Temperature dependence of very deep emission from an exciton bound to an isoelectronic defect in polycrystalline $CuInS_2$

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Zero-phonon lines (ZPLs) of deep exciton bound to isoelectronic deep-donor–deep-acceptor pair in $CuInS_2$ are studied by photoluminescence. These ZPLs have peak positions at 0.6241 eV (*A* line) and 0.6220 eV (*B* line), followed by two series of phonon replicas with phonon energies of 8 and 40.5 meV. Temperature dependence of the intensity of these ZPLs is explained by electron-phonon coupling to a single phonon mode with energy of 8 meV and shows that the lines are originated from two excited state levels of the same exciton. The (anomalously strong) temperature broadening of ZPLs follows $\sim T^{2.6}$ law and can be explained by assuming a strong vibronic coupling between two excited states. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2266597]

Polycrystalline I-III-VI_2 chalcopyrite semiconductors are currently under intense investigation for the application in thin film photovoltaics. Among them, the ternary compound $CuInS_2$ (CIS) has the potential of reaching a high solar-to-electric efficiency due to its direct band gap of about 1.5 eV. However, these semiconductors are usually accompanied by a large number of intrinsic defects. While in other typical semiconductors these native defects usually have a very detrimental effect on the performance of optoelectronic devices, polycrystalline chalcopyrite compounds would seem to be, somehow, very good electronic materials. This indicates that, in spite of the detailed theoretical studies, see, for example, Ref. 1, the specific defect structure and the full role of these intrinsic defects on optoelectronic properties are still far from being completely understood.

Photoluminescence (PL) spectroscopy is known to be a very sensitive tool for the characterization of defects in semiconductors, but the high concentration of intrinsic defects in the chalcopyritic materials usually leads to wide structureless PL bands. However, there is a certain progress also, because many groups have grown CIS crystals which show sharp excitonic emission.[2–6] At the same time deep defects in CIS are still less studied. In Ref. 7 the systematic experimental study of some deep PL bands in $CuInS_2$ and $CuGaSe_2$ was performed. It was shown that in $CuInS_2$ the so-called *D*1 and *D*2 PL bands, having the peak positions at 0.954 and 0.864 eV, respectively, are caused by the recombination within a deep-donor–deep-acceptor (DD-DA) complex. The underlying model was that the *D*1 and *D*2 bands are formed via a donor-acceptor pair recombination between pairs of the closest neighbors and between pairs of the next-closest neighbors, respectively. Later even deeper PL bands were found in CIS and in many other ternaries, corresponding to the next larger distances between the deep donor and the deep acceptor.[8,9] These very closely situated DD-DA pairs can be treated as neutral isoelectronic centers. It is known that isoelectronic centers (and neutral defect complexes) in many semiconductors can bound excitons, see, for example, Refs. 10–14. The simple model adopted by Hopfield *et al.*[15] appears to be useful in most cases of neutral ("isoelectronic") defects; these may be classified as either dominantly hole attractive or electron attractive, even for complex defects. The primary particle bound at a neutral defect typically has a very localized wave function, which is not possible to describe in an effective-mass-like model. The localized nature of the bound hole at hole-attractive neutral complex defects makes it very sensitive to the symmetry of the local defect potential, and thus these bound excitons can be used to study deep defects. In case of isoelectronic defects, the exciton zero-phonon line (ZPL) spectra were explained in terms of a split excited state due to the electron-hole *j-j* (exchange) coupling and an unsplit ($J=0$) ground state. The model for the chalcopyrite structure[16] predicts the spectrum of an exciton bound to an isoelectronic defect consisting of three transitions, two of which are allowed and one is forbidden. Although in some chalcopyrites deep excitons bound to isoelectronic defects were observed,[13,17] there were no indications of such excitons in I-III-VI_2 chalcopyrite semiconductors. In Ref. 18 very sharp lines corresponding to deep PL emission in CIS were observed. This emission showed two zero-phonon lines (ZPLs) at 0.6237 and 0.6216 eV followed by two series of phonon replicas with phonon energies 8 and 40.5 meV. In this letter the temperature dependence of these ZPLs in CIS is studied.

The polycrystalline $CuInS_2$ material was synthesized from a stoichiometric mixture of the constituent elements (5*N* purity). The sealed ampoule with the starting materials was heated up to 1360 K in a tunnel furnace and held for 3 h. After that, the temperature was lowered to 1110 K and held for 12 h, followed by cooling of the furnace to room temperature. Small pieces with a size about 2 mm were broken off the ingot for annealing and/or photoluminescence studies. The Cu annealing was arranged in small evacuated quartz ampoules containing some $CuInS_2$ pieces and a 5*N*-purity Cu piece. The annealing time was 12 h and the annealing temperatures were 670 or 770 K. Finally a slow cooling to 470 K at a rate of 2–3 K/h was performed.

For the PL measurements reported here, a He–Cd laser with a wavelength of 441 nm was used for excitation. The

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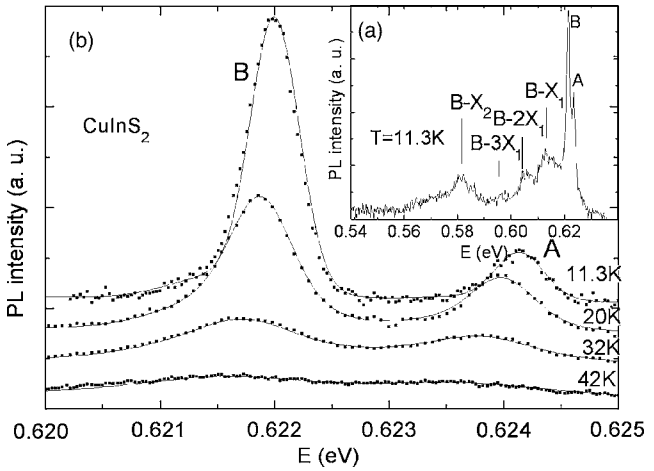

FIG. 1. (a) Low-resolution PL spectrum of deep excitons in $CuInS_2$ measured with PbS detector. Two zero-phonon lines (A and B) are resolved. Phonon sidebands show coupling with two phonons (X_1 and X_2); (b) high-resolution PL spectra of A and B peaks measured with InGaAs detector at different temperatures. Experimental points (dots) are fitted (lines) using Voigt function.

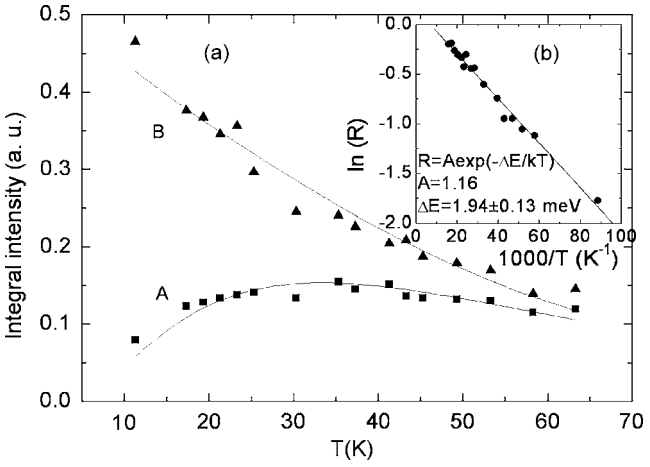

FIG. 2. (a) Temperature dependence of the integral intensity of ZPLs A and B (dots) and the results of fitting using Eqs. (1) and (2) (lines); (b) temperature dependence of the ratio $R=I_A/I_B$ (dots) and the fitting (line) showing the activation energy of 1.94 meV.

samples were mounted inside a closed cycle He cryostat ($T=11-300$ K). The PL spectra were recorded with a computer controlled SPM-2 grating monochromator ($f=0.4$ m). The chopped signal was detected with an InGaAs or PbS detector using the conventional lock-in technique. The emission spectra were corrected for the grating efficiency variations and for the spectral response of the detectors.

Typical PL spectrum taken at 11.3 K from the $CuInS_2$ sample is presented in Fig. 1(a). Two ZPLs at 0.6241 eV (A line) and 0.6220 eV (B line) can be seen followed by phonon replicas. As in Ref. 17, two phonons (X_1 and X_2) can be detected. These phonons have energies of 8 and 40.5 meV, respectively. Very similar phonons were also observed in other chalcopyrite semiconductor $ZnGeP_2$ (Ref. 13) where the X_1 phonon was assigned to a local mode. The X_2 phonon is probably connected with CIS lattice. At this point it is quite speculative to assign the X_2 phonon to any lattice mode of CIS because several phonons occur near 40.5 meV. Figure 1(b) shows both ZPLs measured at different temperatures with improved spectral resolution due to more sensitive InGaAs detector. Spectra have been displaced vertically for clarity. Experimental spectral lines were fitted using a Voigt shape, where the Gaussian component (width of 0.49 meV) was representing an inhomogeneous broadening and an apparatus function of the spectrometer. This component was assumed to be temperature independent, while the Lorentzian component of the Voigt curve represented the temperature dependent shape of the ZPLs. Results of this fitting are presented as continuous lines in Fig. 1(b). It can be seen that the energetic distance between A and B lines is 2.1 meV, and this distance is constant over the full temperature region studied. The energetic shift of ZPLs is linear in temperature with a coefficient of -0.01 meV/K for both lines.

The temperature dependence of the integral intensities of two ZPLs is given in Fig. 2(a), whereas the inset in Fig. 2(b) presents the Arrhenius plot for the ratio $R=I_A/I_B$ of two intensities. One can see from the latter figure that the ratio R can be described by a single activation energy ΔE which is practically equal to the spectral energy separation between A and B peaks.

In the framework of linear electron-phonon coupling when the main interaction includes only one phonon, the temperature dependence of the integral intensity of each ZPL is given by[19]

$$I_j(T) = n_j(T) \cdot D_j \exp\left[- S_j \cdot \coth\left(\frac{\varepsilon_j}{2kT} \right) \right] \quad (j = A,B), \tag{1}$$

where S is the Huang-Rhys parameter, ε is the phonon energy, n is the occupation of the initial level, and D is a preexponential factor. In case of two excited state electronic levels with energy separation ΔE, the thermalization changes the occupation of both levels (A and B):

$$n_A(T) = \frac{1}{1+\exp(\Delta E/kT)}, \quad n_B(T) = \frac{\exp(\Delta E/kT)}{1+\exp(\Delta E/kT)}. \tag{2}$$

Assuming the same electron-phonon coupling for both transitions (i.e., $\varepsilon_A=\varepsilon_B$ and $S_A=S_B$), the ratio of integral intensities for ZPLs A and B is given by a simple exponent

$$R(T) = \frac{I_A(T)}{I_B(T)} = \frac{D_A}{D_B} \exp\left(- \frac{\Delta E}{kT} \right) \tag{3}$$

as it was observed according to Fig. 2(b). At the same time, the integral intensity of each peak also follows the theory, see Fig. 2(a). Experimental points were fitted using Eqs. (1) and (2) assuming that we have only one phonon X_1 with energy $\varepsilon=8$ meV and that $\Delta E=2.1$ meV. The fitting results are shown as solid lines in Fig. 2(a). The fitting parameters are $D_A=2.0\pm0.3$, $S_A=1.3\pm0.1$, $D_B=2.1\pm0.3$, and $S_B=1.5\pm0.1$. As it can be seen from Fig. 2, there is a slight deviation between experiment and theory at low temperatures. We indeed observed that the laser emission caused small heating of our sample, and therefore the temperature inaccuracy is probably the main reason of this deviation and not the fact that we did not take into account coupling with other phonons. The Huang-Rhys factors found from fittings, see Fig. 2(a), are at the same range with the factor obtained from Fig. 1(a) using the intensity distribution of X_1 phonon sidebands, i.e., $S\sim1.0-1.5$. Finally we note that the intensities of two lines tend to equalize at higher temperatures (i.e., $D_A/D_B\sim1$), which shows that the two transitions have simi-

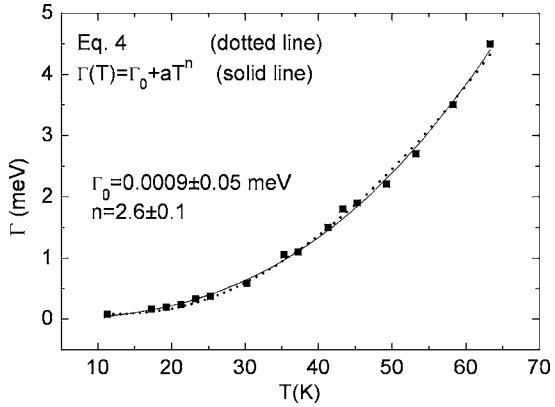

FIG. 3. Temperature dependence of the linewidth of the ZPL (Lorentzian component): measured values (dots) and fitted with Eq. (4) (dotted line) and with a function $\Gamma(T)=\Gamma_0+aT^n$ (solid line). Fitting parameters are also given.

lar probabilities. This is different from the situation observed for a bound exciton in $ZnGeP_2$ (where ZPL B is strongly forbidden),[13] but is similar for A and B lines of Ag-related defect in Si.[14]

In Fig. 3 the temperature dependence of the width of the ZPL (Lorentzian component) is shown. Both peaks have approximately the same width, and therefore only one of them is given in Fig. 3. This temperature dependence could be fitted with the formula

$$\Gamma(T) = \Gamma_0 + \frac{b}{\exp(\varepsilon/kT) - 1}\left(1 + \frac{1}{\exp(\varepsilon/kT) - 1}\right), \qquad (4)$$

which describes ZPL broadening due to the second order coupling of the electronic transition to a phonon mode with energy ε and has been frequently used for describing the experimental data (see, e.g., Refs. 20 and 21). Γ_0 is the linewidth at $T=0$ K, and b is the coupling constant. It can be seen in Fig. 3 that Eq. (4) is a very good fitting function, indeed, and the phonon energy obtained from the fitting ($\varepsilon = 8.3 \pm 0.5$ meV) corresponds well to the X_1 phonon energy. A closer look reveals, however, that the value of the coupling constant obtained from fitting ($b = 11 \pm 2$ meV) is far too big for the validity of formula (4). This formula has been derived using perturbation theory[22] and is therefore valid only in the case of weak coupling when $(b/\gamma)^{1/2} \ll 1$.[23] Parameter γ in the latter condition is the half-width of the spectral peak in the phonon density of states, which arises due to the finite lifetime of the phonon (i.e., γ is given by the inverse value of phonon's lifetime). Obviously this half-width γ should be smaller than the energy ε of the phonon, which means that $\gamma < 8$ meV and the above condition is far from being satisfied. The application of the results of nonperturbative theory, generalizing the result (4) for an arbitrary coupling strength (but still dealing with an electronic transition between two isolated nondegenerate levels),[23,24] completely failed to describe so significant ZPL broadening as observed in the experiment. Both couplings to a local vibration or to Debye phonons[25,26] were assumed at this stage but were unsuccessful. Recently a theory was developed for accounting the influence of (pseudo-) Jahn-Teller effect on ZPL broadening.[27,28] It predicts approximately $\Gamma \sim T^3$-type dependence in a relatively wide temperature limits. Fitting our results with a function $\Gamma(T)=\Gamma_0+aT^n$ resulted in a value of n close to 3 (see Fig. 3). This result shows that a serious dynamic perturbation of the bound exciton must take place, most probably due to pseudo-Jahn-Teller effect involving two close excited state levels.

In summary, the temperature dependence of the zero-phonon lines related to deep-donor–deep-acceptor neutral defect bound excitons can be explained by the linear electron-phonon interaction with a phonon mode with energy of 8 meV and by quadratic electron-phonon interaction involving vibronic mixing of the excited state levels separated by 2.1 meV.

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[1] S. B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
[2] K. Wakita, H. Hirooka, S. Yasuda, F. Fujita, and N. Yamamoto, J. Appl. Phys. **83**, 443 (1998).
[3] J. J. M. Binsma, L. J. Gilliny, and J. Bloem, J. Lumin. **27**, 55 (1982).
[4] K. Yoshino, T. Ikari, and S. Shirakata, Appl. Phys. Lett. **78**, 742 (2001).
[5] S. Shirakata and H. Miyake, J. Phys. Chem. Solids **64**, 2021 (2003).
[6] M. V. Yakushev, A. V. Mudryi, I. V. Victorov, J. Krustok, and E. Mellikov, Appl. Phys. Lett. **88**, 011922 (2006).
[7] J. Krustok, J. H. Schön, H. Collan, M. Yakushev, J. Mädasson, and E. Bucher, J. Appl. Phys. **86**, 364 (1999).
[8] J. Krustok, J. Raudoja, J.-H. Schön, M. Yakushev, and H. Collan, Thin Solid Films **361-362**, 406 (2000).
[9] J. Krustok, J. Raudoja, M. Krunks, H. Mändar, and H. Collan, J. Appl. Phys. **88**, 205 (2000).
[10] J. Weber, H. Bauch, and R. Sauer, Phys. Rev. B **25**, 7688 (1982).
[11] T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1968).
[12] C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968).
[13] C. I. Rablau and N. C. Giles, J. Appl. Phys. **90**, 3314 (2001).
[14] G. Davies, T. Gregorkiewicz, M. Z. Iqbal, M. Kleverman, E. C. Lightowlers, N. Q. Vinh, and M. Zhu, Phys. Rev. B **67**, 235111 (2003).
[15] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).
[16] J. Shah and E. Buehler, Phys. Rev. B **4**, 2827 (1971).
[17] R. E. Nahory, Jagdeep Shah, R. C. C. Leite, E. Buehler, and J. H. Wernick, Phys. Rev. B **1**, 4677 (1970).
[18] J. Krustok, J. Raudoja, and H. Collan, Thin Solid Films **387**, 195 (2001).
[19] K. K. Rebane, *Impurity Spectra of Solids* (Plenum, New York, 1970).
[20] A. Freiberg and L. A. Rebane, Phys. Status Solidi B **81**, 359 (1977).
[21] C. Hecht, R. Kummer, M. Thoms, and A. Winnacker, Phys. Rev. B **55**, 13625 (1997).
[22] M. A. Krivoglas, Sov. Phys. Solid State **6**, 1340 (1964).
[23] I. S. Osadko, Fiz. Tverd. Tela (Leningrad) **19**, 1683 (1977).
[24] D. Hsu and J. L. Skinner, J. Chem. Phys. **83**, 2097 (1985).
[25] I. S. Osadko, Sov. Phys. Usp. **22**, 311 (1979).
[26] D. Hsu and J. L. Skinner, J. Chem. Phys. **81**, 5471 (1984).
[27] V. Hizhnyakov, H. Kaasik, and I. Sildos, Phys. Status Solidi B **234**, 644 (2002).
[28] V. Hizhnyakov, V. Boltrushko, H. Kaasik, and I. Sildos, J. Chem. Phys. **119**, 6290 (2003).