Feedback mechanism for the stability of the band gap of $CuInSe_2$

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We report on experimental results on band gap and lattice distortion in $CuInSe_2$ for various degrees of Cu deficiency. The band gap is measured by optical methods, and the Cu vacancy density and anion displacement parameter are determined by neutron scattering. Our data show that the band gap decreases for Cu-poor compositions, and the anion displacement is weakly dependent on the concentration of Cu vacancies. This is in apparent contradiction with *ab initio* calculations that always predict a larger band gap in presence of Cu vacancies. To shed light on this issue, we studied the overall dependence of the band gap on the anion displacement and on the concentration of Cu vacancies using a self-consistent GW approach and hybrid functionals, including a feedback mechanism that was recently proposed. Our calculations illustrate consistently the remarkable stability of the band gap of chalcopyrite semiconductors and explain the experimental observations by a coupled effect of Cu vacancies and lattice distortions within the feedback model.

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Chalcopyrites, e.g., $CuInSe_2$, are complex ternary semiconductors whose electronic structure is challenging for *ab initio* calculations.[1,2] Their band gap is remarkably stable with respect to deviations from stoichiometry or from the equilibrium structure,[3,4] a feature of great practical importance since the main application of these materials is in thin-film solar cells. It has been known for a long time that *ab initio* calculations predict a strong dependence of the band gap on the anion displacement u, which measures the deviation of the anion from the ideal tetrahedral position.[1,5–7] However, a large range of anion displacements has been observed experimentally,[8] while the band gap remains stable. A recent study based on GW calculations explains this stability for $CuInS_2$ and $CuInSe_2$ by a feedback mechanism[1]: if a distortion of the lattice occurs, the variation of u affects significantly the size of the band gap. However, this variation of u also acts upon the concentration of Cu vacancies, since the formation energy of this defect is modified by a shift of the valence-band maximum (VBM). As a result, the variation in the density of Cu vacancies induces a change in the band gap that counterbalances the initial change due to the distortion.

In fact, while experiments probe directly variations of the band gap (total derivatives), theoretical models allow us to evaluate separately the effect due to the variation of each parameter (partial derivatives). It is then necessary to add the resulting partial derivatives before comparing theory and experiments. This is the main concept embedded in the feedback model. Similar feedbacks have been predicted and observed also for the doping level.[9]

Several aspects of this feedback loop model are accessible to experimental tests. Neutron powder diffraction with careful refinement allows us to evaluate at the same time structural parameters, like the anion displacement, and the density of Cu vacancies.[10] The band gap can be determined by optical transmission or by photoluminescence (PL) measurements.[11] Assuming that the density of Cu vacancies scales with the Cu deficiency, one can test the relation between a higher density of Cu vacancies and the size of the band gap. The band gap of $CuInSe_2$ as a function of the composition, particularly of Cu content, has been investigated, indicating a constant band gap as long as the material is grown under Cu excess and hinting that the band gap decreases with Cu deficiency.[12,13] A detailed investigation of the band gap over a large range of compositions extending into the Cu-poor region is missing. *Ab initio* calculations, independently of the level of theory and the approximations used, always predict that an increased concentration of Cu vacancies should induce a larger band gap.[1,6,14,15] This has usually been justified by the experimental observation that very Cu-deficient samples show, in fact, a higher band gap.[16,17] However, these reported results do not represent chalcopyrite, but another phase, namely $CuIn_3Se_5$, also called the ordered defect compound (ODC).[18] On the contrary, when measuring the $CuInSe_2$ band gap for slightly Cu-poor compositions, which are within the existence region of the chalcopyrite phase, we show here, that the band gap, in fact, is smaller for Cu-poor material.

To shed light on this issue, we performed *ab initio* calculations, considering both the effect of Cu vacancies V_{Cu} and of lattice distortions, i.e., variations of u, on the quasiparticle band gap E_g. We applied many-body schemes for electronic excitations based on density functional theory (DFT), such as hybrid functionals and GW approaches, which proved to give excellent results in similar systems.[1,19,20] It is well known that standard DFT, in combination with semilocal functionals misrepresents the hybridization between Cu d states and Se p states with dramatic consequences on both electronic and structural properties. In fact, the Kohn-Sham DFT band gap of $CuInSe_2$ is negative. Moreover, and in spite of the fact that lattice constants are well reproduced, the anion displacement u is underestimated by more than 5%. These shortcomings

can be corrected at a moderate computational cost using the Heyd-Scuseria-Ernzerhof[21] (HSE) hybrid functional, as implemented in the code VASP,[22,23] which yields $u = 0.229$ and $E_g = 0.85$ eV.

Vidal *et al.*[1] showed that self-consistent (sc) GW[24–26] gives the most accurate description of band structures and band-gap derivatives. We use here the same scGW scheme,[1,26] implemented in the code ABINT.[27] More details on the calculations can be found elsewhere.[1,19] Despite that our band gaps are converged to better than 0.01 eV, one should not forget that the underlying approximations (pseudopotentials, choice of the exchange-correlation functional, construction of supercells, etc.) impose an error bar of about 10% on the value of the calculated band gaps. However, the accuracy on the estimate of energy differences is higher, about 1%, thanks to error cancellations.

Experimentally, we studied the composition-dependent band-gap behavior of polycrystalline and single-crystalline $CuInSe_2$ absorber films by PL and optical transmission spectroscopy. Measurements on both sample types were performed to demonstrate that the observed composition dependence is a general behavior of $CuInSe_2$ thin films, independent of the preparation procedure and crystallinity. The neutron diffraction experiments for the extraction of the anion displacement parameter were performed on powder reference samples to allow for an isotropic distribution of crystal orientations. This is necessary for a reliable refinement analysis of the diffraction patterns. Due to the different experimental requirements of the methods, it was not possible to perform all studies for the same series of samples.

Single-crystalline $CuInSe_2$ layers were grown by metallorganic vapor phase epitaxy on GaAs (001) wafer substrates in an MOCVD (metal organic chemical vapor deposition) reactor at 50-mbar pressure and 470 °C reactor temperature. The precursors are cyclopentadienyl-copper-triethylphosphine, trimethylindium, and ditertiarybutylselenide. The partial pressures and flow rates of each precursor are kept constant to maintain fixed conditions throughout the entire growth process. The samples have a thickness of 700–800 nm and are grown under various Cu/In-ratios and under Se excess. The growth procedure and resulting sample structures were discussed in detail before.[28,29] Polycrystalline $CuInSe_2$ thin films were grown on molybdenum/glass substrates by a modified three-stage coevaporation process.[30] Cu-rich films were obtained by stopping the process after the second stage and varying the duration of the second stage. Cu-poor films were grown by the full three-stage process with different durations of the third stage. The entire process was carried out under Se excess. After the growth process, the Cu-rich samples were immersed into KCN aqueous solution (10 wt%) for 5 min to remove the secondary copper selenide phase. The resulting sample thickness is about 2 μm. Powder samples of $Cu_{1-y}In_ySe_{1/2+y}$ with various y ($0.49 < y < 0.60$) were prepared by solid state reaction of the pure elements (99.9999% purity) in sealed, evacuated silica tubes at T = 850 °C with final fast (200 K/h) cooling. This procedure was repeated three times, with the samples homogenized in between by grinding them in an agate mortar.

The [Cu]/[In]-ratio of the thin films was measured by energy dispersive x-ray analysis (EDX), calibrated by elemental and chalcopyrite standards. For the comparably very thin epitaxial films the calibration was double checked by low-temperature PL measurements at 10 K by comparing specific fingerprints of the spectral shape of the PL at 10 K.[31] This reduces the error that usually occurs with EDX on very thin films. The analysis of the chemical composition of the powder samples was performed by means of wavelength dispersive x-ray analysis (WDX). The system was calibrated using elemental standards.

The optical transmission measurements were performed in a NIR-VIS-UV (near infrared-visible-ultra violet) spectrometer. The recorded optical transmission data were evaluated by an optical modeling tool kit in the program Diplot.[32] This evaluation allows for the extraction of the absorption coefficient of the $CuInSe_2$ absorber. The band-gap values E_g were extracted from linear extrapolation of the $\alpha(E)^2 \cdot E$ plot toward zero. The uncertainty of this method is <2 meV. Transmission was measured only on the epitaxial samples and not on the polycrystalline samples, as the latter ones contain an opaque molybdenum back contact. The PL measurements were done on both sample types to obtain a complete set of results for samples, which have various compositions and are produced by both growth techniques. These PL measurements were performed at room temperature. The excitation source was the 514.5-nm line of an Ar^+ laser. The collected PL light was spectrally dispersed in a spectrometer and detected with an InGaAs detector array. The samples were measured at various excitation intensities; no influence on the extracted band-gap values could be observed. The evaluation of the measured PL spectra was realized by application of the Planck generalized law:[33]

$$Y_{\mathrm{PL}}(\omega) = C \cdot A(\omega) \cdot \omega^2 \left(\exp\left(\frac{\hbar\omega - \mu}{kT} \right) - 1 \right)^{-1}, \qquad (1)$$

where Y_{PL} is the photon spectrum of the PL, C is the apparatus specific const, $A(\omega)$, the absorptivity, $\hbar\omega$ the photon energy, and $\mu = E_{Fn} - E_{Fp}$ is the splitting of quasi-Fermi levels of electrons and holes, respectively. The band-gap values were extracted by a method described in detail elsewhere,[11] fitting the parameters of Eq. (1) to the measured spectra and extracting the band gap from the obtained spectral absorptivity $A(\omega)$ by intercepting it at $A(\omega) = 1/e$. The uncertainty of this method is <3 meV.

Neutron powder diffraction data were collected at the Berlin Research Reactor BERII at the "Helmholtz-Zentrum Berlin für Materialien und Energie" at the fine-resolution powder diffractometer E9 using a wavelength of $\lambda = 1.79776$ Å. Data treatment was done by full-pattern Rietveld refinement[34] using the FullProf Suite software package.[35] In the refinement the chalcopyrite-type crystal structure was used as structural model. Additional phases (copper selenides or the ODC $CuIn_3Se_5$), if present, were included in the Rietveld refinement.

The refined structural parameters for the chalcopyrite-type phase were the lattice constants a and c, the anion x coordinate, site occupation numbers for Cu and In sites, as well as anisotropic atomic displacement parameters $\boldsymbol{b}_{ii}^{A}$ (A = Cu, In; i = 1–3).

For the determination of intrinsic point defects in the chalcopyrite-type phase from neutron powder diffraction data,

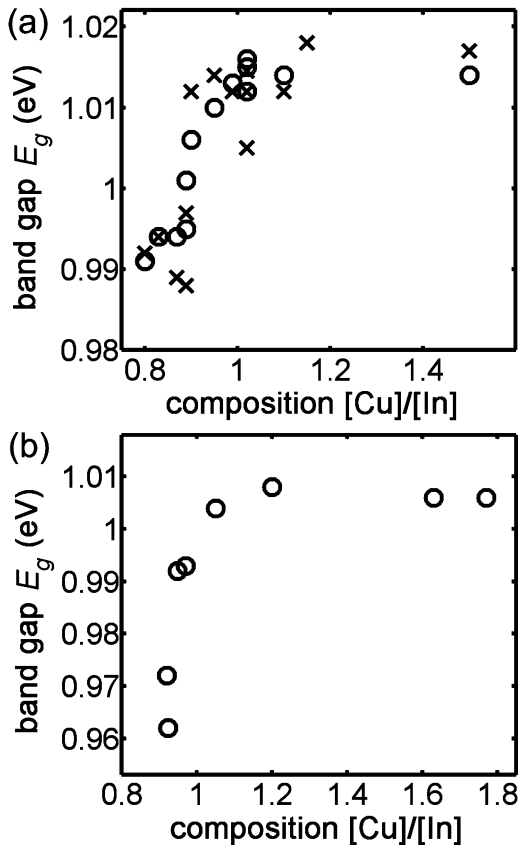

FIG. 1. Band-gap results for the series of epitaxial (a) and polycrystalline (b) samples; results obtained by optical transmission (crosses) and PL (circles).

we applied the method of the average neutron scattering length, described in detail elsewhere.[10]

Figure 1(a) shows the band-gap results for the series of epitaxial samples as a function of the [Cu]/[In]-ratio. There are two regimes visible: in the Cu-poor regime [Cu]/[In] < 0.9, we find band-gap values of around $E_g \approx 0.99$ eV; the regime with higher Cu-content [Cu]/[In] > 0.9 exhibits higher values of $E_g \approx 1.015$ eV. The results obtained by both methods agree well, showing the same two regimes with a very similar step of $E_g \approx 25$ meV at [Cu]/[In] ≈ 0.9.

Figure 1(b) shows band-gap results for the polycrystalline samples. Consistent with the epitaxial sample series, the graph shows two regimes for higher and lower Cu content. The values for the Cu-rich regime ([Cu]/[In] > 1) amount to $E_g \approx 1.01$ eV, which is in acceptable agreement with the results from the epitaxial absorbers. Generally, deviations of this amount (5–10 meV) for thin films from different growth techniques can be generated by strain of the absorber layer, which depends on the growth technique and temperature.[36] The results for the Cu-poor regime show a significantly lower band gap of $E_g < 0.99$ eV.

Note that all Cu-poor samples of both series are in the range where chalcopyrite is a single phase and no contributions from ODC phases are expected. Both sample series show the same clear trend of a higher band gap for material grown under Cu excess, where a considerably lower density of Cu vacancies can be safely assumed, and a lower band gap for Cu-poor compositions, where the density of Cu vacancies is higher.

In apparent contrast with this result, *ab initio* calculations predict a significant increase of the band gap in presence of Cu vacancies.[1,9–12] The opening of the gap is physically explained by the relaxation of the *p-d* repulsion at the top of the valence bands when Cu atoms are removed. DFT calculations show that the band gap approaches from above to the band gap of the perfect crystal when the concentration of Cu vacancies increases. HSE and perturbative GW calculations[37] for 15-, 31-, and 63-atom supercells of $CuInSe_2$ confirm this trend. The selected supercell sizes correspond to [Cu]/[In] ratios in the interval $0.75 \leqslant$[Cu]/[In] < 0.94, which is compatible with the experimentally explored range. The exact relation between E_g and the concentration of Cu vacancies $[V_{\mathrm{Cu}}]$ is not known. We find numerically a linear dependence of E_g on $\ln[V_{\mathrm{cu}}]$ (consistently with what is reported in Ref. 1 for $CuInS_2$): $\partial E_g/\partial[V_{\mathrm{Cu}}] = \mathrm{A}/[V_{\mathrm{Cu}}]$, where the coefficient A is 0.10 eV using the PBE functional [38] within DFT, 0.16 eV using HSE, and 0.17 eV using perturbative GW. Ideally, one should perform scGW calculations of the supercells, including Cu vacancies to obtain the most accurate estimate of A. Moreover, one would like to explore also the region of low Cu deficiency, i.e., $0.95 <$ [Cu]/[In] < 1, where V_{Cu} can be safely assumed to be the only relevant defect.[39] Unfortunately, scGW calculations of a 63-atom cell are already unfeasible. Nevertheless, we know that A must decrease when [Cu]/[In] approaches 1, since the gap saturates to its value in the perfect crystal. Accordingly, we can expect a compensation of errors between the underestimation of A due to the choice of the HSE functional and the overestimation of A in the region of higher Cu deficiency. We can conclude then that $A = 0.16$ eV is a reliable estimate for the coefficient A. In conclusion, if we considered the changes on the band gap due to the inclusion of Cu vacancies *alone*, we would erroneously conclude that *ab initio* calculations predict a *sizable* increase of the band gap (of about 0.13 eV) when the [Cu]/[In] ratio goes from 0.99 to 0.95.

However, we know that experiments do not measure the simple variation of the gap with respect to only one physical variable, while the other variables remain fixed (partial derivatives), but the total variation of the gap due to variations of the concentration of Cu vacancies and the induced variations of u. Following a modified version of the feedback model that is described in detail in Ref. 1, where it was used to determine the total variation of the gap with respect to a variation of u, we assume that E_g is a function of both $[V_{\mathrm{Cu}}]$ and u, and we write its total variation as

$$\Delta E_g \cong \left(\frac{\partial E_g}{\partial[V_{\mathrm{Cu}}]} + \frac{\partial E_g}{\partial u}\frac{\partial u}{\partial[V_{\mathrm{Cu}}]}\right)\Delta[V_{\mathrm{Cu}}]. \qquad (2)$$

We have already evaluated the first term

$$\frac{\partial E_g}{\partial[V_{\mathrm{Cu}}]} = \frac{0.16\ \mathrm{eV}}{[V_{\mathrm{Cu}}]}. \qquad (3)$$

The numerical determination of the second term requires calculations using scGW, the variations of the band gap and the VBM of $CuInSe_2$ when u varies in the interval [0.21,0.24]. Note that we obtained $E_g = 0.96$ eV for the measured anion

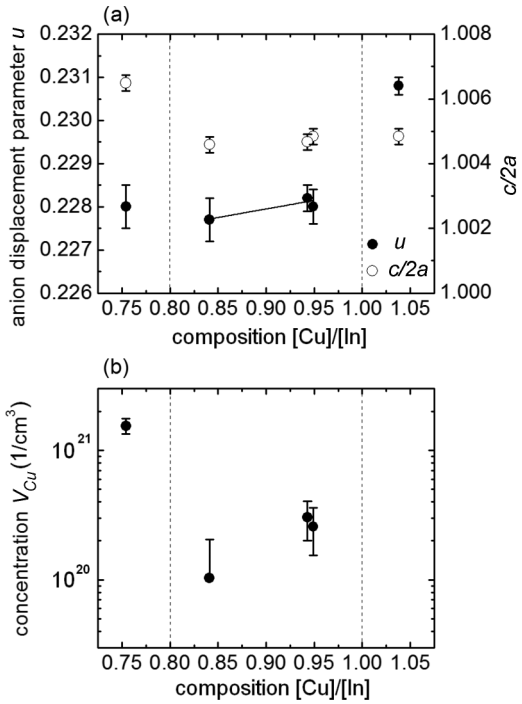

FIG. 2. Anion displacement parameter and $c/2a$ values extracted from the Rietveld analysis of neutron powder diffraction data (a) and the density of Cu vacancies (V_{cu}) (b) as a function of the Cu/In ratio in the chalcopyrite-type phase. The dashed lines indicate regions of different phase content: chalcopyrite and ODC/pure chalcopyrite/chalcopyrite and copper selenides (from left to right).

displacement $u = 0.228$, in close agreement with experimental data. For the slope of the linear dependence of the band gap on u, we obtained $\partial E_g/\partial u = 38.18$ eV, and $\partial E_{\mathrm{VBM}}/\partial u = -9.95$ eV. Gathering all the data (for more details see the supplemental material of Ref. 1), one finally gets

$$\frac{\partial E_g}{\partial u}\frac{\partial u}{\partial [V_{\mathrm{Cu}}]} = -38.18\frac{k_B T}{[V_{\mathrm{Cu}}]}\frac{\mathrm{eV}}{9.95} = -0.20\,\mathrm{eV} \quad \text{at} \quad 600\,\mathrm{K}. \tag{4}$$

Combining Eq. (3) with Eq. (4) in Eq. (2) the compensation of the two terms of similar magnitude, due to the coupled mechanism, leads to an overall *small* (negative) variation of the band gap for increasing Cu deficiency: $\Delta E_g = -0.04\ \mathrm{eV}\frac{\Delta[V_{\mathrm{Cu}}]}{[V_{\mathrm{Cu}}]}$. This corresponds to a reduction by 0.03 eV of the band gap when the [Cu]/[In] ratio goes from 0.99 to 0.95. The result is in agreement with our experimental results and explains the decrease of the band gap with decreasing Cu content, although the partial derivative with Cu deficit predicts an increase of the band gap.

The anion displacement parameter u as well as the lattice parameter ratio $c/2a$ results for the powder samples and the density of Cu vacancies in the chalcopyrite-type phase as a function of the Cu/In ratio are presented in Figs. 2(a) and 2(b), respectively. There is a clear decrease in the anion displacement parameter u when changing from [Cu]/[In] > 1 (Cu rich) to [Cu]/[In] < 1 (Cu poor), whereas within the Cu-poor region the anion displacement parameter remains quite constant.

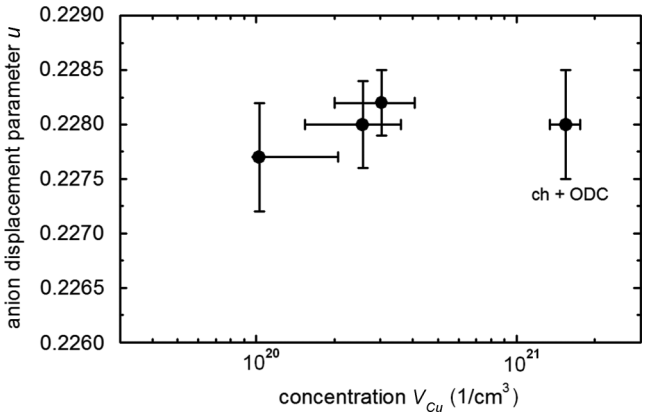

FIG. 3. Anion displacement parameter u of the chalcopyrite-type phase in dependence on the density of Cu vacancies V_{cu}. The sample showing the highest V_{cu} density in the chalcopyrite-type phase (ch) contains as secondary phase the ODC $CuIn_3Se_5$.

This is consistent with *ab initio* calculations of the distribution of the local u in a 64-atom supercell that proved that the relaxation of the lattice has only a mild effect on the anion displacement except in a region localized around the Cu vacancy.[1]

On the other hand, the ratio of the lattice parameter $c/2a$, indicating the tetragonal deformation, remains quite constant over the whole Cu/In range, where no ODC $CuIn_3Se_5$ occurs as a second phase. In the $CuInSe_2 + CuIn_3Se_5$ regime, the tetragonal deformation is being increased.

Thus, significant changes in both parameters, u and $c/2a$, depend more on the occurrence of secondary phases (like copper selenides in the Cu-rich region and the ODC in the Cu-poor region) than on the stoichiometry variations of the chalcopyrite-type phase. The observed behavior of the anion displacement is in relative good agreement to previous results[8] in the region where the chalcopyrite phase exists exclusively. Our results are, however, in disagreement to Merino *et al.* for [Cu]/[In] > 0.95 and in the very Cu-poor region, where the ODC phase $CuIn_3Se_5$ exists as secondary phase. The reason could be different preparation methods, which lead to the different occurrence of secondary phases. We believe that our powder method is closest to thermal equilibrium. Concerning the compositional region where only the chalcopyrite-type phase exists, the anion displacement parameter u increases only slightly with increasing [Cu]/[In] ratio. It should be noticed, that within this region the density of Cu vacancies has a trend to increase with increasing [Cu]/[In] ratio. However, on the Cu-rich side the density of Cu vacancies is below the detection limit of 2%, which justifies our assumption that over a larger compositional range, we can relate the Cu deficiency with the density of Cu vacancies.

Moreover, there is a correlation between the anion displacement parameter u and the density of V_{Cu} (see Fig. 3), especially in the region where only the chalcopyrite-type phase exists. Our results show a weak trend of an increase in the anion displacement parameter u with increasing V_{Cu} density.

As in the case of the gap, the coupled action of variations of u with respect to the gap and the concentration of Cu vacancies leads to a stabilization of the trend compared to the partial

derivatives that can be obtained from calculations resulting in a weak dependence between u and $[V_{Cu}]$.

In conclusion, we have performed experiments measuring the band gap and the anion displacement of $CuInSe_2$ for varied amounts of Cu deficiency. Our band-gap results appeared in clear contrast to theoretic calculations reported before. In view of that we performed state-of-the-art *ab initio* calculations and compared them with our experimental data. Transmission and PL measurements on epitaxial and polycrystalline films both show a clear decrease of the band gap with increased Cu deficiency. Increased Cu deficiency relates to higher Cu vacancy density, at least across the whole compositional range considered here. The anion displacement, obtained from neutron powder diffraction, turned out to be weakly dependent on the concentration of Cu vacancies. Despite the fact that *ab initio* calculations always predict a larger band gap in supercells containing Cu vacancies, we showed that if one considers the coupled effect of variations of the concentration of Cu vacancies and lattice distortions within a feedback model, the agreement between experiment and theory is restored.

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