Thin-film solar cells made of Cu(In,Ga)Se₂ (CIGS) allow cost reduction and high efficiency, and compete today as successors of the dominating silicon technology. Nevertheless, there are concerns about their large scale production due to the increasing price of In and Ga. Quaternary chalcogenides Cu₂ZnSn(S,Se)₄ (CZTS) have recently been proposed as alternative absorbers. Their crystal structures and electronic properties are very similar to those of the parent CIGS, while their constituent elements are naturally abundant and non-toxic. The alloys Cu₂ZnSnSₓSe₁₋ₓ have optimal gaps according to the Shockley-Queisser limit and their use as absorbers in thin film solar cells is getting established by a growing energy conversion efficiency (almost 10% for lab cells). However, the understanding of the properties of the different phases of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ is still rather superficial, and only few recent studies have addressed their structural, electronic, and defect properties.

The zincblende-derived kesterite structure (I₄) of CZTS is recognized to be the most stable. The energy difference per atom with respect to the stannite structure is known to be large. The anion bond lengths, which induce a displacement of the anion displacement parameters (anion bond lengths), prove that kesterite and stannite phases can coexist in experimental samples, and explaining the reported disagreement with density functional theory (DFT) calculations, using semi-local or hybrid functionals, which obtained systematically a smaller gap for Se compounds. More recent measurements delineate a gap of about 1 eV for Cu₂ZnSnSe₄, explaining the previous overestimation with the presence of ZnSe in the sample.

Note that the current workhorse ab initio theory is, in fact, DFT, in combination with the local density approximation (LDA) or generalized gradient approximations (GGA). However, this approach is totally inadequate to study the electronic structure of materials where the band gap is controlled by the hybridization of the d states of a transition metal with p states, such as in CIGS or Cu₂ZnSnS₄. Moreover the anion-cation bonds can be poorly described, leading to anion displacements outside the experimental range, even if lattice constants are as usual well reproduced. In particular, for CuIn(S,Se)₂, LDA and GGA yield structural internal parameters with an error of about 5% for a₁, a₂, c. Such an error leads to an underestimate by more than 50% of the band gap in a calculation at the theoretical geometry.
In this letter, we solve these problems by using state-of-the-art ab initio approaches that go beyond standard DFT to determine accurate quasiparticle band structures of both kesterite and stannite Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$. These calculations are based on a restricted self-consistent (sc) GW scheme, which has the advantage of being independent of the starting point (i.e., the poor LDA Kohn-Sham states) at the price of a larger computational complexity. Such approach, that we will refer to as scGW, consists in performing a self-consistent GW calculation within the Coulomb hole plus screened exchange (COHSEX) approximation followed by a perturbative GW on top of it. This method has been applied to many transition-metal compounds, yielding excellent results for the band gaps and the quasiparticle band structure. Standard LDA or GGA, and scGW calculations were performed using the code ABINIT. We included semicore states in the valence to build the norm-conserving pseudopotentials for Cu, Zn and Sn. We also used the code VASP for Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional and GGA+U calculations. Due to the similarity of CZTS materials with the CIGS family, the convergence parameters turned out to be the same reported in Refs. [17].

In Fig. 1 we display band structures for kesterite Cu$_2$ZnSnS$_4$, obtained using different theoretical schemes at the experimental geometry. In the left panel, the Kohn-Sham LDA band structure is compared with the scGW bands. We observe that scGW corrections upshift almost rigidly the lowest conduction states. Concerning the valence: (i) the dispersion of the S p–Cu d antibonding states at the top of the valence remains fairly unaltered, even if the overlap of LDA and quasiparticle wavefunctions shows remarkable variations in this region. (ii) The band width of the S p–Cu d bonding states (located between -3.5 and -6.7 eV) slightly increases. (iii) The bands associated to the (Zn,Sn)-S bond (between -8 and -10 eV) are inverted and downshifted by about 2 eV with respect to LDA. (iv) Also the Ss states are moved down by about 2 eV. In the right panel of Fig. 1 we show the same bands as obtained from GGA+U and HSE06 calculations. In this case HSE06 bands are remarkably similar to scGW bands. This is not particularly surprising as the Hartree-Fock mixing of HSE06 is particularly suited for materials with gaps of about 1–2 eV. As expected, GGA+U shifts down the states with Cu d character, thereby opening the gap to a reasonable value. However, it is evident from the figure, that the overall description of the band dispersions is quite inaccurate.

It is by now known that the band gap in CIGS materials is extremely sensitive to structural distortions and the remarkable stability of the band gap found experimentally can only be explained by compensating effects induced by intrinsic defects. In order to establish if a similar behavior is also found in CZTS compounds, we performed calculations for kesterite (see Fig. 2) and stannite Cu$_2$ZnSnS$_4$ by varying the anion displacements. We also verified that sensible variations of $a$ and $c$ lattice parameters have negligible effects on the gap, in analogy to the case of CIGS. We observe a strong variation of the band gap with $u$, which is due to similar variations of both valence and conduction band edges. Note that the position of the top valence has important implications for the formation energies of charged defects. The slopes are substantially larger for scGW calculations than for DFT-LDA, and even than for HSE06. In fact, they are controlled by the screening, which is essential to include in a self-consistent way, as in scGW.

In Fig. 3 we can see the scGW band structures of the four compounds of the CZTS family. For the kesterite Cu$_2$ZnSnS$_4$ and stannite Cu$_2$ZnSnSe$_4$ the experimental geometries were used. For the remaining compounds, the experimental anion displacements are not reported and it was therefore necessary to resort to the theoreti-
 TABLE I. Band gaps and valence-band shifts with respect to LDA (in eV) for all the structures considered in this work.

|        | LDA | GGA+U | HSE | scGW | exp. |
|--------|-----|-------|-----|------|------|
| kesterite | $E_g$ | 0.09 | 0.86 | 1.52 | 1.64 |
|         | $\Delta E_v$ | 0.00 | -0.52 | -0.81 | -0.49 |
| stannite | $E_g$ | -0.24 | 0.34 | 0.94 | 1.02 |
|         | $\Delta E_v$ | 0.00 | -0.27 | -0.55 | -0.31 |

Furthermore, we found a remarkable similarity between the electronic properties of the stannite and kesterite compounds, and to a large extent between these and the CIGS family. This once more points to the direction that CZTS materials are excellent candidates to replace the more costly CIGS in the absorbing layer of thin film photovoltaic cells.

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