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A photoluminescence study of excitonic grade $CuInSe_2$ single crystals irradiated with 6 MeV electrons

M. V. Yakushev,[1,2,3,a)] A. V. Mudryi,[4] O. M. Borodavchenko,[4] V. A. Volkov,[2] and R. W. Martin[1,b)]
[1]*Department of Physics, SUPA, Strathclyde University, G4 0NG Glasgow, United Kingdom*
[2]*Ural Federal University, Ekaterinburg 620002, Russia*
[3]*Institute of Solid State Chemistry of RAS, Ekaterinburg 620990, Russia*
[4]*Scientific-Practical Material Research Centre of National Academy of Science of Belarus, 220072 Minsk, Belarus*

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High-quality single crystals of $CuInSe_2$ with near-stoichiometric elemental compositions were irradiated with 6 MeV electrons, at doses from 10^{15} to $3 \times 10^{18}\,cm^{-2}$, and studied using photoluminescence (PL) at temperatures from 4.2 to 300 K. Before irradiation, the photoluminescence spectra reveal a number of sharp and well resolved lines associated with free- and bound-excitons. The spectra also show broader bands relating to free-to-bound transitions and their phonon replicas in the lower energy region below 1.0 eV. The irradiation with 6 MeV electrons reduces the intensity of the free- and the majority of the bound-exciton peaks. Such a reduction can be seen for doses above $10^{16}\,cm^{-2}$. The irradiation induces new PL lines at 1.0215 eV and 0.9909 eV and also enhances the intensity of the lines at 1.0325 and 1.0102 eV present in the photoluminescence spectra before the irradiation. Two broad bands at 0.902 and 0.972 eV, respectively, are tentatively associated with two acceptor-type defects: namely, interstitial selenium (Se_i) and copper on indium site (Cu_{In}). After irradiation, these become more intense suggesting an increase in the concentration of these defects due to irradiation. [http://dx.doi.org/10.1063/1.4934198]

I. INTRODUCTION

$CuInSe_2$ is a semiconductor compound with chalcopyrite structure which attracts great interest due to its successful application in the absorber layer of thin film solar cells. Efficiencies exceeding 21% have been demonstrated for laboratory size cells with $Cu(In,Ga)Se_2$ absorber layers, which is currently the world record conversion efficiency for thin film photovoltaic (PV) devices.[1]

A specific advantage of $CuInSe_2$-based PV devices is their exceptionally high tolerance to radiation. Measurements of the principal solar cell parameters after irradiation demonstrate almost total insensitivity of the conversion efficiency to high-energy electrons up to doses of $10^{16}\,cm^{-2}$.[2,3] Investigations of $Cu(In,Ga)Se_2$-based solar cells irradiated with higher doses of MeV electrons confirmed a considerable stability of their performance. The conversion efficiency dropped by less than 10% after a dose of $10^{17}\,cm^{-2}$.[4,5] Theoretical studies suggest that the origin of this stability is the high mobility of copper atoms combined with the low formation energies of the defect complexes ($2V_{Cu}$-In_{Cu}).[6] However, experimental evidence about these effects would be highly beneficial in order to provide further knowledge about the material properties. Furthermore, the radiation hardness is linked with the general understanding of intrinsic defects in $CuInSe_2$ which is important for further advances in the solar cell performance. High-energy electrons are convenient particles to generate structural defects in semiconductors as they create spatially uniform populations of defects which can then be studied to clarify the nature of intrinsic defects in complicated materials such as $Cu(In,Ga)Se_2$.[7]

Photoluminescence (PL) is an important method for the study of defects in semiconductors.[8,9] Reports on the effects of high energy electron irradiation on PL spectra of $Cu(In,Ga)Se_2$ can be found in the literature.[10–12] However, such reports provide limited information on the physical nature of the defects generated by radiation or on the mechanisms of the extraordinary radiation hardness of $CuInSe_2$. The main reason for this is the high level of doping of the materials used for such studies, which were thin polycrystalline films with [Cu]/[In+Ga] ratios smaller that unity. At such elemental compositions, the high concentrations of charged defects lead to formation of band-tails and the presence of potential fluctuations dramatically reduces the information which can be gained from PL. The spectra are dominated by a broad and asymmetric band associated with band-to-tail transitions.[13–15] Optical spectroscopy studies on semiconductors with low defect concentrations showing excitonic features in their spectra can provide significantly more information.[8,16] However, there are relatively few reports revealing resolved excitonic features in the PL spectra from $CuInSe_2$ because of the challenges facing the growth of high-quality material.[17–20]

This paper presents a study of the effects of 6 MeV electron radiation on high purity $CuInSe_2$ single crystals with a number of sharp excitonic features in the PL spectra. These features are used as sensitive indicators to monitor changes in the structural quality and defect balance of the material due to electron irradiation.

[a)]Author to whom correspondence should be addressed. Electronic mail: michael.yakushev@strath.ac.uk
[b)]r.w.martin@strath.ac.uk

II. EXPERIMENTAL DETAILS

High-quality $CuInSe_2$ single crystals were grown by the vertical Bridgman method from a near stoichiometric melt of high purity Cu, In, and Se.[21] Samples were cut from the middle part of the ingot. The elemental composition was measured using energy dispersive x-ray (EDX) analysis (Cu:25.2; In:24.7; Se:50.1 at. %) and found to be near-stoichiometric with a copper to indium ratio [Cu]/[In] of 1.02. Freshly cleaved surfaces of the as-grown samples were pre-characterised using PL at 4.2 K in an optical closed-cycle helium cryostat. The 514 nm line of a 300 mW Ar^+ laser was used for excitation. The PL signal was focused on the entrance slits of a 1 m single grating monochromator and the intensity measured by a thermoelectrically cooled InGaAs Hamamatsu photomultiplier tube (H9170-75) sensitive in the spectral ranges from 0.95 to 1.7 μm.

The pre-characterised samples were then irradiated with 6 MeV electrons at doses from 10^{15} to $3 \times 10^{18}\,cm^{-2}$ using current densities of about $2 \times 10^{12}\,cm^{-2}\,s^{-1}$ delivered by a linear electron accelerator. During the irradiation, the sample temperature was kept below 50 °C by a water-cooled stage. Following irradiation, the samples were reanalysed using PL at temperatures from 4.2 to 100 K and excitation power densities from 2 to 43 W/cm^2.

III. RESULTS AND DISCUSSION

A. PL emission in virgin $CuInSe_2$

A typical 4.2 K PL spectrum from the non-irradiated material is shown in Fig. 1(a). The spectrum is dominated by the near-band-edge sharp lines which have previously been assigned to free excitons and excitons bound to shallow defects.[17–19] The lower energy region reveals broader bands N ($\sim$1.002 eV), P ($\sim$0.972 eV), and K ($\sim$0.972 eV) along with some phonon replicas with $E_{LO} \approx 29$ meV.[22] The shape of the K band is modified by water absorption in the region of 0.9 eV. The possible origin of these emission bands has been proposed in Ref. 19 analysing theoretical estimates of the defect formation energies, energy levels in the band gap, and comparing them with the experimental data.[23,24] We have followed these assignments in our analysis of the PL spectra measured before and after irradiation.

The spectral positions of the N, K, and P bands do not shift with changing excitation power. As the temperature is increased from 4.2 K to 70 K, they shift towards higher energies by about 2–3 meV, which is close to kT/2 and suggest that the recombination mechanism is a free-to-bound transition.

The P band has been assigned to recombination of conduction band electrons with holes bound at the copper on indium site (Cu_{In}) anti-site acceptor defect. This generates a level at about 77 meV above the valence band.[19] The K band was also attributed to free-to-bound recombination of conduction band electrons and an acceptor level at 147 meV above the valence band, which has been assigned to interstitial selenium (Se_i).[19] The N band was assigned to copper vacancies (V_{Cu}) with a level at 49 meV above the valence band.[19]

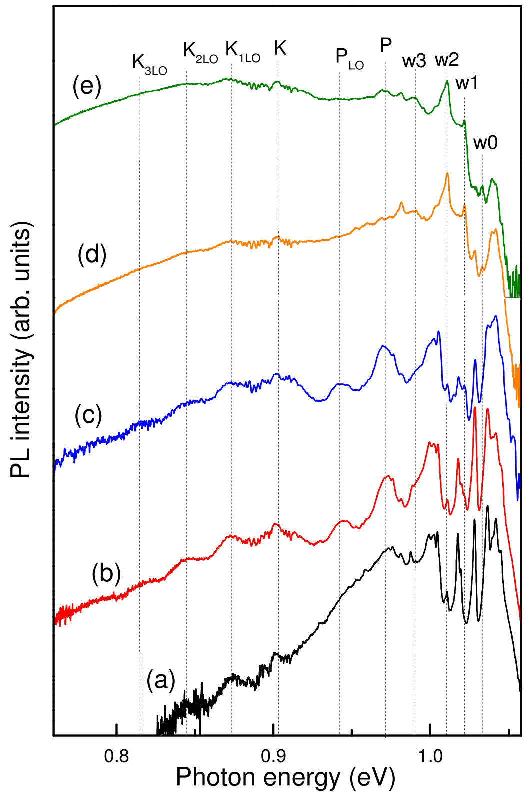

FIG. 1. The evolution of the 4.2 K PL spectrum of $CuInSe_2$ single crystals with irradiation dose. Non-irradiated (a), irradiated with doses of 10^{16} (b), 4×10^{16} (c), 10^{18} (d), and 3×10^{18} (e) cm^{-2} of 6 MeV electrons. The PL intensity is shown on a logarithmic scale. The spectra are shifted on the intensity scale for clarity.

The near-band-edge region of the spectrum from the non-irradiated $CuInSe_2$ is shown in more detail in Fig. 2 and compared with the $10^{18}\,cm^{-2}$ dose spectrum. The non-irradiated spectrum reveals peaks assigned to A ($\sim$1.0417 eV) and B ($\sim$1.0448 eV) free excitons.[17–20]

The chalcopyrite crystal structure of $CuInSe_2$ can be derived from the sphalerite one of ZnSe by the ordered substitution of zinc with alternating indium and copper. Such a substitution results in a chalcopyrite structure with different lengths of the chemical bonds for the Cu-Se and In-Se pairs. This generates a tetragonal distortion which splits the triply

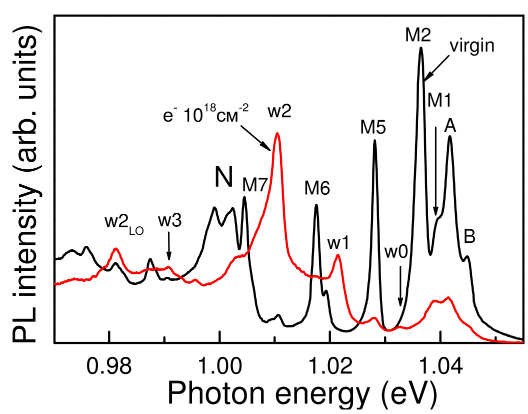

FIG. 2. The near-band-edge region of the PL spectra measured in the virgin $CuInSe_2$ single crystals (red) and after irradiation with a dose of $10^{18}\,cm^{-2}$ of 6 MeV electrons (black) shown on a linear scale.

degenerated valence band of ZnSe into A, B, and C sub-bands.[25] Such a splitting can be described as the simultaneous influence of the non-cubic crystal-field and the spin-orbit interaction. The low temperature PL spectra of high quality $CuInSe_2$ reveal A and B free excitons comprising an electron from the conduction band and a hole from either the A or B sub-valence band, respectively.[17,18] Fig. 2 also reveals other sharp lines: M1 at ∼1.0394, M2 at ∼1.0365, M5 at ∼1.0280, M6 at ∼1.0175, and M7 at ∼1.0045 eV.

The M1 line, reported earlier as a multiplet with three[18] or four[20] components and assigned in Ref. 19 to interstitial copper atom (Cu_i) donors, appears in the PL spectrum in Fig. 2 as a non-resolved shoulder of the A exciton. The M2 exciton, assigned in Ref. 19 to the indium on copper (In_{Cu}) antisite donor appears as a single line not resolved into additional peaks as observed in Refs. 18 and 20, suggesting an inferior structural quality of the present $CuInSe_2$ crystals with respect to those analysed in those papers. The M5 line is assigned to the copper on selenium (Cu_{Se}) acceptor antisites or to indium vacancies (V_{In}).[19] The M6 and M7 lines have not yet been assigned to any specific defects.

B. PL emission from irradiated material

6 MeV electron irradiation induces considerable changes to the PL spectrum as shown in Fig. 1 for increasing doses of electrons with the same laser excitation power for each measurement. The PL spectral intensity is seen to increase in the lower energy region and decrease in the near-band-edge region.

Considering the lower energy region of the spectra, irradiation with doses of 10^{16} and $4 \times 10^{16}\,cm^{-2}$ clearly increases the intensity of the P and K bands, whereas the N band intensity does not grow. The background emission for energies up to 1 eV is seen to gradually increase with irradiation dose. Following doses exceeding $10^{18}\,cm^{-2}$, the intensities of the K, P, and N bands and their phonon replicas are reduced.

In the near-band-edge region of the PL spectra, shown in Fig. 3, the irradiation reduces the intensity of the A and B free excitons, as well as that of the M2, M5, M6, and M7 bound-excitons. Their peaks also become broader, with the full width at half maximum (FWHM) of the M5 line increasing from about 1 meV to 1.5 meV after a dose of $10^{18}\,cm^{-2}$. Small red shifts of up to 2 meV are observed after irradiation with doses exceeding $10^{18}\,cm^{-2}$ for the free and bound excitons, as well as for the free-to-bound P and K peaks.

A reduction of the absolute intensity of the A and B free-excitons as well as of the M2, M5, M6, and M7 bound-excitons has been observed after the lowest dose of $10^{16}\,cm^{-2}$. This suggests that high structural quality material with low concentrations of intrinsic defects and an elemental composition close to ideal stoichiometry is not radiation hard. As seen in Figs. 1 and 3, the irradiation results in a considerable redistribution of the PL intensity from the higher energy near-band-edge region towards the lower energy one.

Alongside this redistribution, five distinct new lines appear in the spectra after irradiation with a dose of $10^{16}\,cm^{-2}$ (w0 at 1.0325 eV, w1 at ∼1.0215 eV, w2 at ∼1.0102 eV, w3 at ∼0.9909 eV, and $w2_{LO}$ at ∼0.98 eV). These lines become even more prominent once the dose increases further as shown in Fig. 3. Fig. 2 shows how they dominate the PL spectrum after a dose of $10^{18}\,cm^{-2}$. Following this dose, the FWHMs of w0, w1, w2 lines have become 1.1, 1.5, and 2.2 meV, respectively, which is close to the FWHM of the M5 excitonic line in the same spectrum (1.5 meV). This suggests that the w-lines can also be associated with excitons bound to defects.

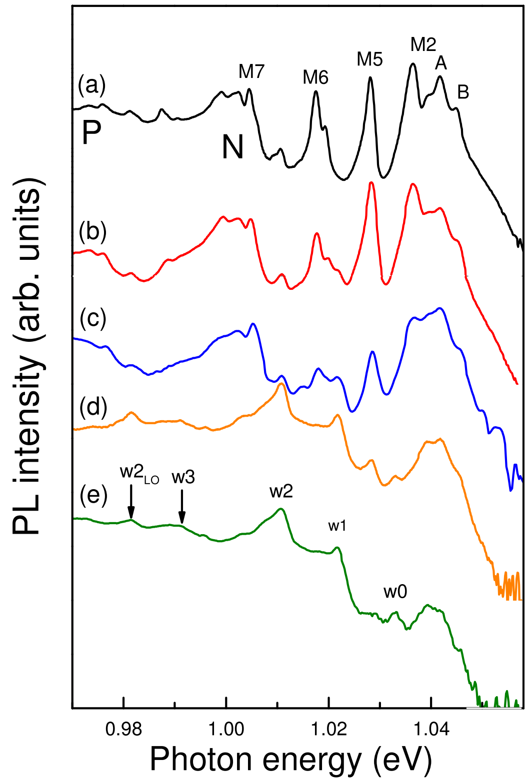

FIG. 3. The evolution of the near-band-edge region of the PL spectrum measured in a $CuInSe_2$ single crystal before irradiation (a), irradiated with doses of 10^{16} (b), 4×10^{16} (c), $10^{18}\,cm^{-2}$ (d), and $3 \times 10^{18}\,cm^{-2}$ (d) of 6 MeV electron radiation. The PL intensity is shown on a logarithmic scale. The spectra are shifted on the intensity scale for clarity.

The spectral position of the w0-line is close to that of the M4-line observed at 1.032 eV in earlier PL spectra from $CuInSe_2$ single crystals[19,26] and thin films.[27] The increasing intensity of this line with irradiation suggests that defects associated with the M4 exciton are being generated by the incident electrons. The w1-line has not been observed in the PL spectra of non-irradiated $CuInSe_2$, suggesting that defects associated with this line are not present in the virgin material but induced by the irradiation. As seen in Fig. 2, the w2-line is present in the spectrum of the virgin $CuInSe_2$, albeit at quite low intensity. This suggests a low concentration of the related defect in virgin material, whereas Figs. 1 and 2 show that it can be resolved after doses as low as $10^{16}\,cm^{-2}$ and becomes dominant after a dose of $10^{18}\,cm^{-2}$. Another component, $w2_{LO}$ follows w2 at a spectral distance of $E_{LO} = 29$ meV and is assigned to an LO phonon replica. The deepest sharp line appearing after electron irradiation (w3) has not been observed in the PL spectra of virgin $CuInSe_2$ and is therefore related to radiation induced defects.

After irradiation with doses in excess of $10^{18}\,cm^{-2}$, the w-lines become broader and gradually shift towards lower energies. This shift and broadening can be explained by an increase in the internal stress induced by high concentrations of radiation generated defects. Similar effects of broadening of the A and B free-excitonic lines as well as their shifts to lower energy have been observed in high-quality $CuInSe_2$ single crystals with small deviations from the ideal stoichiometry.[26] Deviations of the In/Cu ratio from unity induce red shifts of their spectral position and an increase in their widths in PL and reflectivity spectra. These effects are also attributed to internal stress due to high populations of intrinsic defects. Structural defects cause spectral shifts of the excitonic lines. The values of the shifts vary from point to point in the crystal so that the observed excitonic peaks, being a superposition of a number of Lorentzian like lines, become inhomogeneously broadened and their shape becomes Gaussian like.[8]

Dependencies of the PL spectra on the excitation power density and temperature have been measured to identify recombination mechanisms of the w-lines.

C. Excitation power dependence of the w-lines

An excitation power dependence of the PL spectrum measured at 4.2 K in the sample irradiated with a dose of $10^{18}\,cm^{-2}$ is shown in Fig. 4(a). It can be seen that excitation power does not change the spectral position of the w-lines which is consistent with attributing these lines to excitons bound to defects.

The nature of radiative transitions can be assessed by analysing the dependence of the PL intensity I on the laser excitation power P. The experimental data are fitted to the function $I \sim P^k$ on a log-log scale.[28] For the w-lines, the background has been approximated by straight lines, as shown in Figs. 4(b) and 4(c), and subtracted from the spectrum. Integral intensities of the peaks have been used to determine the k power coefficients. Their values were found to be smaller than unity: $k_{w0} = 0.21 \pm 0.05$, $k_{w1} = 0.44 \pm 0.03$, $k_{w2} = 0.55 \pm 0.02$, $k_{w3} = 0.57 \pm 0.04$.

Values of k between 1 and 2 are expected for free excitons and for excitons bound to shallow hydrogenic defects.[28] The free exciton emission intensity is proportional to the product of the concentrations of holes and electrons, each of which is proportional to the excitation power P. Excitons bound to shallow hydrogenic defects also increase their intensity with $1 < k < 2$ because they are in thermal equilibrium with free excitons. However, for excitons bound to non-hydrogenic defects, k can be smaller than unity. Foreign atoms, isoelectronically substituting host atoms in the silicon lattice, have been reported to capture separate charge carriers forming at first a charged state which then in turn attracts opposite charge carriers creating a bound exciton.[29] The concentration of excitons bound to such isoelectronic defects is proportional to the concentration of the charge carriers as well as to the defect concentration resulting in $k \leq 1$. Krustok *et al.*[30] reported excitons bound to closely located neutral donor-acceptor pairs acting as isoelectronic traps in $CuInS_2$, a chalcopyrite ternary compound with electronic properties similar to those in $CuInSe_2$.[25]

The k values, determined for the w-lines, suggest that defects, associated with these lines, are not simple shallow hydrogenic ones but have a more complex nature and can be neutral isoelectronic traps similar to those reported in Ref. 30.

D. Temperature dependence of the w-lines

A temperature dependence of the PL spectrum from $CuInSe_2$ irradiated with a dose of $10^{18}\,cm^{-2}$ is shown in Fig. 5. After a dose of $10^{18}\,cm^{-2}$, the 4.2 K PL spectrum of $CuInSe_2$ reveals a relatively high intensity of non-resolved A and B free-excitons. The M1 bound-exciton line is present, whereas the M2 and M6 bound exciton lines have almost disappeared. It can be seen in Fig. 2 that the M5 and M7 excitons retain considerable intensity. After this dose, the w-lines have become the dominant emission in the 4.2 K spectrum. The w0 line can be seen, although not well resolved. Both the w1 and w3 lines have gained significant intensity and the w2 line dominates the spectrum.

The LO replica $w2_{LO}$ can be seen at a spectral distance of E_{LO} from w2. Increasing temperature reduces the intensity of all the observed lines. The w0 quenches first, at temperatures of about 15 K, although the small intensity of this unresolved line makes it difficult to analyse quantitatively. The

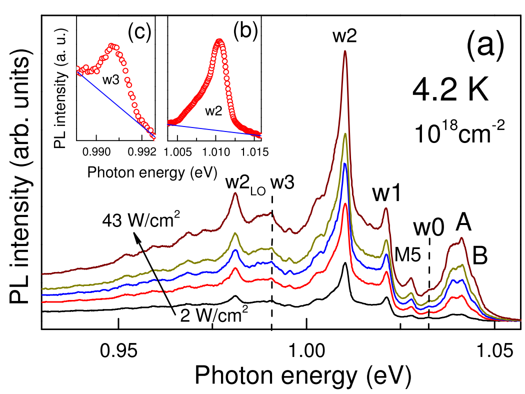

FIG. 4. The excitation power dependence of 4.2 K PL spectrum in $CuInSe_2$ after a dose of $10^{18}\,cm^{-2}$ of 6 MeV electron irradiation (a), approximation of the background by straight lines for the w3 (b), and w2 (c) lines.

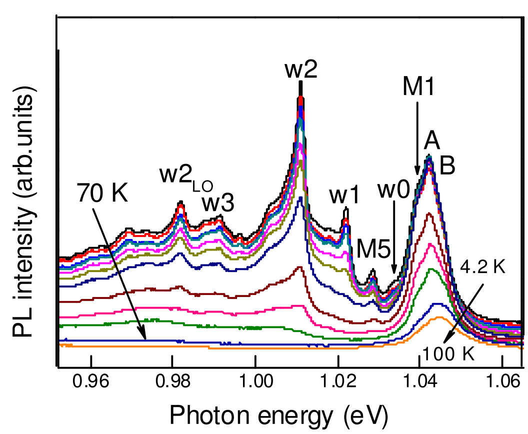

FIG. 5. Temperature dependence of the PL spectrum in $CuInSe_2$ after irradiation by 6 MeV electrons with a dose of $10^{18}\,cm^{-2}$.

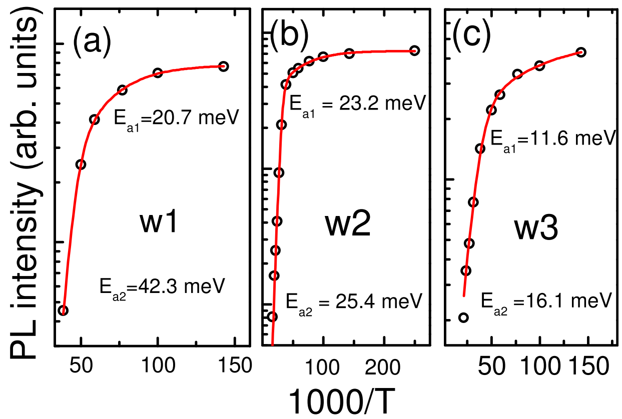

FIG. 6. Arrhenius plots of the integrated PL intensities of the w1 (a), w2 (b), and w3 (c) lines fitted using Eq. (1) for PL spectra of $CuInSe_2$ irradiated with a dose of $10^{18}\,cm^{-2}$ of 6 MeV electrons.

w1 line quenches at temperatures of 30 K. The deeper w2 and w3 lines can be seen to quench at about 70 K. The $w2_{LO}$ quenches simultaneously with w2, confirming its assignment as a LO phonon replica of w2. By 70 K, all the w-lines as well as the M-bound excitons quench leaving only a merged peak of the A and B free excitons in the PL spectrum. Such a quenching behaviour can be taken as another experimental evidence of the bound exciton nature of the w-lines. Arrhenius plots of the temperature quenching of the w1, w2, w3 integrated intensities I, calculated as areas under the peaks in PL spectra, are shown in Fig. 6.

To determine integral intensities of the w peaks and analyse their quenching parameters, the background has been approximated by straight lines, as shown in Figs. 4(b) and 4(c), and subtracted from the spectrum. The best fitting for the three data sets is achieved using a model with two competing recombination channels[31,32]

$$I = I_0/[1 + C1\,\exp(-E_{a1}/kT) + C2\,\exp(-E_{a2}/kT)], \quad (1)$$

where I_0 is the PL intensity at 4.2 K, E_{a1} and E_{a2} are activation energies of the levels corresponding to the first and second recombination channels, respectively, $C1$ and $C2$ are process rate parameters, inversely proportional to the concentration of non-radiative centres.[32]

The best fits of the experimental data points for the w1-, w2-, and w3-lines are shown in Fig. 6. The activation energies (thermal depths) and the spectral distances of these lines to the free A and B excitons (optical depths) of the w-lines are shown in Table I. For compound semiconductors where the crystal field and spin-orbital coupling have split the valence band into sub-bands, the bound excitons can involve holes belonging to deeper sub-bands as well as the topmost one as reported for GaN (Ref. 32) and $CuInSe_2$.[20] Therefore, the determined activation energies should be compared with spectral distances to both the A and B free excitons.

TABLE I. Spectral distances (optical depths) of the w-lines to the A and B free excitons, E_A-wX and E_B-wX (X = 1,2,3), respectively, E_{a1} and E_{a2} activation energies (thermal depths) of the two recombination channels for $CuInSe_2$ irradiated with a dose of $10^{18}\,cm^{-2}$.

wX	E_A-wX (meV)	E_B-wX (meV)	E_{a1} (meV)	E_{a2} (meV)
w1	20.2	23.3	21 ± 3	42 ± 6
w2	31.5	34.6	23 ± 2	25 ± 1
w3	50.8	53.9	11 ± 2	16 ± 7
$w2_{LO}$	61.7	64.8	20 ± 5	26 ± 5

The spectral distances of the w1 line from the A and B free excitons are 20.2 and 23.3 meV, respectively. These values are close to E_{a1}, the thermal depth of w1, suggesting than the hole in the w1 exciton can be associated with either A or B sub-band. Both E_{a1} and E_{a2} are significantly greater than the binding energies of the A and B free excitons of 8.5 and 8.4 meV,[33,34] respectively, indicating that the w1 exciton is formed not by the capture of free excitons but by the capture of separate charge carriers. The two activation energies can be related to the localisation energies of the captured electron and hole.

The activation energies of both w2 and w3 differ significantly from their optical depths with respect to the A and B free excitons. The Arrhenius analysis of these lines also demonstrates clear two channel recombination. Therefore, they are both likely to be associated with non-hydrogenic defects. Thermal quenching first releases one of the charge carriers, dissociating it with activation energy E_{a1} at lower temperatures. Then, at higher temperatures, the other charge carrier dissociates with activation energy E_{a2}. The activation energies determined for the $w2_{LO}$ line are very close to those of w2, as expected.

E. Possible defects associated with w-lines

MeV electrons generate primary displacement defects, vacancies and interstitials, excite phonons, and ionise the host atoms. The resulting primary structural defects are unstable at room temperature. Interactions with other defects and with the crystalline lattice lead to formation of more stable defect complexes, which minimise the total energy of the defect system in equilibrium with the lattice and free charge carrier gas.[35] The total energy required to form an intrinsic structural defect can be considered as the sum of the structural change and electronic energy which depends on the position of the defect level with respect to the Fermi level. The electronic energy influences whether the formed secondary defects are n or p-type, favouring the formation of deep and compensating states.[36] Irradiation of semiconductors results in a reduction of the charge carrier mobility due to scattering on radiation induced defects, removal of the charge carriers by the deep states working as traps and resulting in an increase of the resistivity.[36]

Similar physical processes can be expected in irradiated $CuInSe_2$. A strong dependence of the defect formation energies on the Fermi level position in $CuInSe_2$ has been demonstrated by *ab initio* calculations.[37] It was shown that deviations from the ideal stoichiometry increase the formation probability of compensating acceptor or donor states in n- and p-type materials, respectively. A decrease in the carrier mobility and their concentration has been observed in $CuInSe_2$ thin films following 3 MeV electron irradiation.[38] An increase in resistivity has also been reported after ion implantation of Xe into $CuInSe_2$ single crystals.[39]

The accumulation of deep compensating defects working as traps is consistent with the observed redistribution of the PL intensity from near band edge towards deeper bands. Radiative recombination through deeper bands and non-radiative recombination mechanisms becomes more probable and reduces the overall intensity of the PL emission. The observed increase in the intensity of the broad bands and sharp lines as well as the appearance of new lines suggests an increase in the population of defects associated with these features.

Following the assignment of the P and K bands to Cu_{In} and Se_i, respectively,[19] we can interpret the increased intensities of these bands after irradiation as a rise in the population of Cu_{In} and Se_i, whereas the concentration of V_{Cu}, associated with the N band, does not grow.

The irradiation reduces the intensity of the A and B free excitons. Such a reduction can take place due to the following three processes: (1) reduction of the mobility of the non-equilibrium charge carriers reducing the lifetime of the free excitons due to scattering by defects generated by the irradiation; (2) localisation of the charge carriers by radiation induced defects; (3) increase in the probability of non-radiative recombination.

The irradiation also reduces the intensity of all the bound excitons observed in the PL spectrum of the virgin $CuInSe_2$. Following a dose of $10^{18}\,cm^{-2}$, some lines have disappeared (e.g., M2 and M6), although the intensity of others remains considerable (M1, M5, and M7) and that of the M4 (w0-line) exciton has increased. The M4-line was preliminary assigned to excitons bound to either Se_i or Cu_{In}.[19,26] Therefore, the observed growth of the intensity of the K band and M4 exciton after the irradiation is consistent with an increase in the concentration of Se_i or Cu_{In}.

The relatively high intensity of the M1 line after a dose of $10^{18}\,cm^{-2}$ can be explained by an increase in the concentration of Cu_i, which was associated with the M1 exciton in Ref. 19. Cu_i is also one of the primary defects generated by the irradiation. The high intensity of M1 suggests that a considerable fraction of such defects might be present after the irradiation.

The acceptor nature of the radiation induced defects Cu_{In} and Se_i is in good agreement with the *n*- to *p*-conductivity type conversion of *n*-type conductive $CuInSe_2$ after ion-bombardment by O^+, He^+, Ne^+, Ar^+, Xe^+, and a number of other ions.[40–42]

Comparative analysis of the defect formation in different semiconductors suggests that the probability of annihilation of a primary defect pair (a vacancy and interstitial atom from the same lattice site) is rather low, whereas the probabilities of their migration and formation of defect complexes are much higher.[35,36] Especially high is the probability of migration for interstitial atoms. According to experimental studies of diffusion coefficients, the mobility of Cu, In, and Se atoms in $CuInSe_2$ differs significantly.[43] The mobility of interstitial atoms of indium In_i and especially copper Cu_i is significantly higher than that of Se_i. Fast migration of Cu_i has been reported earlier.[44] Ionisation of the host lattice atoms caused by electron irradiation, should further increase the mobility of copper. Therefore, the probability of migration from the place of formation to a vacancy of indium V_{In} should be rather high, whereas the formation energy of the Cu_{In} defect is low and can be negative.[22]

The chalcopyrite structure assumes an ordering of copper and indium on the cation sublattice, whereas violation of such an order can be considered as an element of sphalerite structure. Transformation of chalcopyrite to sphalerite structure has been observed after bombardment of $CuInSe_2$ single crystals with 1.5 keV Ar ions.[45] Therefore, after irradiation by electrons, we also can expect high concentrations of Cu_{In} and In_{Cu}. Due to the mixed covalent and ionic type of the bonding in $CuInSe_2$, the formation of cation-anion antisite defects, such as Se_{Cu}, observed on a freshly cleaved surface of a $CuInSe_2$ single crystal by atomic scale scanning tunnelling microscopy,[46] cannot also be ruled out.

$CuInSe_2$ single crystals, grown with a significant copper excess ([Cu]/[In] = 1.67), have been irradiated with a dose of $10^{18}\,cm^{-2}$ of 2 MeV electrons at 4.2 K and then *in-situ* studied using positron annihilation at temperatures from 90 to 450 K.[47] Analysis of the material before the irradiation suggested that the concentration of neutral and negatively charged vacancies was below $5 \times 10^{15}\,cm^{-2}$, the threshold of the sensitivity of this method. Analysis of the irradiated material carried out at 90 K revealed the presence of high concentrations of divacancies. An increase of the temperature up to 300 K led to the disappearance of vacancy type defects. It was concluded that annealing of the irradiated samples at room temperature results in the formation of defect complexes not containing negatively charged vacancies or containing only positively charged vacancies, undetectable by the positron lifetime spectroscopy. It was proposed that at room temperature, antisite defects should be present in the material. According to Ref. 48, the selenium vacancy donor type defects (V_{Se}) can be charged positively, but the formation of donors contradicts the trend of the acceptor-type nature of radiation induced defects in $CuInSe_2$.[40,41]

The positron annihilation analysis rules out the possibility of the presence of high concentrations of copper (${V_{Cu}}^-$) and indium vacancies (${V_{In}}^-$) as well as the defect complexes involving two copper vacancies plus indium on copper site ($2{V_{Cu}}^- + {In_{Cu}}^{2+}$). Instead, the study suggested the generation of Cu_{In} antisites and the defect complexes involving Cu_{In} and two interstitial copper atoms ($Cu_{In} + 2Cu_i$), as more probable candidates. High concentrations of Cu_{In} ($3 \times 10^{20}\,cm^{-3}$) and no V_{Cu} were found in $CuInSe_2$ with [Cu]/[In] = 1.05 using neutron scattering.[49]

According to *ab initio* calculations[22] at small excesses of copper, we can expect the following order of the formation energies for defects in $CuInSe_2$ (without defects related to selenium, which were not considered in this study): $Cu_{In} < V_{Cu} < V_{In} < Cu_i < In_{Cu}$. Excluding the vacancies, whose formation has been ruled out in Refs. 47 and 49, we can conclude that the most likely defects can be Cu_{In}, Cu_i, In_{Cu} as well as their neutral complex $Cu_{In} + 2Cu_i$.

It is difficult to unambiguously identify the defects associated with the w-lines. Their small FWHM and quenching at temperatures below 70 K suggest that they might be excitons bound to defects. That the spectral positions of the w-lines do not shift with excitation intensity change supports their excitonic nature. Their intensity dependence on the excitation power indicates that the defects are deep and non-hydrogenic. They could be neutral donor-acceptor pairs similar to those observed in $CuInS_2$.[30] Antisite defects Cu_{In}, In_{Cu} as well as interstitials Cu_i and Se_i are likely to be components of these defects.

Considering the list of the defects expected in this material, we should also take in account possible contaminants like hydrogen and carbon present at concentrations exceeding the concentrations of some of the intrinsic defects in the as grown material. These contaminants significantly complicate the analysis of the nature of the irradiation induced lines w_1, w_2, and w_3. Further investigation is required for unambiguous identification of their nature.

IV. CONCLUSION

The irradiation of $CuInSe_2$ single crystals by 6 MeV electrons with doses from 10^{15} to $3 \times 10^{18}\,cm^{-2}$ resulted in a reduction of the PL intensity of both free- and bound-excitonic lines observed in the virgin material. Such a reduction can be observed from quite a low dose of $10^{16}\,cm^{-2}$, suggesting that high-quality stoichiometric material with low concentrations of intrinsic defects is not quite radiation hard. The irradiation induces new PL lines w1 at 1.0215 eV and w3 at 0.9909 eV and enhances the intensity of the lines w0 and w3 at 1.0325 and 1.0102, respectively, which were present in the PL spectra before the irradiation. The intensity of two deeper broad bands, associated with free-to-bound recombination at the acceptor-type defects, interstitial selenium (Se_i), and copper on indium site (Cu_{In}), have also increased, suggesting a rise in the concentration of these defects due to irradiation.

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[1] P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, and M. Powalla, Phys. Status Solidi RRL **9**, 28 (2015).
[2] C. F. Gay, R. R. Potter, D. P. Tanner, and B. E. Anspaugh, in *Proceedings of the 17th IEEE Photovoltaic Specialists Conference* (IEEE, 1984), p. 151.
[3] M. Yamaguchi, J. Appl. Phys. **78**, 1476 (1995).
[4] A. Jasenek and U. Rau, J. Appl. Phys. **90**, 650 (2001).
[5] A. Jasenek, H. W. Schock, J. H. Werner, and U. Rau, Appl. Phys. Lett. **79**, 2922 (2001).
[6] J. F. Guillemoles, U. Rau, L. Kronik, H. W. Schock, and D. Cahen, Adv. Mater. **11**, 957 (1999).
[7] G. D. Watkins, J. Cryst. Growth **159**, 338 (1996).
[8] *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press, 1972), p. 321.
[9] G. D. Gilliland, Mater. Sci. Eng. Rep. **18**, 99 (1997).
[10] A. V. Mudryi, V. F. Gremenok, A. V. Ivanyukovich, M. V. Yakushev, and Ya. V. Feofanov, J. Appl. Spectrosc. **72**, 883 (2005).
[11] Y. Hirose, M. Warasawa, K. Takakura, S. Kimura, S. F. Chichibu, H. Ohyama, and M. Sugiyama, Thin Solid Films **519**, 7321 (2011).
[12] A. V. Mudryi, A. V. Karotki, M. V. Yakushev, F. Luckert, and R. W. Martin, Proceedings of PV Science, Application and Technology (PVSAT-5), Wrexham, Institute of Physics: Materials and Characterisation Group (The Solar Energy Society UK, 2009), p. 127.
[13] I. Dirnstorfer, M. D. Wagner, M. Hofmann, M. D. Lampert, F. Karg, and B. K. Meyer, Phys. Status Solidi A **168**, 163 (1998).
[14] J. Krustok, H. Collan, M. Yakushev, and K. Hjelt, Phys. Scr. **79**, 179 (1999).
[15] A. Jagomagi, J. Krustoka, J. Raudojaa, M. Grossberga, M. Danilsona, and M. Yakushev, Physica B **337**, 369 (2003).
[16] E. H. Bogardus and H. B. Bebb, Phys. Rev. **176**, 993 (1968).
[17] S. Chatraphorn, K. Yoodee, P. Songpongs, C. Chityuttakan, K. Sayavong, S. Wongmanerod, and P. O. Holtz, Jpn. J. Appl. Phys. Part 2 **37**, L269–L271(1998).
[18] A. V. Mudryi, M. V. Yakushev, R. D. Tomlinson, I. V. Bodnar, I. A. Viktorov, V. F. Gremenok, A. E. Hill, and R. D. Pilkington, Appl. Phys. Lett. **77**, 2542 (2000).
[19] M. V. Yakushev, Y. Feofanov, R. W. Martin, R. D. Tomlinson, and A. V. Mudryi, J. Phys. Chem. Solids **64**, 2011 (2003).
[20] F. Luckert, M. V. Yakushev, C. Faugeras, A. V. Karotki, A. V. Mudryi, and R. W. Martin, J. Appl. Phys. **111**, 093507 (2012).
[21] R. D. Tomlinson, Sol. Cells **16**, 17 (1986).
[22] H. Tanino, T. Maeda, H. Fujikake, H. Nakanishi, S. Endo, and T. Irie, Phys. Rev. B **45**, 13323 (1992).
[23] S. B. Zhang, S. H. Wei, A. Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
[24] C. Rincon and R. Marquez, J. Phys. Chem. Solids **60**, 1865 (1999).
[25] J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors-Growth, Electronic Properties, and Applications* (Pergamon, 1975).
[26] M. V. Yakushev, A. V. Mudryi, and R. D. Tomlinson, Appl. Phys. Lett. **82**, 3233 (2003).
[27] M. V. Yakushev, A. V. Mudryi, V. F. Gremenok, V. B. Zalesski, P. I. Romanov, Y. V. Feofanov, R. W. Martin, and R. D. Tomlinson, J. Phys. Chem. Solids **64**, 2005 (2003).
[28] T. Schmidt, K. Lischka, and W. Zulehner, Phys. Rev. B **45**, 8989 (1992).
[29] J. Weber, W. Schmid, and R. Sauer, Phys. Rev. B **21**, 2401 (1980).
[30] J. Krustok, J. Raudoja, and R. Jaaniso, Appl. Phys. Lett. **89**, 051905 (2006).
[31] D. Bimberg, M. Sondergeld, and E. Grobe, Phys. Rev. B **4**, 3451 (1971).
[32] M. Leroux, N. Grandjean, B. Beaumont, G. Nataf, F. Semond, J. Massies, and P. Gibart, J. Appl. Phys. **86**, 3721 (1999).
[33] M. V. Yakushev, F. Luckert, C. Faugeras, A. V. Karotki, A. V. Mudryi, and R. W. Martin, Appl. Phys. Lett. **97**, 152110 (2010).
[34] B. Gil, D. Felbacq, and S. F. Chichibu, Phys. Rev. B **85**, 075205 (2012).
[35] V. L. Vinetskiy and L. C. Smirnov, Fiz. Tkh. Poluprovodn. **5**, 176 (1971) [Sov. Phys. Semicond. **5**, 153 (1971)].
[36] W. Walukiewicz, Phys. Rev. B **37**, 4760 (1988) and references therein.
[37] S. B. Zhang, S. H. Wei, and A. Zunger, Phys. Rev. Lett. **78**, 4059 (1997).
[38] H.-S. Lee, H. Okada, A. Wakahara, T. Ohshima, H. Itoh, S. Kawakita, M. Imaizumi, S. Matsuda, and A. Yoshida, J. Phys. Chem. Solids **64**, 1887 (2003).
[39] R. D. Tomlinson, M. V. Yakushev, and H. Neumann, Cryst. Res. Technol. **28**, 267 (1993).
[40] G. A. Medvedkin, Yu. V. Rud, and M. V. Yakushev, Cryst. Res. Technol. **11**, 1299 (1990).
[41] R. D. Tomlinson, A. E. Hill, M. Imanieh, R. D. Pilkington, M. A. Slifkin, M. V. Yakushev, and A. Roodbarmohammadi, J. Electron. Mater. **20**, 659 (1991).
[42] R. D. Tomlinson, A. E. Hill, G. A. Stephens, M. Imanieh, P. A. Jones, R. D. Pilkington, P. Rimmer, M. Yakushev, and H. Neumann, in *Proceedings of 11th European Solar Energy Conference I* (IEEE, 1992), p. 791.
[43] H. J. von Bardeleben, J. Appl. Phys. **56**, 321 (1984).
[44] V. Nadazdy, M. Yakushev, E. D. Djebbar, A. E. Hill, and R. D. Tomlinson, J. Appl. Phys. **84**, 4322 (1998).
[45] P. Corvini, A. Kahn, and S. Wagner, J. Appl. Phys. **57**, 2967 (1985).
[46] L. Kazmerski, Vacuum **43**, 1011 (1992).
[47] A. Polity, R. Krause-Rehberg, T. E. M. Staab, M. J. Pushka, J. Klais, H. J. Moller, and B. K. Meyer, J. Appl. Phys. **83**, 71 (1998).
[48] S.-H. Wei and S. B. Zhang, J. Phys. Chem. Solids **66**, 1994 (2005).
[49] C. Stephan, S. Schorr, M. Tovar, and H.-W. Schock, Appl. Phys. Lett. **98**, 091906 (2011).