

Effects of Electronic and Lattice Polarization on the Band Structure of Delafossite Transparent Conductive Oxides

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We use hybrid functionals and restricted self-consistent *GW*, state-of-the-art theoretical approaches for quasiparticle band structures, to study the electronic states of delafossite $\text{Cu}(\text{Al}, \text{In})\text{O}_2$, the first *p*-type and bipolar transparent conductive oxides. We show that a self-consistent *GW* approximation gives remarkably wider band gaps than all the other approaches used so far. Accounting for polaronic effects in the *GW* scheme we recover a very nice agreement with experiments. Furthermore, the modifications with respect to the Kohn-Sham bands are strongly \mathbf{k} dependent, which makes questionable the common practice of using a scissor operator. Finally, our results support the view that the low energy structures found in optical experiments, and initially attributed to an indirect transition, are due to intrinsic defects in the samples.

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Many high-technology devices, such as flat panel displays, touch screens, or even thin-film solar cells, require the use of thin transparent contacts. These contacts are usually built from insulating oxides that, for a certain range of doping, become conductive while retaining transparency in the visible spectrum. The most common examples of these so-called transparent conductive oxides (TCOs) are electron (*n*-)doped SnO_2 , In_2O_3 , and ZnO . Hole (*p*-) doping of wide-gap semiconductors was for a long time very hard to obtain [1]. It is therefore not surprising that the discovery of *p* doping in CuAlO_2 thin films with a carrier mobility of about $10 \text{ cm}^2/(\text{V s})$ attracted great interest [2]. Other members of the delafossite family, like CuGaO_2 [3] and CuInO_2 [4], were discovered shortly after. The latter compound is particularly interesting as it exhibits bipolar (*n*- and *p*-type) conductivity by doping with appropriate impurities and tuning the film-deposition conditions [4]. This opens the way to the development of transparent *p*-*n* junctions, and therefore fully transparent optoelectronic devices, functional windows, and stacked solar cells with improved efficiency.

CuAlO_2 is by far the most studied system of the family of delafossite TCOs. However, there is still no agreement either on the origin of the *p*-type conductivity, or on the electronic bands of the pure crystal. Measurements of the direct optical band gap (E_g^{dir}) of CuAlO_2 fall in the range from 2.9 to 3.9 eV [2,5–8], with most values in the interval 3.4–3.7 eV. These experiments also yield a large dispersion of indirect gaps (E_g^{ind}), from 1.65 to 2.1 eV, with one experiment measuring 2.99 eV [8]. Unfortunately, there is only one photoemission experiment [5], that yields 3.5 eV for the quasiparticle band gap. Note that the optical and quasiparticle gaps differ by the exciton binding energy.

Concerning CuInO_2 , optical experiments measured E_g^{dir} between 3.9 and 4.45 eV [4,9,10], with only one estimation of E_g^{ind} at 1.44 eV [10].

From the theoretical perspective, the situation is also quite complex, even if the full $\text{Cu } 3d$ shell should exclude the strongly correlated electron regime. These materials are usually studied within density functional theory (DFT), using the standard local density (LDA) or generalized gradient approximations (GGA). However, it is well known that the Kohn-Sham band structures systematically underestimate the band gaps. For similar compounds, like Cu_2O and $\text{CuIn}(\text{S}, \text{Se})_2$, Kohn-Sham LDA calculations lead to unreasonable band structures, in particular, due to the misrepresentation of the hybridization between the *d* electrons of the metal and *p* electrons of the anion [11,12]. To overcome this situation, hybrid functionals have been recently proposed, with very promising results [13], especially for materials with small and intermediate band gaps [14,15]. Other approaches include $\text{LDA} + U$, that tries to improve the description of correlation through the introduction of a mean-field Hubbard-like term. This method has been quite successful in the study of strongly correlated systems, but it relies on a parameter *U*, that is often adjusted to experiments.

Arguably the most reliable and used *ab initio* technique to obtain quasiparticle band structures is the many-body *GW* approach [16]. The common practice within this framework is to start from a DFT calculation, and evaluate perturbatively the *GW* energy corrections to the band structure. This procedure, which we will refer to as G_0W_0 , is justified when the departure wave functions and band structure are already close to the quasiparticle ones. This is indeed the case in many systems, explaining why

G_0W_0 has been extremely successful in describing electron addition and removal energies for metals, semiconductors and insulators [17]. However, it has been recently shown that G_0W_0 fails for many transition metal oxides [11,18].

To solve this problem one can perform restricted self-consistent (sc) GW [19]. This technique has the advantage of being independent of the starting point at the price of a larger computational complexity. Fortunately, there is an alternative procedure that yields wave functions that are extremely close to those obtained in a full sc- GW calculation, namely, sc-COHSEX as explained in Ref. [20]. The dynamical effects that are absent in COHSEX calculations can then be accounted for by performing a final perturbative GW step. This method, that we will refer to as sc- GW , has been applied to many oxide compounds, yielding excellent results for the band gaps and the quasiparticle band structure [11,12,18,20].

Note that these theoretical techniques yield quasiparticle bands, and not optical gaps. To evaluate these latter quantities one mostly resorts to the solution of the Bethe-Salpeter equation. For the delafossite structures there is one such calculation starting from a GGA + U band structure [21]. It yields for CuAlO_2 a very large exciton binding energy of about 0.5 eV for the first direct transition. The choice of U was found to have strong consequences on the width of the band gap, but it did not affect significantly the exciton binding energy. We can thus assume that 0.5 eV is a reasonable estimate.

In the following, we present calculations of the band structures of CuAlO_2 and CuInO_2 using some of the most accurate theoretical tools available in the community. These include the standard LDA, hybrid functionals (namely B3LYP [22] and two flavors of Heyd-Scuseria-Ernzerhof, HSE03 and HSE06 [23]), LDA + U , G_0W_0 , and sc- GW . As discussed above, we expect sc- GW to be the most accurate *ab initio* approach. When the comparison was possible, we found our results in excellent agreement with previous calculations (Refs. [5,7,8,24–26] for LDA, Ref. [26] for B3LYP, and Ref. [27] for GGA + U).

The hybrid and LDA + U calculations were performed with VASP [28] and ABINIT [29], respectively, using the PAW formalism and an energy cutoff of 44 Ha. The parameter U was set to 8 eV as in Ref. [21]. Our GW calculations were performed with ABINIT, starting from LDA band structures and using norm-conserving pseudopotentials with semicore states ($3s$ and $3p$ for Cu and $4s$ and $4p$ for In) included in the valence. The energy cutoff was 120 Ha for the ground state calculation, and the \mathbf{k} -point grid was a $4 \times 4 \times 4$ Monkhorst-Pack. As the experimental and LDA relaxed geometries are very close (within 1%), and the small contraction of the lattice in LDA has a negligible effect on band structures (≤ 0.05 eV), we employed experimental lattice parameters [26]. Note that it was absolutely essential to use the method of Ref. [30], due to the extremely slow convergence with respect to the number of empty states.

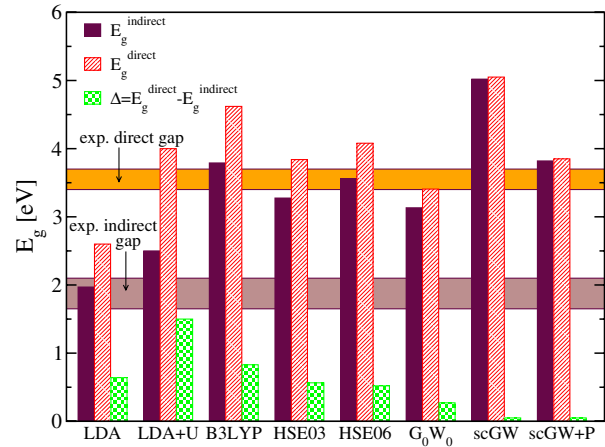


FIG. 1 (color online). Band gaps of CuAlO_2 using: LDA, LDA + U , hybrid, G_0W_0 , sc- GW , and sc- GW including model polaronic corrections. The horizontal zones contain data extracted from various optical experiments (see text).

In Figs. 1 and 2 we show direct and indirect photoemission gaps and the band structures of CuAlO_2 obtained using different theoretical approaches. The minimum E_g^{dir} of CuAlO_2 is always found at L , where the dipole transition between the band edge states is allowed [25]. All calculations, except sc- GW , give a fundamental E_g^{ind} between the conduction band minimum at Γ and the valence band maximum along the Γ - F line. The experimental data for optical gaps are also presented with an error bar that reflects the dispersion of the most likely values found in literature. LDA exhibits, as expected, the smallest gaps. Basically every approach beyond it opens up the gap by different amounts and modifies the band dispersions. The direct and indirect gaps have similar behaviors in the different theories, and both increase when going from $\text{LDA} < G_0W_0 < \text{HSE03} < \text{HSE06} < \text{B3LYP} < \text{sc-}GW$. On the other hand, the difference $E_g^{\text{dir}} - E_g^{\text{ind}}$ seems to decrease with the sophistication of the method, reaching nearly zero for the sc- GW calculation. This is a consequence of the drastic change of the conduction band dispersion, which

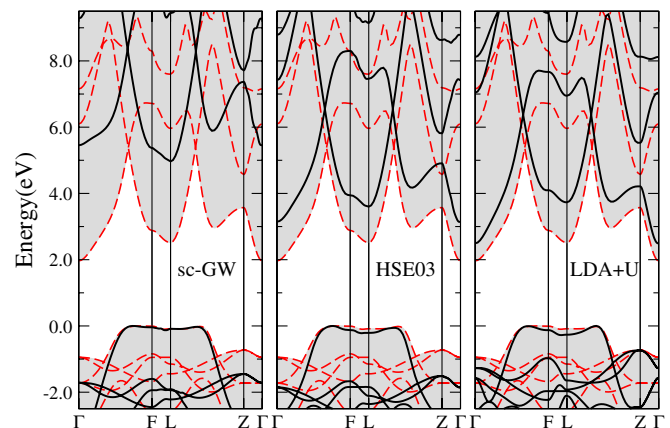


FIG. 2 (color online). Band structures for CuAlO_2 : comparison of LDA (red dashed lines) with sc- GW (left panel), HSE03 (central panel), and LDA + U (right panel).

displaces the conduction minimum from Γ to L when sc-GW is applied (see Fig. 2). Only LDA + U does not follow the trend, as it is the only case in which $E_g^{\text{dir}} - E_g^{\text{ind}}$ gets significantly larger than in LDA.

Looking at the direct gap, we point out that most of the methods give results that are within the experimental range, when an exciton binding energy of around 0.5 eV [21] is considered. This is true for LDA + U , G_0W_0 , the hybrids HSE03 and HSE06. However, for sc-GW and even for B3LYP, the theoretical gap is larger by about 1–1.5 eV than the experimental findings. For CuInO_2 (see Fig. 3) we have to make the comparison with care, as the smallest E_g^{dir} is located at Γ , where optical transitions are forbidden [25]. A meaningful comparison with experiments must consider the gap at L . Thus, we find that both trends and quantitative results are analogous to those for CuAlO_2 . In particular, sc-GW yields again E_g^{dir} larger by 1–1.5 eV than the experimental range.

We stress again that, to date, sc-GW is arguably the best method available to estimate band gaps of wide-gap semiconductors, and that it gives excellent results for compounds like Cu_2O and $\text{CuIn}(\text{S}, \text{Se})_2$ [11,12]. It is unlikely that the presence of defects can lead to such a large shrinkage of E_g^{dir} . However, there is another effect that has been neglected up to now: the change of screening due to the polarization of the lattice [31]. In fact, according to the experimental data [32], unfortunately available only for CuAlO_2 , the polaron constant for this system is large ($\alpha_p \sim 1$), indicating a non-negligible contribution of the lattice polarization to the electronic screening. In other ionic compounds with similar polaron constants this can lead to a shrinkage to the band gap by about 1 eV [33]. A full sc-GW calculation including in an *ab initio* framework the effects of the lattice polarization is to date beyond reach. However, a reliable estimate can be obtained using the model proposed by Bechstedt *et al.* [33], which gives a static representation of the polaronic effects based on the

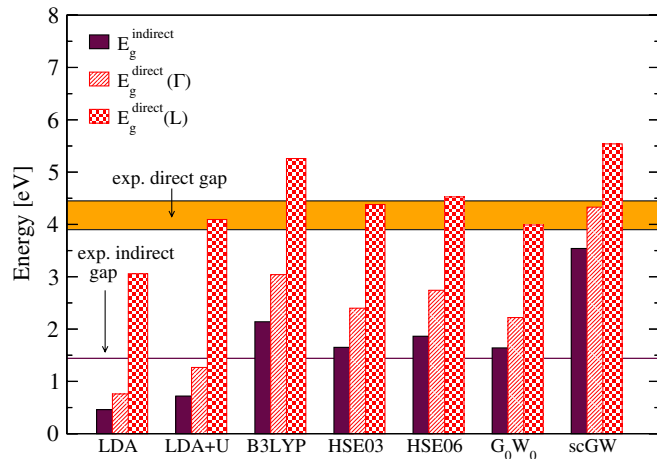


FIG. 3 (color online). Band gaps of CuInO_2 using LDA, LDA + U , hybrid, G_0W_0 , sc-GW. The horizontal zones contain data extracted from optical experiments (see text).

difference of experimental static dielectric constants. By performing a perturbative GW step including model polaronic effects on top of the sc-COHSEX, we found a uniform (\mathbf{k} -independent) shrinkage of the band gap by 1.2 eV. As we can see in Fig. 1, this correction brings our results for E_g^{dir} well within the experimental range (once the excitonic correction of about 0.5 eV is also considered). As it is observed in Ref. [33], the polaronic model employed can only overestimate the correction. All these results point to the conclusion that the agreement of the other methods with experiment was fortuitous and due to a cancellation of errors.

Looking now at the indirect gap, we focus on Fig. 1 as there are more experimental data for CuAlO_2 . All the hybrids and GW calculations yield indirect gaps much larger than the experimental range 1.65–2.1 eV, even taking into account any possible excitonic and polaronic effects. Moreover, sc-GW, the best method used in this work, yields the highest E_g^{ind} at around 5 eV, while the difference $E_g^{\text{dir}} - E_g^{\text{ind}}$ is in general much smaller than the experimental value (≈ 2 eV), and even vanishing for the sc-GW calculation. From Fig. 3 we realize that these conclusions are as well valid for CuInO_2 , where the best estimates for the indirect band gap are much larger than the experimental value of 1.44 eV [10].

These are very strong arguments in favor of Robertson *et al.* [26] that suggested that the experimental “indirect gap” absorption was due to defects, and should not be present in the defect-free compound. Also Pellicer-Porres *et al.* [8] questioned the interpretation of the low energy peaks as indirect transitions, as the absorption coefficient is more than 2 orders of magnitude larger than in typical indirect absorption edges. The most promising defects are oxygen interstitials O_i , as LDA calculations predict low formation energies and the introduction of states in the gap at 0.7 and 1.4 eV [34]. However, a full clarification of this issue will require sc-GW or hybrid calculations for these, and other more complex defects.

Finally, we analyze more in detail the band structures of CuAlO_2 shown in Fig. 2. LDA calculations (red dashed lines) are compared with sc-GW, HSE03, and LDA + U calculations. The main effect of LDA + U is to open the LDA gap by an amount that can be controlled by the parameter U . The difference $E_g^{\text{dir}} - E_g^{\text{ind}}$ is in this approximation enhanced, due to a change of the character of the lowest conduction band along the symmetry lines. Hybrid calculations using HSE03 give a comparable E_g^{dir} and a modified dispersion of both valence and conduction states close to the Fermi energy, which reduces $E_g^{\text{dir}} - E_g^{\text{ind}}$. The conduction band minimum (CBM) within HSE03 is still located at Γ , but the difference between the CBM at L and Γ gets significantly smaller. For sc-GW, besides the further increase of the band gaps, the dispersion of the bands is strongly affected by the many-body effects. In fact, the GW corrections exhibit an unusual dispersion of around 1 eV when looking at the different \mathbf{k} points, displacing the CBM

from Γ to L . We note that often in semiconductor physics one assumes that the quasiparticle corrections can be modeled by a rigid shift (the so-called scissor operator). From our results it follows that one should refrain from using this simple approximation for these important materials. We can also conclude that hybrid calculations give a better description of band dispersions than LDA + U , even if the two approaches yield similar band gaps.

In conclusion, it is clear that the delafossite family exhibits complex and unusual band gap physics that cannot be captured by standard theoretical approximations. We found that the direct band gap is well reproduced by the best many-body approaches if polaronic effects are taken into account. We can expect that this situation, of a large gap that is reduced substantially by polaronic effects, is quite general and is present in many more materials than previously expected. In fact, the apparent good agreement between calculated gaps (with hybrid functionals or G_0W_0) and experimental gaps for materials as simple and widely studied as LiF can be accidental, as preliminary calculations confirm: the underestimation of the gap by these methods (the scGW gap is indeed 2 eV larger than the experimental and G_0W_0 gap) is compensated by the neglect of large polaronic effects. Furthermore, the modifications with respect to the LDA Kohn-Sham bands are strongly \mathbf{k} dependent, which makes questionable the common practice of using a scissor operator. The band dispersion obtained by hybrid functional calculations is in between the LDA and sc-GW dispersion, while the LDA + U calculations open up the gap but do not give a significant improvement of the band dispersion. Finally, our calculations rule out the interpretation of the low energy features in the absorption spectra as arising from a putative indirect band gap. These structures should rather come from intrinsic defects, as proposed in Refs. [8,26]. However, a complete understanding of the electronic and excitation properties of these systems will only be achieved, in our opinion, by a high-level theoretical scheme (like sc-GW) including defects and effects from the lattice polarization in an *ab initio* framework. Work along these lines is in progress.

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- [1] S. Nakamura, M. Senoh, and N. Iwasa, *Jpn. J. Appl. Phys.* **31**, L139 (1992); J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.* **75**, 4452 (1995).
- [2] F. Benko and F. Koffyberg, *J. Phys. Chem. Solids* **45**, 57 (1984); H. Kawazoe *et al.*, *Nature (London)* **389**, 939 (1997).
- [3] K. Ueda *et al.*, *J. Appl. Phys.* **89**, 1790 (2001).
- [4] H. Yanagi *et al.*, *Appl. Phys. Lett.* **78**, 1583 (2001).
- [5] H. Yanagi *et al.*, *J. Appl. Phys.* **88**, 4159 (2000).
- [6] C. Ong and H. Gong, *Thin Solid Films* **445**, 299 (2003); T. Dittrich *et al.*, *Appl. Phys. Lett.* **85**, 742 (2004); E. Alkoy and P. Kelly, *Vacuum* **79**, 221 (2005); A. Banerjee, R. Maity, and K. Chattopadhyay, *Mater. Lett.* **58**, 10 (2004); A. Banerjee and K. Chattopadhyay, *J. Appl. Phys.* **97**, 084308 (2005); A. Banerjee *et al.*, *Physica (Amsterdam)* **370B**, 264 (2005); R.-S. Yu *et al.*, *Appl. Phys. Lett.* **90**, 191117 (2007).
- [7] S. Gilliland *et al.*, *Phys. Status Solidi (b)* **244**, 309 (2007).
- [8] J. Pellicer-Porres *et al.*, *Appl. Phys. Lett.* **88**, 181904 (2006).
- [9] C. W. Teplin *et al.*, *Appl. Phys. Lett.* **85**, 3789 (2004).
- [10] M. Sasaki and M. Shimode, *J. Phys. Chem. Solids* **64**, 1675 (2003).
- [11] F. Bruneval *et al.*, *Phys. Rev. Lett.* **97**, 267601 (2006).
- [12] J. Vidal *et al.*, *Phys. Rev. Lett.* **104**, 056401 (2010).
- [13] E. N. Brothers *et al.*, *J. Chem. Phys.* **129**, 011102 (2008).
- [14] J. Paier, M. Marsman, and G. Kresse, *Phys. Rev. B* **78**, 121201(R) (2008).
- [15] J. Hafner, *J. Comput. Chem.* **29**, 2044 (2008).
- [16] L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- [17] W. G. Aulbur, L. Jönsson, and J. W. Wilkins, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, New York, 2000), Vol. 54, p. 1.
- [18] M. Gatti *et al.*, *Phys. Rev. Lett.* **99**, 266402 (2007).
- [19] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, *Phys. Rev. Lett.* **93**, 126406 (2004); M. van Schilfgaarde, T. Kotani, and S. Faleev, *Phys. Rev. Lett.* **96**, 226402 (2006).
- [20] F. Bruneval, N. Vast, and L. Reining, *Phys. Rev. B* **74**, 045102 (2006).
- [21] R. Laskowski *et al.*, *Phys. Rev. B* **79**, 165209 (2009).
- [22] P. Stephens *et al.*, *J. Phys. Chem.* **98**, 11623 (1994).
- [23] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003); J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006).
- [24] B. J. Ingram *et al.*, *Phys. Rev. B* **64**, 155114 (2001); L. Shi, Z. Fang, and J. Li, *J. Appl. Phys.* **104**, 073527 (2008).
- [25] X. Nie, S. Wei, and S. Zhang, *Phys. Rev. Lett.* **88**, 066405 (2002).
- [26] J. Robertson *et al.*, *Thin Solid Films* **411**, 96 (2002).
- [27] M. N. Huda *et al.*, *Phys. Rev. B* **80**, 035205 (2009).
- [28] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [29] X. Gonze *et al.*, *Z. Kristallogr.* **220**, 558 (2005).
- [30] F. Bruneval and X. Gonze, *Phys. Rev. B* **78**, 085125 (2008).
- [31] W. B. Fowler, *Phys. Rev.* **151**, 657 (1966); A. B. Kunz, *Phys. Rev. B* **6**, 606 (1972).
- [32] J. Pellicer-Porres, A. Segura, and D. Kim, *Semicond. Sci. Technol.* **24**, 015002 (2009).
- [33] F. Bechstedt *et al.*, *Phys. Rev. B* **72**, 245114 (2005).
- [34] I. Hamada and H. Katayama-Yoshida, *Physica (Amsterdam)* **376B-377B**, 808 (2006).