the influence of magnetic field with the Bohr radius a_B as follows^[8]

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

where $\mu = (1/m_e + 1/m_h)^{-1}$ is the exciton reduced mass combining the electron m_e and hole m_h effective masses. Using $\epsilon = 11.25$ ^[19] the average value of static dielectric constants along and perpendicular to the tetragonal axis in CuInTe₂, we determined the reduced masses of A and B excitons as $\mu_A = 0.0575m_0$ and $\mu_B = 0.0568m_0$, respectively (m_0 is the free electron mass).

Table 1. Diamagnetic shift rates c_d , reduced masses μ , effective Rydbergs (Ry^*), and Bohr radii (a_B) of the A and B free excitons.

Band	c_d [eV T ⁻²]	μ [m_0]	Ry^* [meV]	a_B [nm]
A	8.2×10^{-5}	0.0575	6.2	10.4
B	8.5×10^{-5}	0.0568	6.1	10.5

Effective Rydbergs of 6.2 and 6.1 meV for the A and B excitons, respectively, were also calculated using the following expression^[8]

$$Ry^* = 13.6\mu/(m_0e^2) \quad (4)$$

These Rydbergs are close to the A exciton binding energy of 6 meV, estimated as a difference between the spectral position of this exciton in the photoluminescence (PL) spectra (measured at 6 K) and E_g , determined by fitting theoretically calculated absorption spectra to experimental ones (also measured at 6 K) for the same sample.^[20,21] Excitonic Bohr radii (a_B) of 10.4 and 10.5 nm, calculated for the A and B excitons, respectively, are shown in Table 1.

The scatter of reported effective masses for the A valence sub-band hole by more than an order of magnitude can be due to the differences in the quality of the examined materials. Some of the studied CuInTe₂ samples were polycrystalline films, whereas others were single crystals of unknown crystalline quality. The effective masses of the A valence sub-band hole $m_h(A)$, determined from infrared reflection spectra measured for oriented single crystals in a study by Weinert et al.^[22] and confirmed in a study by Marin et al.,^[23] are assumed to be more reliable. The average value of $0.78m_0$ for masses of $0.66m_0$ and $0.85m_0$, measured in the study by Weinert et al.,^[22] for the electric field vector E parallel and perpendicular to the optical axis c , respectively, was used to calculate the effective masses of the electron as $m_e = 0.062m_0$ and of the B valence sub-band hole as $m_h(B) = 0.70m_0$.

The diamagnetic shift rate determined here for the A exciton in CuInTe₂ ($8.2 \times 10^{-5} \text{ eV T}^{-2}$) is significantly greater than that reported for the better-known chalcopyrites: CuInSe₂ ($2.7 \times 10^{-5} \text{ eV T}^{-2}$),^[15] CuGaSe₂ ($0.99 \times 10^{-5} \text{ eV T}^{-2}$),^[4] and CuInS₂ ($0.46 \times 10^{-5} \text{ eV T}^{-2}$).^[16] Because of this increased shift rate, the size of the exciton in CuInTe₂, estimated by the Bohr radius of 10.4 nm, is twice as large as that of CuInSe₂, the nearest competitor among these compounds in terms of the diamagnetic shift rate magnitude with a_B of 5.1 nm.^[15] The large diamagnetic shift rate and Bohr radius for the A exciton in CuInTe₂ result in the smallest reduced exciton mass of $\mu = 0.0575m_0$ ($0.081m_0$ ^[15] in CuInSe₂, $0.115m_0$ ^[4] in CuGaSe₂, and $0.141m_0$ ^[24] in CuInS₂) and effective electron mass ($0.09m_0$ ^[22] in CuInSe₂, $0.14m_0$ ^[4] in CuGaSe₂, and $0.16m_0$ in CuInS₂^[25]) among these chalcopyrite compounds. Such lightness of the masses promises a high potential for charge carrier mobility and consequently the high potential performance of solar cells based on CuInTe₂. To compare electron effective masses as well as diamagnetic shift rates (c_d) and reduced masses (μ) of the A exciton in CuInTe₂, CuInSe₂, CuGaSe₂ and CuInS₂, we show these values in Table 2.

Table 2. A comparison of electron effective masses (m_e), diamagnetic shift rates (c_d), and reduced masses (μ) of the A exciton in CuInTe₂, CuInSe₂, CuGaSe₂, and CuInS₂.

Material	m_e [m_0]	c_d [V T^{-2}]	μ [m_0]
CuInTe ₂	0.062	8.2×10^{-5}	0.0575
CuInSe ₂	0.09	2.7×10^{-5}	0.081
CuGaSe ₂	0.14	0.99×10^{-5}	0.115
CuInS ₂	0.16	0.46×10^{-5}	0.141

3. Conclusion

High-structural-quality single crystals of CuInTe₂ were studied by MR at 4.2 K in magnetic fields B up to 20 T. Zero field OR spectra of the crystals revealed A and B free excitons. The spectral energies of these excitons demonstrated significant blue shifts at increasing magnetic fields. Diamagnetic coefficients of 8.2×10^{-5} and $8.5 \times 10^{-5} \text{ eV T}^{-2}$ for the A and B free excitons, respectively, were determined by fitting quadratic functions into the experimental points assuming a low field limit. Excitons' reduced masses of $0.0575m_0$ and $0.0568m_0$, Rydbergs of 6.2 and 6.1 meV, and Bohr radii 10.4 and 10.5 nm were calculated by applying an isotropic hydrogenic model of a free Wannier exciton in magnetic fields. An effective mass of the electron of $0.062m_0$ and B sub-band hole mass of $0.70m_0$ were calculated assuming a literature A sub-band hole mass of $0.78m_0$.

4. Experimental Section

Single crystals of CuInTe₂ were grown using the vertical Bridgman technique.^[17,26] Crystals from the middle part of the ingot were cleaved and then examined at zero magnetic fields for the presence of excitons in the PL and OR spectra. Such spectra, measured at liquid helium temperatures, were reported earlier.^[17] The elemental composition of the samples was measured by wave-length dispersive spectrometry as Cu:25.4, In:25.3, and Te:49.3 at% corresponding to $[\text{Cu}]/[\text{In}] = 1.00$ and $[\text{Te}]/[\text{Cu} + \text{In}] = 0.97$. The samples were placed in the Faraday configuration (the sample surface being always perpendicular to the magnetic field direction B and the direction of the excitation light from a halogen tungsten lamp) into the bore of a 10 MW resistive magnet at the Grenoble High Magnetic Field Laboratory providing fields B up to 20 T. Light from the lamp was delivered to the samples by an optical fiber. Another fiber was used to collect the MR signal and deliver it to the slits of a 0.5 m focal length single-grating ($1800 \text{ grooves mm}^{-1}$) spectrometer with a liquid nitrogen-cooled InGaAs array detector. The MR spectra were measured at a spectral resolution of 0.2 meV. The orientation of the lattice structure of the crystals with respect to the magnetic field direction was not examined. More details on the experimental set up can be found in Refs. [4,15].

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CuInTe₂, effective masses, excitons, magnetic fields

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