# Energy of excitons in $CuInS_2$ single crystals

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High-quality single crystals of $CuInS_2$, grown by the traveling heater method in an indium solvent, were characterized using photoluminescence (PL) and reflectance (RF) at temperatures from 4.2 to 300 K. A number of well-resolved sharp excitonic peaks have been observed in the near-band-edge region of the PL and RF spectra at 4.2 K. The lines at 1.536 and 1.554 eV in the RF spectra were associated with $A$ and $(B,C)$ free-excitonic transitions, respectively. In the PL spectra the $A$ exciton revealed a well-resolved splitting into two peaks at 1.5348 and 1.5361 eV assigned to the lower and upper branches of exciton polariton, respectively. Other sharp lines were assigned to excitons bound at shallow impurities. The experimental temperature variation of the band gap was analyzed using the Bose–Einstein model. Two deeper bands in the PL spectra were identified as free-to-bound optical transitions followed by phonon replicas. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2152114]

Solar cell technologies, using I-III-$VI_2$ direct band-gap chalcopyrite semiconductors as the absorber layer, have attracted great interest in the last years.[1] One of these chalcopyrites, $CuInS_2$, has the band gap ($E_g \sim 1.53$ eV) almost ideally matching the solar spectrum. Its absorption coefficient is one of the highest amongst the known semiconductors. However, the level of understanding of the material's physics is very low. It is reflected in the difference between the record conversion efficiency of 12% of $CuInS_2$-based solar cells[2–4] and a theoretical limit for a one-junction solar cell of 30%. The detailed band structure near the fundamental band edge has not been established yet. The nature of its intrinsic defects is unclear. Single crystals of $CuInS_2$ have been studied using photoluminescence (PL) (Refs. 5–12), reflectivity (RF) (Ref. 5), photoreflectance (PR) (Refs. 7 and 12), and electroreflectance (ER) (Ref. 5) Although several excitonic transitions have been reported, their spectral positions remain controversial because of the large width of the peaks associated with these transitions due to low quality of the crystals.

The goal of this study is to establish the fine structure of the free- and bound-exciton features in the PL and RF spectra, and their temperature dependence from 4.2 to 300 K measuring high-quality $CuInS_2$ single crystals.

Single crystals of $CuInS_2$ grown by the traveling heater method (THM) using an indium solvent were studied by PL and RF. The PL spectra were measured using excitation with the 488-nm line of an $Ar^+$ laser. A 400-W tungsten halogen lamp was used for the RF measurements. Both the PL and RF spectra were obtained using a liquid He cryostat and 0.6-m grating monochromator with 2.6 nm/mm dispersion. Optical signals were detected by either a photomultiplier tube (Hamamatsu R7400U-20) or a liquid-nitrogen-cooled Ge $p$-$i$-$n$ diode. An electrical signal was amplified using low-noise phase-sensitive lock-in techniques. The RF spectra were taken in a reflection geometry at 20°–25° between the incident light and the sample surface. The elemental composition of the crystals, measured by energy dispersive x-ray analysis (EDX), was Cu: 24.3, In: 25.8, and S: 49.9 at. %. The PL and RF spectra were taken from as-cleaved surfaces of crystals at temperatures from 4.2 to 300 K.

Typical PL spectra taken at 4.2 and 78 K from the $CuInS_2$ single crystals are presented in Fig. 1. The 4.2-K spectrum contains relatively broad peaks $M$ (at $E_M = 1.379$ eV), $N$ (at 1.478 eV), and a number of higher-energy sharp lines shown separately in Fig. 2(a). The $M$ peak is followed by a well-defined sequence of the four phonon replicas $M_{1A_1}$(1.342 eV), $M_{2A_1}$(1.305 eV), $M_{3A_1}$(1.266 eV), and $M_{4A_1}$(1.229 eV) separated by approximately (37±2) meV. These replicas may be attributed to an electronic transition with the participation of zone-center phonons $\Gamma_1$ ($A_1$ mode). The $A_1$ transversal optical mode, detected earlier using infrared absorption and Raman techniques, at either 294 $cm^{-1}$

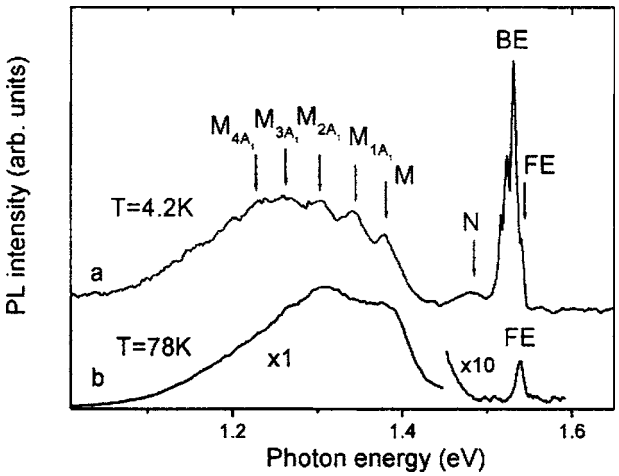


FIG. 1. Photoluminescence spectra from $CuInS_2$ single crystals at (a) 4.2 K and (b) 78 K (FE and BE are free and bound excitons, respectively).

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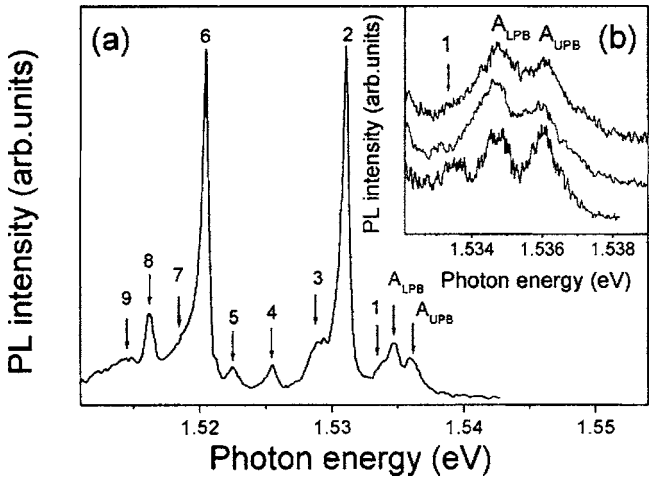


FIG. 2. (a) High-resolution band-edge emission spectra from $CuInS_2$ single crystals at 4.2 K. (b) The *A* excitonic region for three different samples; the spectral resolution is about 0.1 meV.

(36.5 meV) (Ref. 13) or 290 $cm^{-1}$ (36 meV) (Refs. 14 and 15), characterizes $CuInS_2$. Recently this vibrational mode has also been calculated using the valence-force-field model and the density-function perturbation theory at 290 $cm^{-1}$ (36 meV) (Ref. 15) and 313 $cm^{-1}$ (38.8 meV) (Ref. 16), respectively. A small blueshift of the *M* peak of about 2–3 meV was observed at a temperature increase from 4.2 to 78 K. The band gap $E_g$ also increases by about 2 meV at such temperature rise[6] [it can be seen in Fig. 3(c)]. No noticeable energy shift was observed for the *M* peak at variations of the excitation power from 0.1 to 10 W $cm^{-2}$. Thus the *M* band can be attributed to a free-to-bound optical transition. To calculate the activation $E_a$ energy of this defect level the band gap of $E_g$=1.556 eV was derived by adding the reported earlier free-exciton binding energy of 20 meV (Ref. 6) to the measured *A* exciton ground state ($E_A$) at 1.536 eV. Recently, the same value of the *A* exciton energy $E_A$=1.536 eV was suggested from PL measurements.[11] The

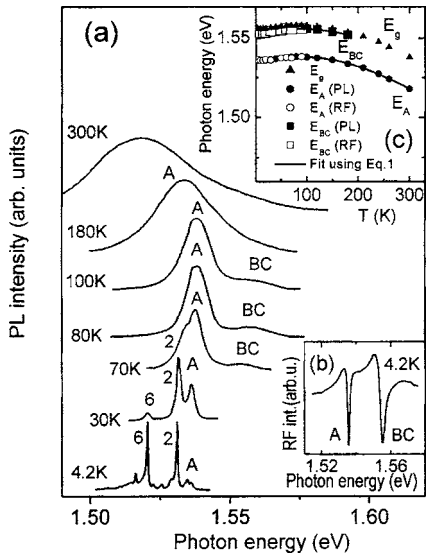


FIG. 3. The temperature dependence of the PL spectra in the near-band-edge region from (a) $CuInS_2$ single crystals; (b) RF spectrum measured at 4.2 K and (c) experimental values of the *A* free-exciton energy $E_A$ [taken from the PL (solid circles) and RF (open circles) measurements] and *BC* free exciton $E_{BC}$ [PL (solid squares), RF (open squares), and $E_g$ energy band gap (solid triangles)] as functions of temperature. The solid lines are numerical fits based on the Bose–Einstein model.

TABLE I. Peak position of free- and bound-exciton lines and their assignment in $CuInS_2$.

| Notation[a] | Energy[b] (eV) | Energy[c] (eV) | Energy[d] (eV) | Notations[d] |
|---|---|---|---|---|
| $A_{UPB}$ | 1.5361 | 1.5355 | 1.535 | $FE_A$ |
| $A_{LPB}$ | 1.5348 | | | |
| | | 1.5347 | | |
| 1 | 1.5336 | | | |
| | | 1.5324 | | |
| 2 | 1.5309 | 1.5298 | 1.530 | EX1 |
| 3 | 1.5289 | 1.5288 | | |
| | | 1.5281 | | |
| 4 | 1.5255 | 1.524 | 1.525 | EX2 |
| 5 | 1.5228 | | | |
| 6 | 1.5203 | 1.5225 | 1.520 | DV |
| 7 | 1.5186 | 1.5173 | 1.5185 | EX3 |
| 8 | 1.5162 | | 1.5165 | EX4 |
| 9 | 1.5138 | 1.5142 | 1.513 | EX5 |

[a]This work.
[b]This work, 4.2 K.
[c]Reference 10, 8 K.
[d]Reference 6, 4.2 K.

activation energy $E_a$ for the *M* recombination center can be found as $E_a=E_g-E_M$=0.177 eV. The elemental composition of our material is slightly In rich. Therefore this transition is very likely to be related to the donor, In interstitial ($In_i$) (Ref. 9). An emission band at 1.38 eV with a satellite 30 meV below has already been observed in the PL spectra of $CuInS_2$ thin films[17] and single crystals.[6,7,9] This emission band was tentatively assigned to a donor-acceptor transition, where the donor is the S vacancy while In vacancy is the acceptor defect.

No considerable shift at excitation power or temperature variation has been observed for the *N* peak, suggesting that this transition can be attributed to a free-to-bound transition between a donor level at about 78 meV and the valence band. Following the assignment of the earlier report[9] we attribute this band to the indium on copper site $In_{Cu}$ defect.

The emission of excitons, bound to donors (or acceptors), dominates the band-edge region above 1.5 eV in the PL spectra at 4.2 K. Their intensity is high with respect to the deeper recombination bands *M* and *N*. The PL spectra, taken at 4.2 K with a spectral resolution of about 0.4 meV, reveal the 11 lines shown in Fig. 2(a). Their energy positions and the proposed assignments, along with those reported by Binsma *et al.*[6] and Yoshino *et al.*,[10] are shown in Table I. The strongest bound-exciton emission lines 2 and 6 have a full width at half maximum (FWHM) of about 0.5 meV. The *A* free-exciton emission exhibits well-resolved doublet structures $A_{LPB}\sim$1.5348 eV and $A_{UPB}\sim$1.5361 eV, shown in Fig. 2(b), and tentatively identified as the lower and upper polariton branches, respectively. This assignment was suggested earlier,[12] however the peaks of this doublet structure were not well resolved. Also the free-exciton splitting of $A_{UPB}-A_{LPB}$=1.3 meV in our experiments is smaller than that measured by Shirakata *et al.*[12] $A_{UPB}-A_{LPB}$=2 meV. This splitting can be clearly seen in Fig. 2(b) and in the inset showing the doublet structure taken at 4.2 K with a spectral resolution of about 0.1 meV for three different $CuInS_2$ samples. The exciton-polariton states and similar doublet structure of free-exciton spectrum have been observed in

other chalcopyrite semiconductors $CuGaSe_2$ (Ref. 18) and $AgGaS_2$ (Ref. 19). The FWHM of the free-exciton lines is about 1.2 meV, which is smaller than that reported earlier,[6,11,12] demonstrating a superior quality of our material. Our spectral positions of the bound-exciton lines 4, 6, and 8 are closer to those determined by Binsma *et al.*[6] rather than those measured by Yoshino *et al.*[10] or Shirakata *et al.*[12]

Line 6 is very narrow and dominates the PL spectra at 4.2 K. The FWHM (0.5 meV) of this line is smaller than $kT$ at temperatures above 6 K, which can be taken as evidence of the excitonic nature of this line. Its temperature-quenching behavior, shown in Fig. 3(a), demonstrates that at 30 K its intensity becomes smaller by about one order of magnitude and by 70 K this line disappears completely due to a dissociation of the bound exciton from the defect when $kT$ exceeds the binding energy of the exciton. Such behavior suggests a bound-exciton origin rather than a donor-level–valence-band transition (DV) proposed by Binsma *et al.*[6] A detailed discussion on binding energies of excitons in $CuInS_2$ will be published shortly in our forthcoming paper. The 1.5347 eV line, reported by Yoshino[10] as a bound exciton, is very likely to be our line $A_{LPB}$ at 1.5348 eV. For the first time we report the exciton lines 1 and 5, shown in Fig. 2(a) and Table I.

Figure 3(a) shows the evolution of the PL spectra at temperature rise from 4.2 to 300 K demonstrating that (1) the intensity of the $A$ free-exciton peak decreases much slower than that of the bound-exciton lines, becoming greater than that of the bound excitons above 50 K, and (2) the bound-exciton lines completely disappear by 80 K, indicating the dissociation of the excitons due to thermal effects, whereas the $A$ free-exciton peak can be observed up to 240 K. The FWHM of the $A$ peak at 80 K was measured to be about 9 meV. At room temperature the PL band at 1.517 eV, with a FWHM of about 41 meV, is associated with the band-to-band transition. The broader PL peak ($BC$) appearing at the high-energy side of the $A$ free-exciton peak at temperatures above 30 K originates from the free-exciton transition belonging to the double degenerate $\Gamma 7$ valence band, which lies near $k=0$ about 18 meV below the $\Gamma 6$ valence band ($A$ exciton).[6] The $A$ and $BC$ excitons, separated by 18 meV due to the spin-orbital interaction, can be seen in Fig. 3(a) well resolved at temperatures from 40 to 180 K, and merged at temperatures above 180 K. They shift towards higher energy up to a maximum at 1.5382 eV ($A$ peak) and 1.5562 eV ($BC$ peak) at 80 K. No noticeable changes in the spectral position of the excitons were observed from 4.2 to 20 K. Above 80 K the $A$ and $BC$ peaks shift towards lower energy. As the temperature increases up to 60 K all the bound-exciton lines shift to higher energies following the $A$ free-exciton peak.

We also measured RF spectra at temperatures from 4.2 to 300 K. As an example a RF spectrum, taken at 4.2 K, is shown in Fig. 3(b). The experimental data on the low-temperature dependence (up to 80 K) for $A$ and $BC$ RF peaks are included in Fig. 3(c).

A Bose-Einstein-type expression[20] has been fitted into the experimental points of the temperature dependence of the $A$ and $BC$ exciton spectral positions

$$E(T) = E(0) - \alpha/[\exp(\Theta/T) - 1], \quad (1)$$

where $\alpha$ represents the strength of the average exciton-phonon interactions and $\Theta$ corresponds to the average phonon temperature. This fitting line is shown by a solid line in Fig. 3(c). The fitting parameters for the Bose–Einstein expression are $E_A$ (80 K)=1.5382 eV, $\alpha$=0.169 eV, and $\Theta$=672 K for the $A$ exciton, and $E_{BC}$ (80 K)=1.5562 eV, $\alpha$=0.1600 eV, and $\Theta$=667 K for the $BC$ exciton. The energy band gap of $CuInS_2$ dependence between 4.2 and 300 K, calculated by adding the exciton binding energy of 20 meV to the $A$ free-exciton transition energy, is shown in Fig. 3(c). The anomalous temperature change of the band gap $E_g$ can be caused by the combined effect of the lattice constant change and electron-phonon interaction. A similar temperature dependence of $E_g$ was established for other chalcopyrite semiconductor for example $CuInSe_2$ (Ref. 21).

In summary, a number of free and bound excitons have been shown resolved in the PL and RF spectra of high-quality $CuInS_2$ single crystals at 4.2 K. The FWHM of about 1.2 and 0.5 meV were measured for the free- and bound-exciton peaks, respectively. For the first time the upper and lower branches with the FWHM of 1.3 meV of the $A$ free-exciton-polariton emission line were resolved at 4.2 K. Two new bound-exciton lines have been observed. Two deeper bands were identified as free-to-bound optical transitions. One of these bands is followed by four phonon replicas. The experimental temperature dependence of the $A$ and $BC$ excitonic peak spectral positions was fitted with a line using the Bose–Einstein model.

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