Strong Interplay between Structure and Electronic Properties in $CuIn(S, Se)_2$: A First-Principles Study

Julien Vidal,[1,2,3] Silvana Botti,[2,3,4] Pär Olsson,[1,5] Jean-François Guillemoles,[1] and Lucia Reining[2,3]

[1]*Institute for Research and Development of Photovoltaic Energy (IRDEP), UMR 7174 CNRS/EDF/ENSCP, 6 quai Watier, 78401 Chatou, France*

[2]*Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau, France*

[3]*European Theoretical Spectroscopy Facility (ETSF)*

[4]*LPMCN, Université Claude Bernard Lyon I and CNRS, 69622 Villeurbanne, France*

[5]*Département MMC, EDF R&D, Les Renardières, 77250 Moret-sur-Loing, France*

(Received 22 April 2009; revised manuscript received 2 December 2009; published 1 February 2010)

We present a first-principles study of the electronic properties of $CuIn(S, Se)_2$ (CIS) using state-of-the-art self-consistent *GW* and hybrid functionals. The calculated band gap depends strongly on the anion displacement u, an internal structural parameter that measures lattice distortion. This contrasts with the observed stability of the band gap of CIS solar panels under operating conditions, where a relatively large dispersion of values for u occurs. We solve this apparent paradox considering the coupled effect on the band gap of copper vacancies and lattice distortions. The correct treatment of d electrons in these materials requires going beyond density functional theory, and *GW* self-consistency is critical to evaluate the quasiparticle gap and the valence band maximum.

DOI: 10.1103/PhysRevLett.104.056401 PACS numbers: 71.10.−w, 71.15.Mb, 71.15.Qe, 72.40.+w

During the past years, copper indium/gallium diselenide $Cu(In, Ga)(Se, S)_2$ (CIGS) thin-film solar cells have emerged as a technology that could challenge the current hegemony of silicon solar panels [1]. This is possible thanks to the peculiar optical and structural properties of CIGS, which possess an extraordinary stability under operating conditions [2]. In fact, these compounds conserve to a very high degree their electronic properties in a large nonstoichiometric range and are remarkably insensitive to radiation damage or impurities. This appears to be a consequence of self-healing mechanisms that compensate for the creation of defects [3]. The origin of this unusual behavior is currently unknown, but it is clear that its understanding would pave the way to the tuning of new materials for more efficient photovoltaic energy conversion. In this context, theoretical calculations that can predict and analyze the interplay between structural and electronic properties can give a crucial contribution to the interpretation of numerous experiments which, in this field, is often far from straightforward.

In this Letter, we are interested in the electronic properties of two paradigmatic CIGS materials: $CuInSe_2$ and $CuInS_2$ (commonly referred to as CIS). Like other ternary chalcopyrites, CIS pure crystals are obtained from the zinc blende structure by replacing the Zn cations alternatively with Cu and In. In this way, each anion (Se or S) is coordinated by two In and two Cu atoms, while each cation is tetrahedrally coordinated by four anions. However, the existence of two different cations results in two different bonding lengths $R_{\mathrm{In}-(\mathrm{S,Se})}$ and $R_{\mathrm{Cu}-(\mathrm{S,Se})}$, leading to two structural anomalies [4]: (i) The tetragonal cell exhibits a distortion, defined by the parameter $\eta = \frac{c}{2a} \neq 1$, the ratio between the lattice constants a and c; (ii) the ideal zinc blende site for the anion is perturbed, yielding a deformation of the anion tetrahedron, which is measured by the anion displacement parameter $u = \frac{1}{4} + (R^2_{\mathrm{Cu}-(\mathrm{S,Se})} - R^2_{\mathrm{In}-(\mathrm{S,Se})})\frac{1}{a^2} \neq \frac{1}{4}$. Both structural anomalies are small, but not negligible. The precise experimental determination of the anion displacement u is more difficult than the measurement of the lattice constants a and c due to inhomogeneity of the samples. Indeed, the dispersion of the measured values is very small for the lattice parameters (usually $<1\%$), while it is significant for the anion displacement ($0.22 < u < 0.235$) [4,5].

Merino *et al.* [5] reported a relatively narrow spread in the band gap ($\approx 10\%$) as a function of the dispersion of the anion displacement u. Unfortunately, experiments alone are not conclusive, due to the lack of information on the composition and uniformity of the samples. The variation of the band gap as a function of u was also addressed theoretically using *ab initio* density functional theory (DFT) [6], in some cases including empirical corrections to get closer to the experimental gap [4,7]. An uncommonly large variation was found, in apparent contradiction with the experimentally proved stability of the CIS gap with respect to any kind of damage or perturbation.

However, DFT—the standard tool in modern condensed matter theory—is plagued by two serious shortcomings when applied to these systems. (i) As is well known, the Kohn-Sham (KS) band gaps of DFT underestimate systematically by 50%–100% the experimental ones. In particular, for CIS compounds the KS band gap is vanishing, in contrast to the experimental values of 1.54 and 1.05 eV for $CuInS_2$ and $CuInSe_2$ [8], respectively. On the other hand, *ad hoc* corrections, like the scissor operator, often used to adjust the DFT band gap to the experimental value, are too

simplistic to analyze the dependence of the band gap on u. (ii) In spite of this problem, the local density (LDA) or the generalized gradient (GGA) approximations to the exchange and correlation energy of DFT usually yield good structural parameters of semiconductors and insulators. Unfortunately, for CIS, the theoretical range of anion displacements obtained within these approximations ($0.215 < u < 0.220$) lies outside the experimental range. It is clear, thus, that to understand the paradox of the band gap dependence on the unit cell deformations in CIS one has to go beyond standard DFT.

In the past years, *GW* [9] has emerged as an invaluable tool to access the one-electron addition and removal energies, also called quasiparticle energies. In principle, the *GW* equations have to be solved self-consistently, as both G, the one-particle Green's function, and W, the screened Coulomb interaction, depend on the quasiparticle wave functions and energies. However, the standard use of this theory, that we will refer to as G_0W_0, starts from a KS calculation, and evaluates perturbatively the quasiparticle corrections to the energy levels ignoring the self-consistent process. This procedure is justified when the KS wave functions and band structures are already close to the quasiparticle ones. In that case it gives results in good agreement with experiments [10].

In spite of the success of the G_0W_0 approach, it has recently been proved that it is insufficient to describe the physics of many materials containing localized d electrons, such as transition metal oxides [11–13]. Several strategies have been proposed to solve this problem, following two main lines: (i) Replacing the LDA with a better starting point, e.g., exact exchange [14], LDA + U [15], or hybrid-functional approaches [16]; (ii) Using an approximate self-consistent approach [12,13,17,18]. In this work we chose to perform a self-consistent (sc) COHSEX (a static approximation to *GW* [9]) calculation, followed by a perturbative G_0W_0 step to include the dynamical effects absent in the COHSEX calculation [18]. This method has given excellent results for several transition metal compounds, very close to the quasiparticle self-consistent *GW* method of Refs. [11,17], retaining however a relative computational efficiency [18]. Furthermore, and unlike some of the strategies listed in (i), our choice does not rely on any nonuniversal parameter.

In this Letter we compare calculations of quasiparticle gaps for a range of anion displacements, obtained from state-of-the-art *ab initio* schemes. We performed standard DFT and *GW* calculations within the plane-wave scheme implemented in ABINIT [19], using norm-conserving pseudopotentials [20] and including semicore states in the valence. Our calculated LDA (and GGA) structural parameters and band structures agree with previous results [6,21,22]: the anion displacement u is systematically underestimated by 5%–10%, and the bottom conduction band overlaps the top valence band, yielding negative band gaps. The negative gap is due to the overestimation of the $p - d$ repulsion [23], which raises the valence band maximum (VBM) beyond the low lying conduction band minimum (CBM), causing a significant hybridization of the CBM with valence states close in energy. Values of u and band gaps in agreement with experiments can be obtained using the Heyd-Scuseria-Ernzerhof (HSE06) [24] hybrid functional, as implemented in the Vienna *ab initio* simulation package (VASP) [25,26]. In fact, the structural relaxation within this scheme yields $u = 0.229$ ($u = 0.227$) for the ideal monocrystal of $CuInS_2$ ($CuInSe_2$). In real samples, however, there is a dispersion of values of u. As a first step, it is therefore most interesting to calculate and analyze the evolution of the gaps as a function of u. To this aim we use *ab initio* schemes that are designed to describe excited states, namely, the *GW* approximation, as well as hybrid functionals which are also known to yield reasonable band gaps for solids. We varied u in the interval $0.2 < u < 0.25$, that encompasses both experimental and theoretical ranges. After verifying that sensible variations of the lattice parameters a and c produce negligible changes on the band structure these parameters were fixed to their experimental values [27]. In the following we will present only calculations for $CuInS_2$, as we found strictly analogous results for $CuInSe_2$.

The dependence on u of the band gap of $CuInS_2$ is shown in Fig. 1. We can see that our KS LDA curve (magenta with filled circles) has the same slope as the theoretical curve (dotted line) obtained by Jiang *et al.* [7] using LDA corrected by a scissor operator. If we apply the perturbative G_0W_0 approach on top of DFT (blue line with crosses), bands are reordered, reversing the sign of the band gap for $u > 0.215$. In any case, G_0W_0 gaps remain quite small, and the slope of the curve do not change for most of the u-range when compared to the KS results. The slope of the G_0W_0 calculation increases when $u = 0.25$,

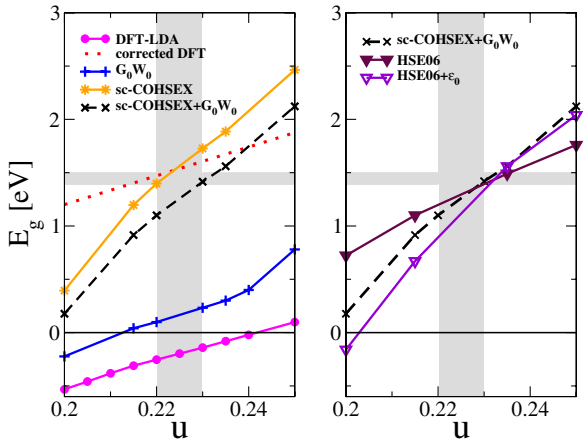

FIG. 1 (color online). Photoemission band gap vs the anion displacement u for $CuInS_2$. The vertical (horizontal) shaded areas give the spread of experimental data for u (band gap). Left panel: calculations using DFT-LDA, G_0W_0, sc-COHSEX, and sc-COHSEX + G_0W_0. The dotted line is from Ref. [7]. Right panel: sc-COHSEX + G_0W_0 and calculations using HSE06 and a modified HSE06 (see the text).

becoming comparable to the slope of the curves obtained applying a self-consistent approach. This is the only case for which the KS gap is already positive and no band reordering occurs.

The sc-COHSEX procedure (yellow lines with stars) leads to a very different result: the gap enlarges (to values slightly larger than the experimental ones), and also the slope of the curve significantly increases. This is due to the progressive modification in the self-consistent iterations of the unsatisfactory LDA starting point.

Finally, when the sc-COHSEX eigenstates are used as a starting point for a perturbative G_0W_0 calculation (black dashed lines), the band gap gets reduced by a constant value of about 0.3 eV, without affecting the slope of the dependence on u. In particular, we find a band gap in agreement with experimental data for the anion displacement measured for the monocrystal [28]. The important finding to stress is however that according to our sc-GW calculation small displacements of the S (Se) atoms lead to even larger variations of the gap than those predicted by previous LDA-based calculations.

In order to further investigate this intriguing feature we performed HSE06 calculations for the gaps (maroon line with filled triangles). The outcome is a curve characterized by an intermediate slope between DFT-LDA and sc-GW. The effect of the HSE06 functional is determined by the fixed amount of Hartre-Fock (HF) exchange included:

$$E_{xc}^{\mathrm{HSE06}} = E_{xc}^{\mathrm{GGA}} + \tfrac{1}{4}E_x^{\mathrm{HF,sr}} - \tfrac{1}{4}E_x^{\mathrm{GGA,sr}}, \qquad (1)$$

where the exchange term $\frac{1}{4}E_{\mathrm{HF,sr}}$ can be seen as an approximated contribution to the self-energy, whose Coulomb interaction is screened by the mixing parameter $\frac{1}{4}$ and the short-range (sr) screening factor, while $\frac{1}{4}E_x^{\mathrm{GGA,sr}}$ is a screened GGA exchange. By contrast, in a GW calculation the exchange part of the self-energy is screened by the inverse dielectric constant, as a first approximation using the static ε_∞; the latter varies for different values of u. To shed light on this point we performed a series of HSE06 calculations using $\frac{1}{\varepsilon_\infty}$, computed within sc-COHSEX for each value of u, to replace the mixing parameter in front of the screened Hartree-Fock exchange. The resulting curve (violet line with open triangles) has the same slope as the sc-COHSEX curve [29].

Hence, all theoretical results, independently of the level of sophistication, point to large band gap variations. Considering as an upper limit for Δu the range where both theoretical and experimental values are included ($\Delta u \lesssim 0.02$), we conclude that the gap variation ΔE_g due to the anion displacement alone would be $\Delta E_g = 32.2 \times \Delta u \approx 0.65$ eV. However, CIS thin films proved to possess stable electronic gaps [5].

This apparent paradox of band gap stability can be solved by considering also the effect on the band gap due to deviations from stoichiometry, which manifest themselves in high concentrations of defects [2]. Cu vacancies V_{Cu} are shallow acceptor defects, which are known to be present in usual samples, consistently with the observation of p-type conductivity. In particular, V_{Cu} is thought to have very low formation energies [30] compared to other intrinsic defects. It is known that already at the KS level the presence of V_{Cu} opens up the band gap [30,31], with a larger effect for increasing Cu vacancy concentration [V_{Cu}], once again in contradiction with the observed stability of experimental band gaps against stoichiometry deviations. We confirmed this trend by performing G_0W_0 calculations for 16-32-64-atom supercells [32], corresponding to concentrations of V_{Cu} in the usual experimental range of off-stoichiometry [5]. The concentration of V_{Cu} is related to the formation energy ΔE_f through a Boltzmann distribution, whose relevant temperature and chemical potentials are set by the growth conditions ($T \approx$ 500–600 °C, copper poor samples) at which defect equilibrium occurs, this equilibrium is moreover assumed to be quenched during the rapid cool down of the samples. However, previous calculations of formation energies were done at the level of DFT and suffer from the unsatisfactory description of the localized states contributing to the VBM. Assuming that a shallow acceptor behaves like the VBM due to their proximity, Lany *et al.* [33] proposed to use LDA + U to correct its formation energy as follows:

$$\Delta E_f = \Delta E_f^{\mathrm{LDA}} - \Delta E_v^{\mathrm{LDA}+U}. \qquad (2)$$

We used this idea evaluating the VBM shift ΔE_v within sc-GW. In Fig. 2 we show the band edge corrections with respect to the KS VBM, calculated using sc-GW, for different levels of self-consistency. In this case, ΔE_v does not correct a shortcoming of KS theory, but improves on the LDA functional, as the exact exchange-correlation functional would give the exact VBM already within DFT. The VBM shift has a dispersion of around 1 eV in the considered range of u. This dispersion is totally absent in DFT ($+U$) calculations [34] (horizontal line). Note that the shifts are significantly different according to whether both wave functions and eigenvalues or only eigenvalues are updated in the self-consistent procedure.

Following the logic of the feedback-loop scheme of Fig. 3, we can now prove that if a distortion of the lattice

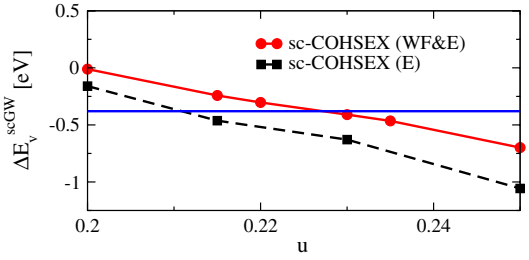

FIG. 2 (color online). The VBM shift ΔE_v of $CuInS_2$ with respect to the LDA band edge versus the anion displacement u. We compare results for sc-COHSEX with self-consistency only in energy (dashed curve) and in both wave functions and energies (continuous curve). The horizontal blue line represents ΔE_v given by DFT + U_d [34] where U is set to 6 eV.

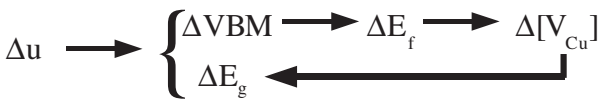

FIG. 3. Scheme of the feedback loop that stabilizes the gap.

occured for any reason (e.g., extended defect, axial strain) it would actually have little influence on the gap value because of two canceling effects: (i) the gap of the CIS compound increases with u and (ii) its VBM is shifted upwards, which causes easier V_{Cu} formation under growth conditions. The loop is closed as the variations of $[V_{\mathrm{Cu}}]$ modify the gap in such a way to compensate to a large extent for the initial change due to the distortion. If we put together our GW calculations of the slopes of the band gap and the VBM as functions of u and $[V_{\mathrm{Cu}}]$, we can estimate the overall change of the band gap (for details see the supplementary material [35]):

$$\Delta E_g \simeq \frac{\partial E_g}{\partial u}\Delta u + \frac{\partial E_g}{\partial [V_{\mathrm{Cu}}]}\Delta [V_{\mathrm{Cu}}]. \quad (3)$$

All derivatives are calculated *ab initio*. When the coupled mechanism is considered, using again $\Delta u = 0.02$, we obtain $\Delta E_g = -1.9 \times \Delta u \approx -0.038$ eV, to be compared with the $E_g = 0.65$ eV found due to lattice distortions alone. It is the opposite sign of the two interplaying terms of Eq. (3) that stabilizes the band gap, making it understandable why large deviations from stoichiometry can have innocuous effects in CIS materials.

In conclusion, we have analyzed the dependence of the band gap and band edge shifts ΔE_v of In based chalcopyrites on the internal displacement parameter u. We have found that this dependence, predicted within DFT, was strongly underestimated. Furthermore, we have demonstrated the necessity of using a self-consistent numerical scheme based on many-body perturbation theory to fully capture the structural dependence of the band gap. The HSE06 hybrid functional gives a satisfactory description of the electronic properties of CIS at a reduced cost. However in order to evaluate important trends correctly, the parameter which controls the amount of Fock exchange should be allowed to vary proportionally to the electronic screening. Finally, we explained the relative stability of the experimental band gap in realistic conditions through a coupled process between defect formation and structural relaxation. This suggestion is consistent with both the prediction of very low formation energies for V_{Cu} and experimental samples showing p-type conductivity with very high intrinsic defect concentration.

We thank Ch. Domain and M. Gatti for fruitful discussions. We acknowledge funding from ANR (NT05-343900, JC05_46741), the European projects Athlet (FP6 n.019670) and EPRI (EP-P23606/C11428), the EC 7th Framework Programme (FP7) under grant agreement n.211956 . J. V. acknowledges support by the EDF/ANR CIFRE.

[1] I. Repins *et al.*, Prog. Photovoltaics **16**, 235 (2008).
[2] U. Rau and H. Schock, Appl. Phys. A **69**, 131 (1999).
[3] J.-F. Guillemoles *et al.*, J. Phys. Chem. B **104**, 4849 (2000).
[4] J. E. Jaffe and A. Zunger, Phys. Rev. B **29**, 1882 (1984).
[5] J. M. Merino *et al.*, J. Appl. Phys. **80**, 5610 (1996).
[6] J. E. Jaffe and A. Zunger, Phys. Rev. B **27**, 5176 (1983).
[7] F. D. Jiang and J. Y. Feng, Semicond. Sci. Technol. **23**, 025001 (2008).
[8] M. I. Alonso *et al.*, Phys. Rev. B **63**, 075203 (2001).
[9] L. Hedin, Phys. Rev. **139**, A796 (1965).
[10] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).
[11] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004).
[12] F. Bruneval *et al.*, Phys. Rev. Lett. **97**, 267601 (2006).
[13] M. Gatti *et al.*, Phys. Rev. Lett. **99**, 266402 (2007).
[14] P. Rinke *et al.*, New J. Phys. **7**, 126 (2005).
[15] E. Kioupakis *et al.*, Phys. Rev. B **77**, 155114 (2008).
[16] F. Fuchs *et al.*, Phys. Rev. B **76**, 115109 (2007).
[17] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).
[18] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).
[19] X. Gonze *et al.*, Z. Kristallogr. **220**, 558 (2005).
[20] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[21] C. Domain *et al.*, J. Phys. Chem. Solids **64**, 1657 (2003).
[22] J. Łażewski, P. T. Jochym, and K. Parlinski, J. Chem. Phys. **117**, 2726 (2002).
[23] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).
[24] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[25] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); , Phys. Rev. B **54**, 11 169 (1996).
[26] P. Blöchl, Phys. Rev. B **50**, 17 953 (1994); G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
[27] H. W. Spiess *et al.*, Phys. Status Solidi B **62**, 183 (1974).
[28] S. C. Abrahams and J. L. Bernstein, J. Chem. Phys. **59**, 5415 (1973).
[29] Our argument for the use of $\frac{1}{\varepsilon_\infty}$ is purely qualitative. It neglects dynamical effects, lowering of the screening at finite distances, the underestimate of ε_∞ in a sc-COHSEX calculation [17], as well as the fact that the HSE06 functional already contains a part of screening. However it corrects the most important shortcoming of the hybrid functionals for the comparison of band gaps, namely, the rigid fixing of the effective screening of the nonlocal Fock part.
[30] S. B. Zhang *et al.*, Phys. Rev. B **57**, 9642 (1998).
[31] H. Z. Xiao, L.-C. Yang, and A. Rockett, J. Appl. Phys. **76**, 1503 (1994).
[32] In particular, as the starting LDA gap of the system with vacancies is already positive, it is enough to perform G_0W_0 calculations to obtain reliable slopes for the variation of the gap vs $[V_{\mathrm{Cu}}]$. This is analogous to what happens in the case of the pure compound when $u > 0.215$ (see Fig. 1) where a positive KS gap allows for the correct slope as a function of u already at the G_0W_0 level.
[33] S. Lany and A. Zunger, Phys. Rev. B **78**, 235104 (2008).
[34] C. Persson and A. Zunger, Appl. Phys. Lett. **87**, 211904 (2005).
[35] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.104.056401.