Electronic Band Structures and Excitonic Properties of Delafossites: A $GW$-BSE study

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We report the band structures and excitonic properties of delafossites CuMO$_2$ (M = Al, Ga, In, Sc, Y, Cr) calculated using the state-of-the-art $GW$-BSE approach. We find that all the delafossites are indirect band gap semiconductors with large exciton binding energies, varying from 0.24 to 0.44 eV. The lowest and strongest exciton, mainly contributed from either Cu 3$d$ → Cu 3$p$ (Al, Ga, In) or Cu 3$d$ → M 3$d$ (M = Sc, Y, Cr) transitions, is always located at L point of the rhombohedral Brillouin zone. Taking the electron-hole effect into account, our theoretical band gaps exhibit nice agreement with experiments.

Keywords: delafossite, $GW$, BSE, exciton

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I. INTRODUCTION

Nowadays transparent conductive oxides (TCO) are widely used in displays, solar cells and light emitting diodes. Such materials require optical transparency with band gap over ~3 eV and good p- and n-type dopability. Most of the high-performance TCOs are n-type semiconductors, such as In$_2$O$_3$, ZnO and SnO$_2$. Their use is rather restricted due to lack of the p-type counterparts. Realization of p-type TCOs is challenging but quite important since many semiconductor devices are based on p-n junctions. p-type conductivity in combination of transparency was achieved in 1997 in thin films of CuAlO$_2$, which crystallizes in delafossite structure belonging to $R3m$ space group. Subsequently, p-type TCOs has been discovered in other delafossites (CuMO$_2$, M = Ga, In, Sc, Y, Cr).

There are many research reports on the electrical and optical properties of delafossites over the past two decades, both theoretical and experimental. However, the agreement with each other is rather limited. The discrepancy comes from the sample fabrication details, measurement conditions and also the different levels of theories used. Among the delafossites, CuAlO$_2$ is by far the most studied, parameter. This makes the method less favorable in the sense of prediction. An alternative is to use hybrid functionals, which incorporate a portion of Hartree-Fock (HF) exact exchange with exchange and correlation from semilocal DFT functionals. Hybrid functionals, balancing out the overestimation of HF and the underestimation of DFT, are found to yield good results for simple semiconductors. However, for more complex systems or semiconductors with $d$ electrons, the general validity of hybrid functional is not clear. As for CuAlO$_2$, the band gap at L, which corresponds to the direct optical transition, was predicted to be 4.5 eV$^{11}$ and 4.8 eV$^{31}$ from B3LYP$^{32}$ and PBE0$^{33,34}$ hybrid functionals. Even including the exciton
binding energy of ~0.5 eV\(^{17}\), these numbers are still too large. sX-LDA\(^{28}\) underestimates the value to be 2.95 eV\(^{35}\). HSE06\(^{36}\) functional seems to predict reasonable band gap of ~4.1 eV\(^{25,31}\), which is comparable to experimental value considering the excitonic effect. However, the HSE06 band gap of CuScO\(_2\) is 3.72 eV as in our calculations, significant underestimation of the experiment values of 4.24-4.35 eV\(^{18,19}\).

A more involved theoretical method is many-body perturbation theory with \(GW\) approximation\(^{37,38}\). The \(GW\) method, including the many-body electron-electron interaction, in general predicts more accurate band structures of solids.\(^{39-43}\) In practice, single shot \(GW\) or \(G_0W_0\) as a perturbative quasiparticle correction to LDA band structure is widely used and shown to yield accurate band gaps for some typical semiconductors,\(^{38,44}\) but generally still gives an underestimation and the error can be large for systems with shallow \(d\) states\(^{45}\). Different levels of \(GW\) approximation exist to improve the agreement with experiments. Partial self-consistency on the Green’s function \(G\) only (\(GW_0\)) and on both \(G\) and screened Coulomb interaction \(W\) (\(GW\)) can further open the band gap.\(^{41}\) The \(GW_0\) scheme, with the screening properties fixed at random phase approximation (RPA) level, shows excellent agreement with experiments\(^{43,44}\), stemming from the fact that the dielectric properties of many systems can be predicted quite well at RPA\(^{45}\). Further update of \(W\), as in the \(GW\) scheme, is found to give too large band gaps of almost all materials due to underestimation of the screening.\(^{43}\) Another approach solving the deficiency of \(G_0W_0\) is based on the generalized Kohn-Sham (gKS) scheme, which uses hybrid functional wave functions as a starting point.\(^{42}\) The gKS scheme is also a practical solution of \(GW\) calculations if LDA or GGA predict completely unreasonable wave functions, as we will see it is the case for CuCrO\(_2\). All the above \(GW\) approximations depends on the starting point of mean field wave functions, different starting points yield varied results. Quasiparticle self-consistent \(GW\) (QSGW)\(^{41}\), developed to optimized the starting point self-consistently, shows systematically improved band structures of many materials, but suffers from an overestimation of the fundamental gaps. The overestimation can be partly remedied by including the vertex correction in the dielectric matrix.\(^{46}\) \(G_0W_0@LDA\) calculations\(^{31,47}\) predict the indirect and direct band gaps of CuAlO\(_2\) of 3.1 eV and 3.4 eV, respectively, which are obviously underestimated given the fact of large exciton binding energy. By using wave functions from scCOHSEX as a starting point, the \(G_0W_0\) band gaps are changed to 5.0 eV and 5.1 eV\(^{31,47}\). A similar large band gap was also obtained by QSGW calculations.\(^{31,47}\) Contrary to all other theories, \(G_0W_0@scCOHSEX\) predicted the conduction band minimum (CBM) located at L instead of \(\Gamma\). The large discrepancy of the band gap compared with experiments was claimed attributed to large polaronic effect which shrinks the band gap by 1.2 eV according to a simple model calculation. By adding up both the excitonic and polaronic contributions, agreement with experiments can be eventually obtained. However, we note that the phonon frequency of CuAlO\(_2\) is \(\omega_{LO} = \sim 80-90\) meV, which is responsible for the polaron shift.\(^{49}\) It is obvious that the phonon modes in the relevant energy is practically not active since the measurements are conducted at room temperature\(^{13}\) or even as low as 20 K\(^{12}\). Therefore, the large band gap must be ascribed to the underestimation of the dielectric constant in scCOHSEX calculation, as found similar to QSGW.\(^{41}\)

As we see there is yet no consistent approach appropriately describing the band structures of delafossites. In addition, the measured exciton binding energies of delafossites are as large as 0.3-0.5 eV\(^{18-20}\). However, there is only one report calculating the exciton absorption of CuAlO\(_2\) by solving the Bethe-Salpeter equation\(^{30-53}\) (BSE) based on LDA+U band structures.\(^{17}\) Though tuning the U parameter can reproduce the experimental band structures and the following BSE could give a reasonable estimate of the exciton binding energy, we claim that more accurate and parameter free calculations are desired from the first-principles point of view. Here, we present \(GW_0\) calculations on the band structures of (CuMO\(_2\), M=Al, Ga, In, Sc, Y) with PBE\(^{34}\) wave functions as the starting point. For CuCrO\(_2\), PBE predicts completely wrong orders of Cr 3\(d\) bands, hence, HSE is adopted. The BSE is solved on top of the \(GW_0\) quasiparticle band structures. The exciton binding energies are found to vary in range of 0.24-0.44 eV for different delafossites. Our \(GW\)-BSE results agree very well with experiments.

II. METHODOLOGY

All the DFT, \(GW\) and BSE calculations are performed using the \textsc{vasp} code\(^{40,55,56}\) and projector augmented-wave (PAW)\(^{37}\) potentials. For Ga and In, the potentials with semicore 3\(d\) and 4\(d\) electrons placed in valence are used, while for Sc, Y and Cr, we use 3\(s\)3\(p\), 4\(s\)4\(p\) and 3\(s\)3\(p\) shells in valence. We use Perdew, Burke, Ernzerhof (PBE)\(^{54}\) exchange-correlation functional to relax the atomic positions while experimental lattice parameters are used for all the delafossites. The force tolerance is 0.01 eV/Å. A \(k\)-grid of 6\(\times\)6\(\times\)6 is found to converge the band structures within 0.01 eV both for DFT and \(GW\) calculations, and a kinetic energy cutoff of 500 eV is used to expanding the wave functions.

We carefully examine the convergence of the \(GW\) calculations, especially the energy cutoff of the response functions \(E_\varepsilon\) and the number of empty states \(N\), since we have \(d\) bands at the band edges of delafossites. It is demonstrated that large \(E_\varepsilon\) and \(N\) are needed to get reliable results of localized states.\(^{58}\) Usually, the band gap converges much faster than the exact band energies due to the error cancellation. Figs. 1a and b show the band energy and band gap convergence with respect to \(E_\varepsilon\) and \(N\),
respectively, at $\Gamma$ for CuAlO$_2$. It is obvious that $N = 100$ and $E_g = 200$ eV are enough to converge the band gap within 0.02 eV. The same accuracy for the exact band energy can only be obtained for at least $N = 1500$ and $E_g = 400$ eV. Contrary to the behavior of $\Gamma$, the convergence is more difficult for $L$, where the CBM converges much faster than VBM, as shown in Figs. 1c and d. As a result, the band gap convergence slows down. We attribute this to the different band characters of VBM and CBM. The VBM is mostly contributed by Cu 3$d$ orbitals at all k points, though a hybridization with 0 2$p$ orbitals exists, as shown in Fig. 3a. The CBM is dominated by Cu 3$p$ orbitals at $\Gamma$ but Cu 3$p$ orbitals at L. Since 3$d$ orbital is more localized than $3p$ orbital, the CBM at L needs more effort to converge. In a word, we choose $N = 1000$ and $E_g = 300$ eV in our $GW$ calculations. This restricts the band gap error within 20 meV. The dielectric function is evaluated at 100 frequency grids on real axis. The self-energy is calculated using the full frequency integration method. After obtaining the $GW$ eigenvalues on a regular k mesh, the band structures on high symmetry lines are interpolated using WANNIER90 code$^{59}$.

![Graph](image)

FIG. 1 Convergence of the band energy and band gap of CuAlO$_2$ with respect to the number of empty states $N$ and energy cutoff of the response function $E_R$ at (a), (b) $\Gamma$ point and (c), (d) L point. The calculations are conducted at a k grid of $2 \times 2 \times 2$, since the convergence behavior is insensitive to the k mesh. For (a) and (c), $E_R = 700$ eV, while for (b) and (d), $N = 2500$.

The excitonic properties are determined by solving the BSE with Tamm-Dancoff approximation$^{60}$ on top of the $GW$ quasiparticle band structure. The indirect transitions are not included in the present study. Two occupied and one unoccupied bands are used and found enough to converge the lowest electron-hole excitation energy $\Omega_1$ which determines the exciton binding energy. It is usually required much finer k mesh in BSE calculations to obtain accurate exciton spectrum, since excitons are very localized in reciprocal space. However, the computation demand is prohibitive even for the $GW$ calculations for many k points. To this end, we use a model BSE (mBSE) scheme$^{61}$. The dielectric function was fitted to $GW$ calculations with the form:

$$\varepsilon^{-1}(q) = 1 - (1 - \varepsilon_{m}^{-1})e^{\varepsilon_{m}^{-1}q^2}$$  

Where $\varepsilon_{m}$ is the ion-clamped static dielectric constant which is evaluated on RPA level. $\varepsilon_{m}$ for different delafossites are listed in Table 1. $q_{TP}$ is the Thomas-Fermi screening length, which is found nearly constant of 1.1 for all the delafossites by fitting. The quasiparticle eigenvalues are evaluated on a finer k mesh through wannier interpolation. We argue that wannier interpolation is more accurate than scissor shift technique$^{61}$ and essential for non-uniform corrections of the $GW$ bands. The PBE wave functions at finer k mesh are used. However, for CuCrO$_2$, PBE wave function is unreliable. The PBE+U method are adopted. We find that the exciton spectrum is insensitive to the U parameter, since the eigenvalues are fixed at $GW$ level. Fig. 2a compares the imaginary part of the dielectric function $\varepsilon_2$ (Hereafter, we ignore the polarization dependence and use $\varepsilon = (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})/3$) of CuAlO$_2$ calculated by $GW$-BSE and the mBSE method using $6 \times 6 \times 6$ k mesh. As can be seen, mBSE reproduce the $GW$-BSE curve quite well. A finer k mesh of 12×12×12 is used in all the mBSE calculations to determine the exciton binding energy. The estimated error is 0.01 eV, as show in Fig. 2b.

![Graph](image)

FIG. 2 (a) The comparison of the imaginary dielectric function $\varepsilon_2$ calculated by GW-BSE and mBSE. (b) The convergence of the lowest exciton energy $\Omega_1$ with respect to the k mesh using mBSE method.

### III. RESULTS AND DISCUSSION

The band gaps and exciton binding energies of delafossites calculated by the present $GW$-BSE approach is summarized in Table I, PBE band gaps and experimental direct optical gaps are also included for comparison. Only CuScO$_3$ is predicted to be direct band gap semiconductor by PBE. Our $GW$ calculations show that all the delafossites are indirect band gap semiconductors. We also include the lowest excitation energy $\Omega_1$ in Table I, which, in general, agrees quite well with the experimental optical gaps. The exciton binding energy $E_{XB} = E_{g}^{0} - \Omega_1$ shows variation for
different delafossites with largest of 0.44 eV for CuAlO₂ and smallest of 0.24 for CuScO₂. These data agree with the reported BSE@LDAU calculation of 0.47 eV\(^{11}\) for CuAlO₂ and the experimental data of 0.3-0.38 eV\(^{18,19}\) for CuScO₂. In what follows, we present more details about the band structures and excitonic properties of different delafossites.

**TABLE I.** Band gaps of delafossites. CMO is shot for CuMO₂, where M is the first letter of Al, Ga, In, Sc, Y and Cr, respectively. \(E_g^d\) is direct band gap, \(E_g^i\) is indirect band gap, \(\Omega_1\) is the lowest electron-hole excitation energy, \(E_{xb}\) is exciton binding energy, and \(E_o\) is the direct optical gap from measurements. \(\varepsilon_{RPA}^{GG}\) is the static ion-clamped dielectric constant evaluated on RPA level with local field effect included.

|       | CAO     | CGO     | ClO     | CSO     | CYO     | CCO     |
|-------|---------|---------|---------|---------|---------|---------|
| PBE   | \(E_g^d\) | 2.68    | 2.58    | 3.09    | 2.21    | 2.69    | 1.30    |
|       | \(E_g^i\) | 1.92    | 0.92    | 0.40    | ---     | ---     | 2.67    | 0.96    |
| GW    | \(E_g^d\) | 3.88    | 3.80    | 4.49    | 4.22    | 4.49    | 3.42    |
|       | \(E_g^i\) | 3.55    | 2.48    | 1.89    | 4.16    | 4.35    | 3.29    |
|       | \(\Omega_1\) | 3.44    | 3.47    | 4.07    | 3.98    | 4.16    | 3.11    |
|       | \(E_{xb}\) | 0.44    | 0.33    | 0.42    | 0.24    | 0.33    | 0.31    |
|       | \(\varepsilon_{RPA}^{GG}\) | 5.3     | 5.6     | 5.0     | 5.5     | 4.6     | 4.9     |
| EXP\(^a\) | \(E_o\) | 3.46    | 3.53    | 3.90    | 3.93    | 3.7     | 3.08    |
|       |         | 3.47    | 3.56    | 4.15    | 3.94    | 3.8     | 3.14    |
|       |         | 3.53    | 3.60    | 4.45    | ---     | 3.5     | 3.18    |

\(^a\)Experimental data are from Refs: 2,3,5,6,12,13,15,18,19,62-69.

### A. CuAlO₂, CuGaO₂ and CuInO₂

As mentioned in the introduction, different levels of self-consistency in \(GW\) calculations can yield quite different band structures. We confirmed this by examining the direct band gap \(E_g^d\) of CuAlO₂ at L, as shown in Table II. For all the \(GW\) calculations, we find the CBM is located at \(\Gamma\), with 0.2-0.3 eV lower than that at L. Our \(G_0W_0\) band gap of 3.5 eV agrees with 3.4 eV reported by Trani et al\(^{31}\). Though the present QSGW calculations are different from what they called scGW (\(G_0W_0@\text{scCOHSEX}\)) in Refs\(^{31,47}\), the obtained band gaps of 5.1 eV are the same. This is because the wave functions produced by the two different approaches are extremely close.\(^{70}\) Christensen et al\(^{48}\) reported a smaller band gap of 4.55 eV with the same QSGW method. We attribute the difference to the different basis sets used in the \(GW\) calculations. Plane waves and PAW potentials are used in our calculations while they adopt full-potential linear muffin-tin orbitals (LMTO). As can be seen from Table II, \(E_g^d\) is increased in the order of \(G_0W_0 < G_0W_0 < GW < QSGW\). The self-consistency of the screened Coulomb potential \(W\) reduces the electronic screening, as indicated by the decreasing of the dielectric constant, hence, deteriorating the agreement with experiments.\(^{43}\) The RPA dielectric constant is 5.3, close to the experimental value of 5.1.\(^{71}\) Hence, a reasonable evaluation of the quasiparticle band structure should be expected to be obtained at \(W_0\) level.

**TABLE II.** The calculated \(GW\) band gaps \(E_g^d\) of CuAlO₂ at L with different levels of self-consistency. \(\varepsilon_{RPA}^{GG}\) is the static ion-clamped dielectric constant evaluated on RPA level with local field effect included.

|       | \(G_0W_0\) | \(G_0W_0\) | GW | QSGW |
|-------|------------|------------|----|------|
| Present work | 3.5 | 3.9 | 4.3 | 5.1 |
| Refs. \(^{31}\) | 3.4 | 5.1 \(^{47}\) | 4.55 | 4.58 |
| \(\varepsilon_{RPA}^{GG}\) | 5.3 | 5.3 | 4.1 | 3.4 |

**FIG. 3** Band structure of CuAlO₂. (a) PBE fat bands with projections on Cu 3d (blue squares), Cu 3p (red circles) and O 2p (green diamonds) orbitals, respectively. (b) Comparison of the PBE (red dash) and \(GW_0\) (blue solid) band structures. The green dots are the VBM positions along \(\Gamma F\) and \(LZ\) lines. (c) The imaginary dielectric function \(\varepsilon_2\) and oscillator strength \(\lambda\) as a function of photon energy \(\hbar\nu\). (d) The lowest exciton amplitude (magenta circle) plotted as a fat-bands style.

Fig. 3a displays the fat bands of CuAlO₂ with projections on Cu 3d, 3p and O 2p orbitals. The Cu 4s orbitals have a small contribution to the CBM at \(\Gamma\), which is not shown here. It is clear that the VBM for all the \(k\) path is mainly Cu 3d orbitals. On the contrary, the CBM exhibits distinct Cu 4s orbitals, with part hybridization with O 2p states. On the contrary, the CBM exhibits distinct Cu 4s orbitals, with part hybridization with O 2p states. The CBM at \(\Gamma\) is mainly Cu 3d and 3p orbitals, which predominate for \(\Gamma\) and \(L\), respectively. Fig. 3b compares the \(GW_0\) band structure with that of PBE. The VBM is located along the \(\Gamma F\) line, as indicated by the green dot, which we denote as \(A\) site. Hence, the indirect band gap is measured from \(A\) to \(L\). It is clear that the VBM for all the \(k\) path is mainly Cu 3d orbitals. On the contrary, the CBM exhibits distinct Cu 4s orbitals, with part hybridization with O 2p states. The CBM at \(\Gamma\) is mainly Cu 3d and 3p orbitals, which predominate for \(\Gamma\) and \(L\), respectively. Fig. 3b compares the \(GW_0\) band structure with that of PBE. The VBM is located along the \(\Gamma F\) line, as indicated by the green dot, which we denote as \(A\) site. Hence, the indirect band gap is measured from \(A\) to \(L\).
calculations. As a general trend, the $GW_0$ corrections shift the conduction and valence bands up and down, respectively. The band renormalizations, however, varies at different k points. The VBM correction $\Delta E_{\text{VBM}}$ is 1.0 eV at L while 1.5 eV at $\Gamma$. The $\Delta E_{\text{VBM}}$ is much smaller with 0.65 eV at $\Gamma$ and 0.2 eV at L. The non-uniform renormalization of the bands invalidates the scissor shift technique in the delafossite structures.

Based on the $GW_0$ band structure, the exciton properties are evaluated by solving the BSE. The exciton oscillator strength and the imaginary part of the dielectric function $\varepsilon_2$ are plotted in Fig. 3c. The first peak of $\varepsilon_2$, corresponding to the lowest excitation energy of 3.44 eV, which is smaller than the related band gap $E_g^0$ of 3.88 eV, indicates a bound exciton with a binding energy of 0.44 eV. Such high exciton binding energy is attributed to the localization of the exciton wave functions in real space and the weak screening environment. The exciton wave functions can be expressed in a coupled electron-hole pair configurations: $|S\rangle = \sum_{cck} A_{cck}^S |vc\rangle$, where $v$ and $c$ are for valence and conduction states, $A_{cck}^S$ is the exciton amplitude with the corresponding excitation energy $\Omega_S$. We plot $|A_{cck}^S|$ for the lowest excitation as fat bands as shown in Fig. 3d. The circle size denotes the absolute value of the amplitude. In practice, BSE is solved on a regular $k$ mesh. To calculate $A_{cck}^S$ for an arbitrary $k$ point as for the purpose of plot, we adopt the Gaussian mapping:

$$A_{cck}^S = \sum_{k'} |A_{cck'}^S|^2 \omega_{kk'}^S \exp \left( -\frac{|k-k'|^2}{2\sigma^2} \right)$$

Where $k'$ is the $k$ point in irreducible Brillouin zone, $\omega_{kk'}^S$ is the corresponding weight, $\sigma = 0.05$ is adopted. It is from Fig. 3d that the lowest exciton is composed almost exclusively of the transitions between the topmost valence and lowest conduction states around L. Those states are localized Cu 3d and 3p orbitals, as shown in Fig. 3a. Hence, the largest probability of excitations is found to be the Cu 3d $\rightarrow$ Cu 3p transitions on the same Cu atom. The delafossites can be considered as layered structures with excitations confined in the Cu planes. The cross-plane dielectric constant $\varepsilon_{\perp}$ is calculated to be 4.5, while the in-plane $\varepsilon_{\parallel}$ is 5.7. The weak electronic screening in the cross-plane direction further enhances the binding of the excitons. After taking account of the exciton binding energy of 0.44 eV, the $GW$-BSE optical band gap is found to be 3.44 eV, which is in good agreement with the experimental value of $\sim 3.5$ eV.

The $GW_0$ band structures and exciton properties of CuGaO$_2$ and CuInO$_2$ are shown in Fig. 4. The VBM of both of them are located at A site along the IF line, with B site 15 meV and 2 meV lower in energy, respectively, for CuGaO$_2$ and CuInO$_2$. The CBM is located at $\Gamma$. The lowest excitation of CuGaO$_2$, corresponding to the first peak of $\varepsilon_2$ in Fig. 4c, is contributed from the transitions around L point, as shown in Fig. 4a. The dominant exciton is still Cu 3d $\rightarrow$ Cu 3p transition similar to CuAlO$_2$. However, the CBM at L also has some Ga 4s character. Hence, Cu 3d $\rightarrow$ Ga 4s transition can also contribute to the lowest excitations. The calculated exciton binding energy is 0.33 eV, which is smaller than that of CuAlO$_2$. The smaller binding energy is related to the spread the exciton wave functions due to Cu 3d $\rightarrow$ Ga 4s excitations and larger dielectric constant, which is calculated as 5.6. For CuInO$_2$, the fundamental direct band gap of 2.5 eV is found at $\Gamma$ point. Nonetheless, the optical transitions at $\Gamma$ is dipole-forbidden. The measured optical gap is composed of the transitions at L point, see the magenta circles in Fig. 4b, which is corresponding to the strongest peak of $\varepsilon_2$ in Fig. 4. However, below this excitation, there are many weak excitations with much smaller oscillator strength. We plot the amplitude of one of these weak excitons in Fig. 4b, as indicated by the black circles. Note, that the amplitude is ten times exaggerated to make suitable to the eye. The weak excitons are composed of the transitions around $Z$ point, contributed from Cu 3d $\rightarrow$ Ga 4s excitations. Since the amplitudes are smaller and the dipole transition probability at $Z$ is also smaller, the optical absorption due to these weak excitons can hardly be observed in experiments.

### B. CuScO$_2$ and CuYO$_2$

Unlike the group IIIA (Al, Ga, In) delafossites, the few low-lying conduction states of the IIIB (Sc, Y) ones are contributed by the partially filled $d$ orbitals, as indicated by the red circles in Fig. 5a. The fat-bands features of the...
valence bands for CuScO$_2$ and CuYO$_2$ are similar to that of CuAlO$_2$ and not shown here. The CBM of both CuScO$_2$ and CuYO$_2$ is located at L, with 0.1 eV lower than that at Γ where the Cu 3$d$ orbitals still predominate. The VBM of CuScO$_2$ is at B site, with 2 meV higher than that of A site. Contrary to experiments, CuScO$_2$ is predicted to be an indirect semiconductor with indirect band gap of 4.16 eV from B to L. The direct band gap at L is 4.22 eV, only 0.06 eV larger than the indirect band gap. Hence, such small difference can hardly be detected in UV-vis measurements. The VBM of CuYO$_2$ is located at A site with 35 meV higher than that of B site. CuYO$_2$ is also found an indirect semiconductor with indirect band gap of 4.35 eV from A to L. The direct band gap at L is 4.49 eV.

The exciton properties of CuScO$_2$ and CuYO$_2$ are quite similar. The lowest excitations or the first absorption peak in ε$_2$ as shown in Figs. 5c and d, are composed of the transitions around L mainly from Cu 3d → Sc 3d or Cu 3d → Sc 3d excitations, as in Fig. 5b. A small contribution can be found for Cu 3d → Cu 3p excitations. Since the excitons are dominated by the inter-atom excitations, the binding energy is expected to be smaller than that of the Cu 3d → Cu 3p excitations. The exciton binding energy of CuScO$_2$ and CuYO$_2$ are 0.24 and 0.33 eV, respectively. The smaller exciton binding energy of CuScO$_2$ can be further ascribed to the larger dielectric constant of 5.5 compared to 4.6 of CuYO$_2$. Our calculated exciton binding energy of 0.24 eV and the optical band gap of 3.98 eV agree quite well with the experimental value of 0.3 eV and 3.94 eV, respectively. However, extra resonate exciton peaks above the band gap, as shown in Fig. 5c, are not observed in experiments. We attribute this discrepancy to the insufficient k point sampling in BSE calculations. Usually, one needs extremely fine k mesh to converge the absorption curve for higher energies. We only check convergence with respect to the k mesh about the first absorption peak, as our focus is on the exciton binding energy. Hence the resonate exciton peaks may not be converged.

C. CuCrO$_2$

CuCrO$_2$ is different from other delafossites, since electrons are strongly correlated due to the half-filled 3$d$ states of Cr. The ground state was found antiferromagnetic with very small difference in energy to that of ferromagnetic state. Here, our calculations are performed on the ferromagnetic state due to its smaller unit cell. The band structure of CuCrO$_2$ is under debate in literatures. The main concern is the Cr 3d position in the valence bands. PBE calculations predict that both the CBM and VBM are mainly composed of Cr 3d states, as shown in Fig. 6a. Arnold et al. reported the band structure of CuCrO$_2$ by using X ray spectroscopy combined with DFT+U calculations and showed that the VBM derived mainly from the Cu 3d states. Yokobori et al. found that Cr 3d states dominate the VBM according to their photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) measurements and also DFT+U calculations. Although the conclusions of the two are contrary to each other, similar valence band spectrum are obtained. The mystery is indeed due to the different U parameters used in their-first-principles calculations, since both of their conclusions depend on the DFT+U calculations. In Ref. 74, U of 5 eV and 4 eV were used for Cu and Cr 3d states, respectively, while U of 2 eV was used for both of the atoms in Ref. 76. The effect of the onsite repulsive U term in the DFT+U framework is to push the corresponding states in conduction and valence bands up and down, respectively. Hence, larger U parameter would push Cr 3d states deep in the valence bands and even deeper than the Cu 3d states, as found in Ref. 74. We believe the U parameter of 2 eV used in Ref. 76 is too small for Cu and Cr 3d states, thus resulting in wrong band structures. In addition to DFT+U, hybrid functionals can also be employed to correct the band orders predicted by normal DFT. sX and HSE06 calculations agree with the DFT+U (U = 4 eV for Cr) calculations with Cu 3d states dominate the VBM. Our HSE (HSE03) calculations also reproduce the correct bands orders, as shown in Fig. 6b. We also check the band structure obtained from QSGW calculations which should give the most accurate wave functions, and find it is consistent with that of HSE calculations qualitatively despite the large band gap of 4.5 eV at L. With the correct band order, DFT+U still underestimates the direct band gap as ~2.6 eV, while HSE06 overestimate it to 3.75 eV, compared to the experimental value of ~3.1-3.2 eV. Although sX
and our HSE calculations predict reasonable band gaps of 3.1 eV and 3.2 eV, experiments\textsuperscript{20} show that the exciton binding energy of CuCrO\textsubscript{2} is large as 0.33 eV.

To improve the description of the band structure of CuCrO\textsubscript{2}, we adopt the GW calculations based on the generalized Kohn-Sham (gKS) scheme\textsuperscript{42}. The gKS+ G\textsubscript{0}W\textsubscript{0} approach shows good performance for typical semiconductors or even compounds with shallow d states. We use HSE wave functions as the starting point for the perturbative G\textsubscript{W\textsubscript{0}} calculations, since HSE reproduces the correct band orders. The G\textsubscript{W\textsubscript{0}}@HSE band structure of CuCrO\textsubscript{2} is shown in Fig. 6c. We note here, that the G\textsubscript{W\textsubscript{0}} improvement of the band structure over G\textsubscript{0}W\textsubscript{0} is quite small for the HSE starting point, only 0.04 eV increase of the band gap. The VBM is located at B site along LZ line for the up spin state, with 1 meV higher than A site. The fundamental direct band gap of 3.42 eV, which is also the lowest spin-allowed optical transition, is found at L for down spin state. The indirect band gap is 3.29 eV from B (up) to L (down). The dielectric function and oscillator strength are shown in Fig. 6d. The first absorption peak corresponds to a bound exciton with binding energy of 0.31 eV, in agreement with the experimental value of 0.33 eV\textsuperscript{20}. The amplitude, as shown in Fig. 6c, indicates that the lowest excitation is mainly composed of Cu 3d-Cr 3d transitions with a small contribution from Cu 3d-Cu 3p transitions. However, this strong absorption peak is usually wrongly assigned to Cu 3d+O 2p → Cu 3d+4s transitions for delafossites in literatures due to incorrect band structures used\textsuperscript{15,17,20,78}. We note that the Cu 3d+4s states in conduction bands is located at Γ point, which is optical inactive due to dipole forbidden. According to our GW-BSE calculations, the lowest excitations are always at L point, mainly derived from either Cu 3d → Cu 3p (Al, Ga, In) or Cu 3d → M 3d (M = Sc, Y, Cr) transitions. The O 2p states hybridize with Cu 3d states in valence bands but with less contribution, we thus neglect the O 2p in the notations.

FIG. 6 (a) PBE (b) HSE (c) G\textsubscript{W\textsubscript{0}@HSE band structures of CuCrO\textsubscript{2}. The red circles and blue squares in (a) and (b) denote projections on Cr and Cu 3d orbitals, respectively. The solid and dash lines in (c) denote the up and down spin states. The magenta circles show the fat-bands of the exciton. (d) dielectric function ε\textsubscript{2} and oscillator strength λ.

IV. CONCLUSIONS

In conclusion, we calculate the band structures and the excitonic properties of delafossites CuMO\textsubscript{2} (M = Al, Ga, In, Sc, Y and Cr) by using the state-of-the-art GW-BSE approach. The HSE wave functions are used as the starting point of the GW calculations for CuCrO\textsubscript{2}, since HSE corrects the band orders wrongly predicted by PBE. For other delafossites, PBE wave functions are employed. We evaluate different self-consistency levels of GW calculations on CuAlO\textsubscript{2}, namely G\textsubscript{0}W\textsubscript{0}, G\textsubscript{W\textsubscript{0}}, GW and QSGW, and find that the G\textsubscript{W\textsubscript{0}} scheme with self-consistent updates on the Green’s function while keeping the screened Coulomb potential on RPA level yields band gaps closest to experiments. Our results show that all of the delafossites are indirect band gap semiconductors with large exciton binding energies, varying from 0.24 to 0.44 eV. The lowest and strongest exciton absorption is always located at L point of the rhombohedral Brillouin zone, mainly contributed from either Cu 3d → Cu 3p (Al, Ga, In) or Cu 3d → M 3d (M = Sc, Y, Cr) transitions. Taking the electron-hole effect into account, the calculated band gaps agree quite well with experiments.

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