# Exchange and Correlation Effects in Electronic Excitations of $Cu_2O$

Fabien Bruneval
*Laboratoire des Solides Irradiés, CEA-CNRS UMR 7642-Ecole Polytechnique, 91128 Palaiseau Cedex, France and European Theoretical Spectroscopy Facility (ETSF), Palaiseau, France*

Nathalie Vast
*Laboratoire des Solides Irradiés, CEA-CNRS UMR 7642-Ecole Polytechnique, 91128 Palaiseau Cedex, France*

Lucia Reining
*Laboratoire des Solides Irradiés, CEA-CNRS UMR 7642-Ecole Polytechnique, 91128 Palaiseau Cedex, France and European Theoretical Spectroscopy Facility (ETSF), Palaiseau, France*

M. Izquierdo and F. Sirotti
*Synchrotron SOLEIL, L'Orme des Merisiers St. Aubin B.P. 48, 91192 Gif-sur-Yvette Cedex, France*

N. Barrett
*CEA-DSM/DRECAM-SPCSI, CEA-Saclay, 91191 Gif-sur-Yvette, France*

(Received 26 April 2006; published 28 December 2006)

State-of-the-art theoretical methods fail in describing the optical absorption spectrum, band gap, and optical onset of $Cu_2O$. We have extended a recently proposed self-consistent quasiparticle approach, based on the *GW* approximation, to the calculation of optical spectra, including excitonic effects. The band structure compares favorably with our present angle-resolved photoemission measurements. The excitonic effects based on these realistic band structure and screening provide a reliable optical absorption spectrum, which allows for a revised interpretation of its main structures.

DOI: 10.1103/PhysRevLett.97.267601 PACS numbers: 79.60.−i, 71.10.−w, 71.20.−b, 71.35.−y

The optical absorption spectrum (OAS) of $Cu_2O$ has been an area of interest for more than 50 years [1], recently boosted by the potential applications of this material in solar energy conversion and catalysis [2]. The spectrum shows numerous excitonic peaks of different nature: the optical transitions in the vicinity of the band gap at $\Gamma$ give rise to a bound exciton at the absorption onset and to excitonic series based on dipole forbidden transitions. These series have been measured [3,4] and well understood theoretically [5]. In contrast, the interpretation of the rest of the OAS has not been clarified. It has been discussed [4] in terms of optical transitions and van Hove edges; however, to our knowledge, no theoretical work has assessed these conclusions so far.

The state-of-the-art approach to calculate *ab initio*, the OAS is a two-step process. First, one determines the band structure (namely, electron addition and removal energies, that are measurable in direct and inverse angle-resolved photoemission). To this end, quasiparticle energies are calculated using the *GW* approximation for the electron self-energy [6,7]. Then this band structure is used as an input for the Bethe-Salpeter equation (BSE) [8]: this effective two-particle equation corrects for the fact that optical absorption is neither electron addition nor removal, but the creation of interacting electron-hole pairs. In this framework, the dielectric function $\varepsilon(\mathbf{r}_1, \mathbf{r}_2, \omega)$ plays a prominent role. First, it screens the additional particle, the hole in photoemission or the electron in inverse photoemission, which are both described by the one-particle Green's function $G$: in the *GW* self-energy, the screened Coulomb interaction $W$ [calculated in the random phase approximation (RPA)] replaces the bare Coulomb interaction $v$ of exchange in Hartree-Fock. Second, $\varepsilon$ screens the electron-hole attraction in the BSE that is approximated by the static limit of $W$.

Today, *GW* calculations are most often performed as a "one-shot" correction to a self-consistent Kohn-Sham (KS) local density approximation (LDA) calculation [9]. Obviously, the accuracy of the Green's function $G$ and of the RPA dielectric function $\varepsilon$ rely on how well the KS wave functions and energies estimate the quasiparticles. This approach, denoted $G_0W_0$, though successful in many applications to solids [7], seems to fail in the case of $d$ electron metals and their oxides [10,11]. It is therefore not clear how well the BSE, based on the resulting band structure and on the electron-hole interaction $W_0$, may describe an optical spectrum for this kind of material.

In this Letter, we focus on the determination and interpretation of the OAS of $Cu_2O$. We will first show the failure of $G_0W_0$ and perform self-consistent *GW* (sc*GW*) calculations. We have implemented the sc*GW* following Faleev *et al.* [12] who recently suggested an "adaptative" static model for the *GW* self-energy calculations. It provides a proper description of the eigenvalues and of the spatial distribution of the strongly localized $d$ states while avoiding the frequency dependence and non-Hermiticity of the self-energy, which might worsen spectral properties [13]. At variance with Ref. [12], our implementation is based on pseudopotentials [14,15]. Because the band structure is an important intermediate result that can be compared with experiment, we have checked it against existing photoemission data of the literature as well as to our own angle-resolved photoemission spectroscopy (ARPES) measurements. Our sc*GW* results provide a much better description of the experimental band structure than the LDA or $G_0W_0$. Furthermore, we demonstrate that only by taking into account the improved band structure both in the independent-quasiparticle response and in the electron-hole screening can the excitonic spectrum of $Cu_2O$ be properly described.

Electron removal and addition energies are presented in Table I. In the first four columns we give theoretical values at the experimental lattice parameter for the photoemission band gap ($E_g$), the absorption threshold ($E_0$), and the photoemission peaks $A1$ to $F1$ labeled in Ref. [16]. These are compared with the experimental values (last column). The parameters of the calculations [17] can be found in Ref. [18]. All calculations presented here consider the semicore states $3s3p$ of Cu explicitly as valence states: as observed for bulk copper [19], this is crucial for *GW* calculations. Here the situation is even more remarkable: when including the $3s3p$ in the core, *GW* approximation predicts wrongly $Cu_2O$ to be metallic. Table I shows that the choice of theoretical approach gives rise to differences of up to half an eV for the valence band features, and up to a factor of 4 for the band gap. $G_0W_0$ improves the LDA results, but band gaps are still far from the experimental values. Self-consistency in *GW* yields further improvement, with a more important influence of the eigenvalues and a weaker role of wave functions. In a material where already $G_0W_0$ corrects the gap by almost a factor of 3, self-consistency must drastically lower the screening and lead to a significant additional gap opening. It is still not obvious that the dispersion of the band structure is correctly described by the pseudopotential sc*GW* approach. The optical spectra, however, is based on the whole band structure. It is therefore important to independently check the band structure before turning to the OAS.

Because the only reported photoemission results are on polycrystalline samples [20], or cover a limited photon energy range [16], we have performed ARPES measurements with horizontally polarized light ($\theta_i = 45°$) on a high quality $Cu_2O(111)$ single crystal at the APE beam line of Synchrotron Elettra (Trieste). The sample was supplied by Surface Science Laboratory and was cleaned *in situ* by several cycles of $Ar^+$ ion sputtering at 600 eV and annealing at 400 °C. The ion energy and annealing temperature were chosen as low as possible in order to prevent lack of oxygen at the surface, but high enough to obtain a sharp $(1 \times 1)$ LEED pattern. In order to verify the delicate surface stoichiometry we checked the presence of the satellite at $-15.3$ eV binding energy in the photoemission spectrum measured at $h\nu = 76$ eV [18]. This satellite is a fingerprint of $Cu_2O$ [21]. The band dispersion along the $\Gamma$-$R$ direction was then extracted from a series of energy-

TABLE I. Band structure elements of $Cu_2O$ (in eV). $E_g$: photoemission band gap; $E_0$: optical absorption threshold. Structures $A1$ to $F1$ are the photoemission peaks measured in Ref. [16] and reported in the calculated density of states in Fig. 1. The binding energies of structures $A1$ to $F1$ has been adjusted using $D1$ as a reference.

| Energies<br>Wave functions | LDA<br>LDA | $G_0W_0$<br>LDA | sc*GW*<br>LDA | sc*GW*<br>sc*GW* | Experiment |
|---|---|---|---|---|---|
| $E_g$ | 0.54 | 1.34 | 1.80 | 1.97 | 2.17[a] |
| $E_0$ | 1.23 | 1.51 | 2.21 | 2.27 | 2.55[b] |
| $A1$ | −8.45 | −8.19 | −7.95 | −8.13 | −7.25[c] |
| $B1$ | −6.90 | −6.83 | −6.47 | −6.60 | −6.04[c] |
| $C1$ | −3.46 | −3.44 | −3.47 | −3.46 | −3.37[c] |
| $D1$ | −2.95 | −2.95 | −2.95 | −2.95 | −2.95[c] |
| $E1$ | −2.46 | −2.27 | −2.16 | −2.18 | −2.00[c] |
| $F1$ | −1.80 | −1.58 | −1.35 | −1.31 | −1.01[c] |

[a] Reference [3]
[b] Reference [4]
[c] Reference [16]

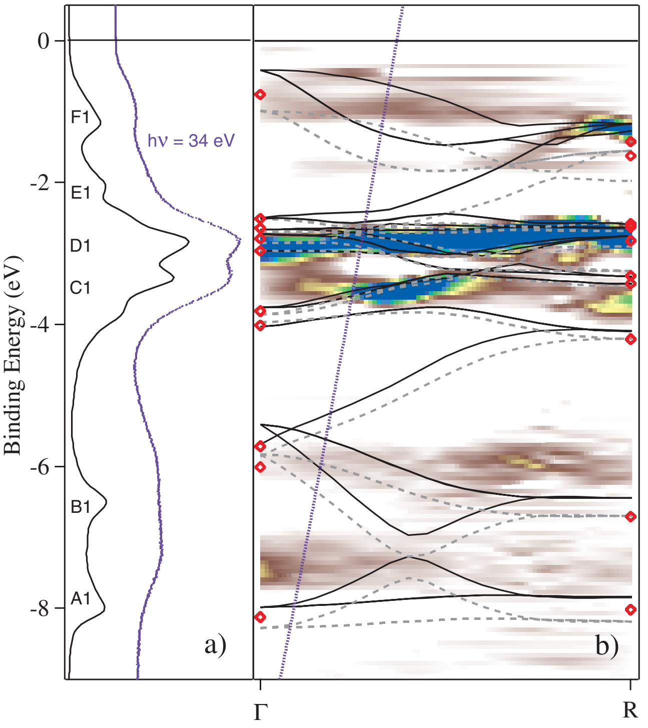

FIG. 1 (color). (a) Spectrum measured at $h\nu = 34$ eV (purple) together with the theoretical sc*GW* DOS (black line). Peaks from $A1$ to $F1$ correspond to those of Table I. (b) Valence band structure deduced from ARPES (displayed as an image of the second derivative of the photointensity). The theoretical bands (arbitrarily aligned to fit the Cu $3d$ peak maximum) are displayed as follows: LDA (dashed lines), $G_0W_0$ (open diamonds), and sc*GW* (solid lines). The straight purple dotted line represents the points in the band structure sampled by the spectrum at $h\nu =$ 34 eV displayed in a).

distribution curves (EDCs) in the photon energy range from 20 to 46 eV, which cover all the **k** points along this high symmetry direction. EDCs were constructed by integrating 1° around normal emission the $\Delta\theta = 12°$ dispersion measured with a SCIENTA-2002 analyzer ($\delta\theta = \pm 0.2°$, $\Delta E < 0.1$ eV). In Fig. 1(a), a spectrum at $h\nu = 34$ eV, representative of the measured data set [18], is displayed (purple line) together with the theoretical DOS (black line). One can distinguish two energy regions: between $-8$ and $-5$ eV (O $2p$ levels); from $-5$ eV up to the Fermi level (mainly Cu character, pure Cu $3d$ between $-4$ and $-2$ eV and hybridized with Cu $4s$ and O $2p$ near the Fermi level). Considering that the calculated DOS is **k** point integrated, whereas the experimental curve is not, the agreement is fair. Figure 1(b) shows the image of the second derivative of the photoelectron intensity (blue color corresponds to the intensity maxima of the spectra) as a function of the electron momentum, which was obtained within a free electron final state model. This representation of the band dispersion along the $\Gamma$-$R$ line allows us to clearly see the splitting at the top valence band when moving from $\Gamma$ to $R$ and the dispersion of the O $2p$ states near the middle of the Brillouin zone. The comparison with the theoretical calculations obtained for sc$GW$ (solid line), LDA (dashed line), and $G_0W_0$ (points at $\Gamma$ and $R$) shows that, in general, the experimental bands are slightly flatter than theoretical predictions, which may be due to a reduced mean free path of the electrons [22]. The best overall agreement is obtained for our sc$GW$ results, which reproduce reasonably well the position and the dispersion of the Cu states. A less satisfactory agreement is obtained for the oxygen states: their dispersion is slightly overestimated and they are too strongly bound within sc$GW$, though half of the LDA and $G_0W_0$ errors are corrected. This discrepancy might be explained by the strong dependence of the binding energy of these states on the lattice spacing, that may vary at the surface [23], and by the finite momentum resolution in the direction perpendicular to the surface [24]. In fact, one should keep in mind that photoemission is a surface sensitive technique whereas the *ab initio* spectroscopy calculations are, as most often, performed for a perfect bulk system. The dispersive band between the O $2p$ bands and the Cu $3d$ group cannot be seen in the measurement because of the small cross section of the Cu $4s$ orbital (a major contribution), the high-dispersion of the band and the numerous secondary photoelectrons arising from the Cu $3d$ states.

We dispose hence of a reliable band structure for the determination of the OAS. Figure 2(a) shows the comparison of the experimental data [4] with the result obtained by a $G_0W_0$ calculation of the band structure and the subsequent solution of the BSE using $W_0$ for the static screened electron-hole interaction. Although at first glance the theoretical and experimental spectra are similar and the structures labeled $A$, $E_1$, and $C$ seem to be reproduced, there are significant discrepancies: the absorption onset is redshifted by 1 eV in the calculation, and the shoulder at 3 eV has no counterpart in the measured spectrum. In Fig. 2(b), we display the solution of the BSE (dot-dashed line) using our sc$GW$ band structure. The absorption onset is much improved with respect to the panel (a) and the peaks $A$, $E_1$, and $C$ reproduce the experiment, though much less pronounced. This may be due to the standard BSE procedure [8] in which $W_0$, calculated from KS ingredients, is used. Because the KS band gap is 4 times smaller than the sc$GW$ one, an important error in the screening can be expected. Moreover, to be fully consistent, $W$ should be the same as in the $GW$ calculation (the screened electron-hole interaction is obtained as the derivative with respect to $G$ of the $GW$ self-energy). Therefore, we have solved the BSE with $W$ evaluated using sc$GW$ energies [25]. The result, shown as a solid line in panel (b), reproduces remarkably well the experimental spectra and, in particular, the sharpness of the peaks [26]. This result finally allows us to interpret with confidence the different structures. The inset of Fig. 2(b) shows (dots) the energy and the weight of the independent-quasiparticle transitions that mix through the electron-hole

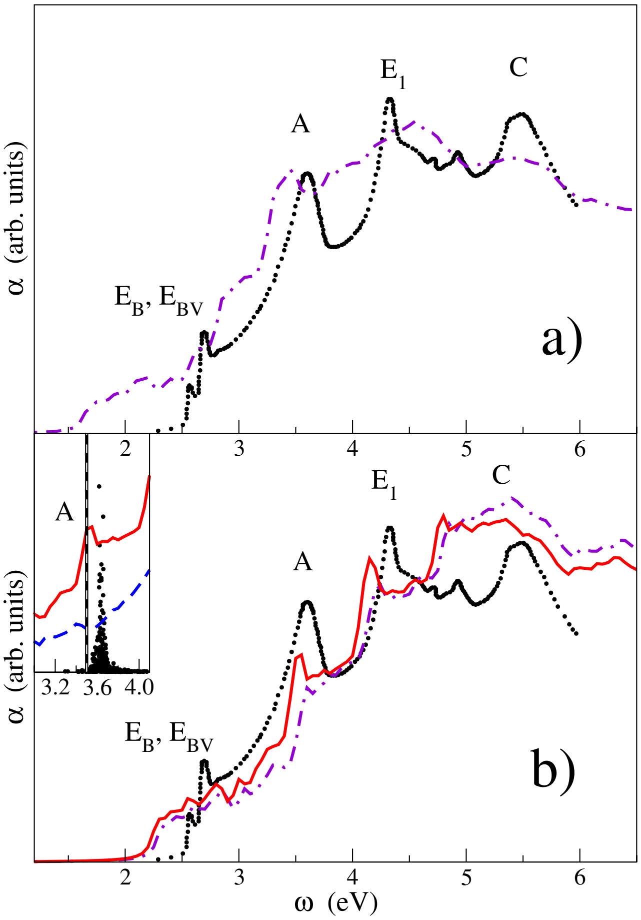

FIG. 2 (color online). Optical absorption of $Cu_2O$: (a) using standard $G_0W_0$ inputs. (b) using sc$GW$ inputs. Experiment from Ref. [4] (full circles), BSE result with LDA dielectric function (dot-dashed line), BSE result with sc$GW$ dielectric function (solid line). The inset in panel (b) shows the transition analysis for peak $A$: contributing transitions (dots) and OAS calculated with sc$GW$ energies but without excitonic effects (dashed line).

interaction and yield the BSE spectrum in the region of peak $A$ marked by the vertical line. Many transitions contribute to this peak (corresponding to the Cu $d$ states in the same energy region), and contrary to what was proposed in Ref. [4], they are not limited to a part of the Brillouin zone. Furthermore, its extinction when excitonic effects are switched off in the calculation (dashed curve of the inset) indicates that it is not a band structure effect associated with a particular van Hove edge, but is created by the electron-hole interaction. The peak $E_1$, however, is not purely excitonic: it is present (though weaker) when excitonic effects are disregarded (not shown). We therefore conclude that the interpretation of the peaks proposed in Ref. [4] should be revised. We stress that the seeming agreement between $G_0W_0$ based BSE spectrum in panel (a) and experiment leads to an erroneous interpretation, because, for example, peak $A$ would have been given a characterization that is more appropriate for peak $E_1$. Only the sc$GW$ approach used consistently for the band structure and the electron-hole screening is able to yield an unambiguous and reliable interpretation of the experiment.

Although $Cu_2O$ is not considered to be a strongly correlated material because its $d$ shell is almost filled, the $d$ electrons play an important role. As they are rather localized, exchange effects are strong and $G_0W_0$ [which correctly describes (screened) exchange] leads to a strong gap opening. Self-consistency weakens the screening. Moreover, it changes the wave functions correcting both the error of coming from the LDA (in particular the self-interaction) and the fact that the local KS potential is the same for conduction and for valence states. In turn, the electron-hole attraction that yields the strong excitonic effects in the OAS is caused by a variation of the exchange due to the optical excitation; correlation leads to screening of this interaction (as opposed to the bare electron-hole attraction of time-dependent Hartree-Fock). $W_0$ overestimates screening and therefore weakens the sharp excitonic peaks, that are instead correctly recovered using the self-consistent $W$.

In conclusion, we have shown that the electronic properties of $Cu_2O$ can be fully understood provided self-consistency beyond perturbative $G_0W_0$ is taken into account. The sc$GW$ band structure, an ingredient that is crucial for a correct description of the OAS, has been confirmed by published as well as our own photoemission data. Furthermore, we have demonstrated that the strong excitonic effects in $Cu_2O$ can be described by solving the BSE, and that the screening of the electron-hole interaction has to be treated consistently to reproduce the peak positions and line shapes in the OAS. Finally, we have clearly stated that the *ab initio* solution of the BSE is a powerful tool to interpret the complex optical spectrum, complementary to models and experiments.

This work has been supported by the EU's 6th Framework Programme through the NANOQUANTA Network of Excellence (No. NMP4-CT-2004-500198). We acknowledge beam time at APE beam line at Elettra Synchrotron, Trieste, Italy, and financial support from the EU Contract No. RII3-CT-2004-506008. We thank G.-C. Panaccione, J. Fujii, and I. Vobornik from APE beam line, and V. Trinité-Quéquet and M.-B. Lepetit. Computer time has been granted by CEA/DSM on the NEC SX6 (Project No. p93), and by IDRIS on the NEC SX5 (Project No. 544).

[1] G. Grosso and G. Pastori Parravicini, *Solid State Physics* (Academic Press, San Diego, London, 2000), Chap. 7, and references therein.

[2] L. Gou and C. Murphy, Nano Lett. **3**, 231 (2003), and references therein.

[3] P. W. Baumeister, Phys. Rev. **121**, 359 (1961).

[4] S. Brahms, S. Nikitine, and J. Dahl, Phys. Lett. **22**, 31 (1966).

[5] R. J. Elliott, Phys. Rev. **124**, 340 (1961).

[6] L. Hedin, Phys. Rev. **139**, A796 (1965).

[7] W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys. **54**, 1 (2000), and references therein.

[8] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002), and references therein.

[9] W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).

[10] F. Aryasetiawan and O. Gunnarsson, Phys. Rev. Lett. **74**, 3221 (1995).

[11] A. Continenza, S. Massidda, and M. Posternak, Phys. Rev. B **60**, 15 699 (1999).

[12] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004).

[13] B. Holm and U. von Barth, Phys. Rev. B **57**, 2108 (1998).

[14] X. Gonze *et al.*, Z. Kristallogr. **220**, 558 (2005).

[15] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).

[16] Z.-X. Shen *et al.*, Phys. Rev. B **42**, 8081 (1990).

[17] A basis set of around 13 000 plane waves is required in order to converge eigenvalues within 50 meV.

[18] F. Bruneval, Ph.D. thesis, Ecole Polytechnique, Palaiseau, France, 2005, http://theory.lsi.polytechnique.fr/people/bruneval/bruneval_these.pdf

[19] A. Marini, G. Onida, and R. Del Sole, Phys. Rev. Lett. **88**, 016403 (2002).

[20] J. Ghijsen *et al.*, Phys. Rev. B **38**, 11 322 (1988).

[21] M. R. Thuler, R. L. Benbow, and Z. Hurych, Phys. Rev. B **26**, 669 (1982).

[22] B. Kim *et al.*, Phys. Rev. Lett. **68**, 1931 (1992).

[23] We have checked this dependence numerically: an increase of 1% of the lattice parameter reduces the binding energy by 0.5 eV within LDA.

[24] V. N. Strocov, J. Electron Spectrosc. Relat. Phenom. **130**, 65 (2003).

[25] Strictly speaking one should also update wave functions. But because all our results point to the fact that this correction is significantly smaller than the influence of the eigenvalues, the effort would not be justified for the presently required precision.

[26] Only the excitonic peaks ($E_B$ and $E_{BV}$) are not present. Because this region is very sensitive to the **k** point mesh, the calculated oscillations are artifacts of this parameter and, considering the number of bands involved, it has been out of reach to converge both parameters in this region.