

Ab initio electronic structure and correlations in pristine and potassium-doped molecular crystals of copper phthalocyanine

Gianluca Giovannetti,^{1,2} Geert Brocks,² and Jeroen van den Brink^{1,3}¹*Institute Lorentz for Theoretical Physics, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands*²*Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*³*Institute for Molecules and Materials, Radboud Universiteit Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands*

(Received 16 May 2007; revised manuscript received 20 October 2007; published 29 January 2008)

We investigate the effect that potassium intercalation has on the electronic structure of copper phthalocyanine (CuPc) molecular crystals by means of *ab initio* density functional calculations. Pristine CuPc (in its α and β structures) is found to be an insulator containing local magnetic moments due to the partially filled Cu d shells of the molecules. The valence band is built out of molecular Pc-ring states with e_g symmetry and has a width of 0.38/0.32 eV in the α/β polymorph. When intercalated to form K_2 CuPc, two electrons are added to the Pc-ring states of each molecule. A molecular low spin state results, preserving the local magnetic moment on the copper ions. The degeneracy of the molecular e_g levels is lifted by a crystal field, resulting in a splitting of 52 meV between occupied and empty bands. Electronic correlation effects enhance the charge gap of K_2 CuPc far beyond this splitting; it is 1.4 eV. The conduction band width is 0.56 eV, which is surprisingly large for a molecular solid. This finding is in line with the observed metallicity of $K_{2.75}$ CuPc, indicating that in this compound the large bandwidth combined with a substantial carrier concentration prevents polaron localization.

DOI: 10.1103/PhysRevB.77.035133

PACS number(s): 71.45.Gm, 71.10.Ca, 71.10.-w, 73.21.-b

I. INTRODUCTION

Chemical doping of molecular crystals can result in a dramatic change of electron transport properties; well-known examples are intercalated fullerenes and organic charge transfer salts. Starting out as insulators, upon doping these compounds can become conducting and in special cases even superconducting.^{1,2} Because of the chemical richness of molecular crystals, building new metals by doping them remains an exciting and ever moving front. In this respect, recent progress was made by Craciun and co-workers, showing that transition metal phthalocyanines (MPc's) FePc, CoPc, NiPc, and CuPc—in their pristine state wide gap insulators—can be turned into a metal through potassium intercalation.³⁻⁵ The MPc molecules are particularly interesting because they possess a magnetic moment and are characterized by substantial intramolecular Coulomb interactions, which opens the way for a display of interesting electron correlation effects. In addition, the MPc's can have orbital degeneracies giving rise to a competition between local Jahn-Teller distortions and the molecular Hund's rule exchange. Upon doping, an intricate interplay between charge delocalization and all these different molecular effects develops, a situation that is reminiscent of strongly correlated ceramics such as for instance doped manganese oxides.⁶ The molecular aspects of organic crystals, however, make metallic MPc's also behave very different from such hard ceramics—in fact they form a class of strongly correlated metals.^{7,8}

The question then arises how exactly the interplay between metallicity, magnetism, Jahn-Teller distortions, and correlation effects unfolds upon intercalation. By performing *ab initio* electronic structure calculations, we set the stage for more involved many-body calculations that can provide detailed answers to such a question. Here, we focus, in particu-

lar, on pristine CuPc and its potassium-doped derivative K_2 CuPc, both of which are of considerable experimental interest,^{3,5,8-13} also because of their close relation to other intercalated phthalocyanines.¹⁴⁻¹⁷ Our specific aims are to establish for potassium intercalated CuPc (i) whether the potassium atoms donate their electrons to the CuPc molecules, and if so, which molecular orbitals they occupy (Cu related or Pc related), (ii) the properties of the valence and conduction bands that are derived from these molecular orbitals, and, in particular, (iii) whether the bandwidth is such that it can explain the observed metallic behavior of $K_{2.75}$ CuPc. This indeed turns out to be the case: the metallicity of $K_{2.75}$ CuPc is due to a relative large bandwidth.

The paper is organized as follows. We will start by investigating the electronic structure of pristine CuPc in its β and α structures. Spin-polarized density functional calculations within the generalized gradient approximation (SGGA) for this compound reveal that a local magnetic moment is present in the open Cu d shell, so that substantial electronic correlation effects can be anticipated due to the strong Coulomb repulsion between the d electrons. We determine the value of the effective Coulomb interaction U_{Cu} with a set of electronic structure calculation for the free, charged CuPc molecule. In the band structure calculations, we subsequently take U_{Cu} into account on a mean field level by incorporating it explicitly within a SGGA+ U scheme. In the last part of the paper, we determine the electronic structure of the intercalated compound K_2 CuPc with SGGA+ U . We will show that the interpretation of this band structure is facilitated by comparing it to the band structure of the virtual crystal K_0 CuPc, indicating that the main consequence of potassium intercalation is a rigid band shift. Before presenting these results, however, we will provide the reader with the details on our computational approaches.

II. COMPUTATIONAL DETAILS

Our spin-polarized calculations (SGGA and SGGA+ U) are performed within the framework of density-functional theory^{18,19} (DFT) using the Vienna *ab initio* simulation package (VASP).²⁰ The Kohn-Sham equations are solved using the PW91 functional,²¹ which describes electronic exchange and correlation within a generalized gradient approximation. The electronic structure is computed using the projector augmented wave method (PAW^{22,23} and PAW+ U ²⁴), and the valence pseudo-wave-functions are expanded in a plane wave basis set with a cutoff energy of 500 eV. All the integrations in the Brillouin zone are performed with the tetrahedron scheme²⁵ using a sampling grid of $5 \times 10 \times 5$ \mathbf{k} points.

The on-site Coulomb interaction U that is needed in the SGGA+ U calculations²⁶ is an input parameter to a VASP calculation. Since in molecular crystals U is basically a molecular property, we can obtain this parameter from calculations on isolated molecules.²⁷ One can express U^{bare} of an isolated molecule as the variation of the energy eigenvalue of a particular orbital with respect to its occupation number.^{28,29} In the case of a CuPc molecule, one can distinguish between orbitals that are localized on the Cu ion in the center, and orbitals that are delocalized over the Pc ring,^{30,31} which leads to two separate parameters $U_{\text{Cu}}^{\text{bare}}$ and $U_{\text{Pc}}^{\text{bare}}$. These parameters are calculated for an isolated molecule using the molecular program GAMESS.³² The electronic structure is calculated within DFT using the BLYP SGGA functional^{33,34} and the 6-31G** Gaussian orbital basis set.

If the molecule is embedded in a crystal, all Coulomb interactions are screened, leading to effective parameters U_{Cu} and U_{Pc} .^{27,35,36} We determine the screening by calculating the electronic polarization that is caused by a charged CuPc molecule placed in a cavity of a homogenous dielectric medium. A value of 3.3 for the static dielectric constant of the medium is used, which is typical for Pc crystals. The polarization energy is then determined by the electrostatic interaction between the molecular charge distribution and the surrounding medium.^{37,38} The effect of screening by the crystal on U_{Cu} is in fact negligible because the dominant (intramolecular) screening by the Pc ring surrounding the localized Cu state is already accounted for in the molecular calculation. Screening by the crystal has, however, an important effect on U_{Pc} .

III. PRISTINE CU PHTHALOCYANINE

The structure of the neutral CuPc molecule and its electronic energy level diagram are shown in Fig. 1. The molecule is planar and has D_{4h} symmetry. It is an open shell molecule; whereas Pc^{2-} is a closed shell system, the copper ion is essentially Cu^{2+} with a d^9 configuration. The b_{1g} state in Fig. 1 is dominated by a contribution from the Cu d orbitals and is localized on the Cu ion. The single electron in this state gives rise to an uncompensated magnetic moment. The a_{1u} and e_g states are mainly derived from the π states of the (conjugated) Pc ring and are delocalized over the ring.

It is important to note that, whereas Fig. 1 indicates that the b_{1g} states form the highest occupied molecular orbital

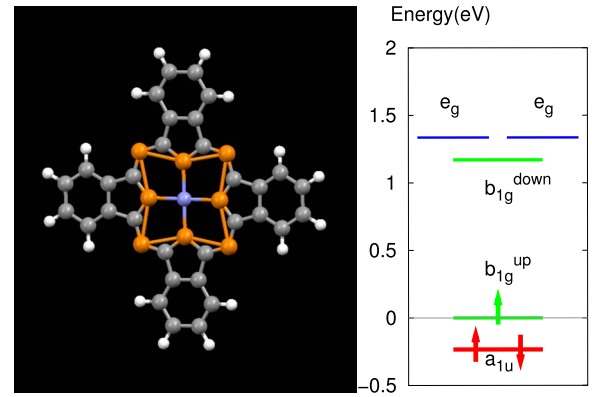


FIG. 1. (Color online) Left: the planar CuPc molecule has D_{4h} symmetry. The central Cu^{2+} ion is surrounded by N atoms, indicated by orange (large) balls; C and H atoms are indicated by gray (medium) and white (small) balls, respectively. The C, N, and H atoms constitute the Pc ring. Right: the SGGA energy levels of the neutral CuPc molecule relative to the HOMO.

and lowest unoccupied molecular orbital (HOMO-LUMO) levels, in reality the first electron addition (removal) state of the CuPc molecule is the Pc-derived e_g (a_{1u}) state. Adding an electron (or even a second and third) will *not* cause a filling of the Cu-derived b_{1g} state. Due to the strong on-site electron-electron repulsion between Cu electrons, the added electrons are forced to occupy the e_g states of the Pc ring (see Table I). This effect is demonstrated by explicit calculations on the charged CuPc ions and is in agreement with the results of previous calculations.^{30,31} One can expect that the order in which the molecular states are occupied also plays an important role in determining how the electronic bands are filled in the doped CuPc crystal.

A. Pristine β -CuPc: SGGA

The crystal structure of pristine β -CuPc (Ref. 39) is shown in Fig. 2. We start with a set of electronic structure calculations to determine the magnetic ground state of the compound. From the SGGA calculations, we find that the antiferromagnetic ordered state (spin up on the first and spin down on the second molecule in the unit cell) is 438 meV per unit cell lower in energy than the spin unpolarized state.⁴⁰ The magnetic moment of each molecule is close to $1\mu_B$, which is consistent with its interpretation as a molecu-

TABLE I. Electronic ground state configurations of various CuPc ions. The a_{1u} and e_g states are derived mainly from the Pc ring and the b_{1g} state is dominantly a Cu orbital.

Ion	Ground state configuration
CuPc ⁺	$(a_{1u})^1(b_{1g})^1(2e_g)^0$
CuPc ⁰	$(a_{1u})^2(b_{1g})^1(2e_g)^0$
CuPc ⁻	$(a_{1u})^2(b_{1g})^1(2e_g)^1$
CuPc ²⁻	$(a_{1u})^2(b_{1g})^1(2e_g)^2$
CuPc ³⁻	$(a_{1u})^2(b_{1g})^1(2e_g)^3$

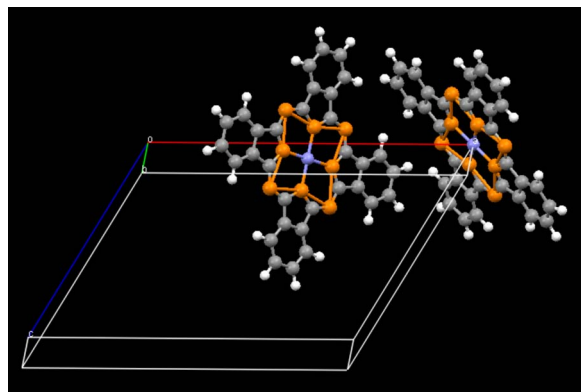


FIG. 2. (Color online) Schematic representation of the β -crystal structure of pristine CuPc. The unit cell is monoclinic with $P2_1/a$ space-group symmetry and contains two CuPc molecules: one in the origin of the cell and a second molecule at $(a/2, b/2, 0)$ (Ref. 39). The unit cell parameters are $a=19.407$ Å, $b=4.790$ Å, $c=14.628$ Å, and $\beta=120.93^\circ$.

lar magnetic moment. We also find that the energy difference between the ferromagnetic and antiferromagnetic orderings is extremely small, i.e., smaller than 1 meV. This indicates that even though local moments are present in this system, the magnetic ordering temperature—if ordering occurs at all—is expected to be very low. This is not important in the following discussion since the band structures that we will present are nearly identical for the ferromagnetically and antiferromagnetically ordered states. We will present results for the antiferromagnetic ordering.

The band structure and density of states of β -CuPc, as calculated by SGGA, is shown in Fig. 3. The bands are arranged in almost degenerate pairs, indicating that the local electronic structure of the two molecules in the unit cell is practically identical. Moreover, the bands show little disper-

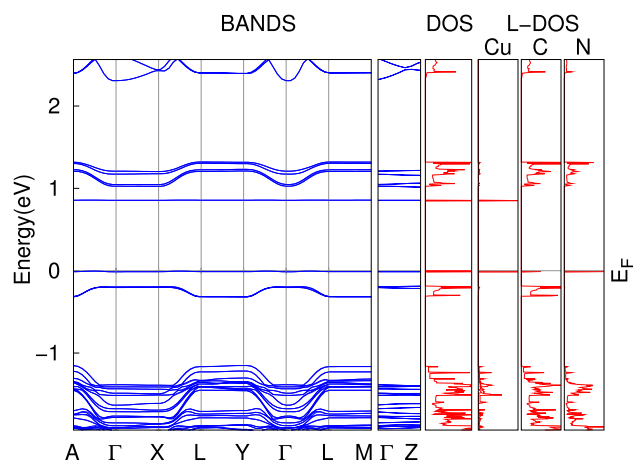


FIG. 3. (Color online) Pristine β -CuPc: band structure, density of states, and atom projected density of states, calculated with SGGA. The energies are plotted along lines in the Brillouin zone, connecting the points $A=(\frac{1}{2}, \frac{1}{2}, 0)$, $\Gamma=(0, 0, 0)$, $X=(\frac{1}{2}, 0, 0)$, $L=(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $Y=(0, \frac{1}{2}, 0)$, $M=(0, \frac{1}{2}, \frac{1}{2})$, and $Z=(0, 0, \frac{1}{2})$. The zero of energy is at the Fermi level.

sion, from which we conclude that the interaction between the molecules is weak. In fact, there is only appreciable dispersion of the bands along the crystallographic b direction, as can clearly be seen from the Γ - Y cut through the Brillouin zone in Fig. 3. Thus, from an electronic point of view, solid β -CuPc is quasi-one-dimensional along the shortest unit cell vector b , in accordance with the measured exciton dispersion in this compound.⁴¹

The width of the highest valence band derived from the molecular e_g states (see below) is ~ 0.3 eV. Such small bandwidths are typical of molecular crystals,²⁷ comprised of relatively weakly interacting molecules. They are consistent with the results of a previous calculation on CuPc crystals.⁴⁰ In a recent calculation on CuPc stacks, bandwidths have been found that are almost an order of magnitude larger.⁴² Note, however, that in Ref. 42 a rather artificial structure has been used with an extremely strong intermolecular bonding.

In Fig. 3, one observes that there is a very flat band at the Fermi level, derived from the localized Cu b_{1g} states. The first band above the Fermi level is derived from the corresponding empty Cu states; the bands just above 1 eV result from the empty e_g states. It is interesting to see that in the band structure, these e_g states, which are doubly degenerate in the molecule, split up into two nondegenerate bands.⁴⁴ This lifting of the molecular degeneracy is due to the crystal fields causing a distortion of the molecule that lowers its fourfold rotation symmetry to a twofold rotation symmetry. In the β structure, the distances between the central Cu ion and its four neighboring N atoms are therefore not the same. There are two shorter Cu-N bonds with $d_1=1.933$ Å and two longer bonds with $d_2=1.946$ Å. Around the Cu ion, the short and long bonds alternate. This is in contrast with the α structure to be discussed below, where the molecular symmetry is preserved and all Cu-N bond distances are the same, $d_1=d_2=1.930$ Å.

The band structure of Fig. 3 corresponds to the energy levels of the CuPc molecule shown in Fig. 1. However, as discussed above, in the molecule the first electron addition and removal states are *not* the Cu b_{1g} states, but the Pc derived e_g and a_{1u} states, respectively (see Table I). It is very unlikely that in the solid this order is altered very much. SGGA calculations on doped CuPc correctly describe that the e_g states (and not b_{1g} state) are filled if electrons are added. However, the SGGA band structure of the undoped CuPc does not reflect the correct order of these states. This can be remedied by explicitly taking the on-site Coulomb interactions between the localized Cu d electrons into account.

B. Single molecule CuPc calculations

A straightforward way to include the intra-atomic Coulomb interactions of Cu d^9 is to use the SGGA+ U scheme,^{28,29} including a parameter U_{Cu} for the electrons in the b_{1g} orbital. We obtained this parameter as described in Sec. II using the relaxed CuPc molecule and CuPc⁻ ion in $(a_{1u})^2(b_{1g})^1(2e_g)^0$ and $(a_{1u})^2(b_{1g})^2(2e_g)^0$ configurations, respectively. We find $U_{Cu}=4.89$ eV, a value that is typical for Cu d^9 . It is also possible to calculate the Coulomb interaction

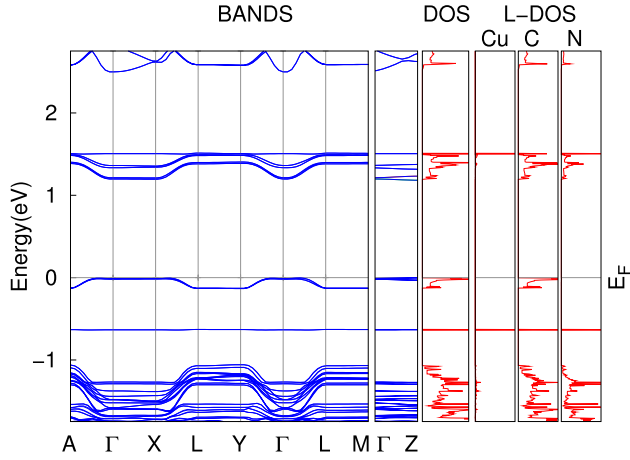


FIG. 4. (Color online) Pristine β -CuPc: band structure, density of states, and projected density of states, calculated with SGGA+ U . The points in the Brillouin zone are the same as in Fig. 3.

$U_{\text{Pc}}^{\text{bare}}$ between electrons in the e_g states of the Pc ring using the CuPc ionic configurations given in Table I. From this, we find $U_{\text{Pc}}^{\text{bare}} = 3.0$ eV.

Note that these single molecule calculations include screening of the Coulomb interaction U_{Cu} by the electrons on the Pc ring of the molecule. As mentioned above, in a crystal, there will be additional screening of the Coulomb interaction by the more distant surrounding molecules, which effectively reduces the value of $U_{\text{Pc}}^{\text{bare}}$.^{27,35,36} We calculate a screening energy of 1.7 ± 0.1 eV, so that the effective Coulomb interaction becomes $U_{\text{Pc}} = 1.3 \pm 0.1$ eV.

From differences between the total energies of the CuPc molecule and the ions in the configurations listed in Table I, one can also determine the molecular energy gap $\Delta_{\text{CuPc}}^{\text{mol}} = I_{\text{CuPc}} - A_{\text{CuPc}}$, where I and A are the molecular ionization potential and electron affinity, respectively. We find $\Delta_{\text{CuPc}}^{\text{mol}} = 4.3$ eV, which is close to values found previously.^{30,31} Molecular charges in a crystal are screened by polarization of the environment. Using the calculated polarization energy of 1.7 ± 0.1 eV, we find a band gap (i.e., a charge transport gap) $\Delta_{\text{CuPc}}^{\text{solid}} \approx 2.6$ for the crystal, which is in fair agreement with the value given in Ref. 45.

C. Pristine β -CuPc: Spin-polarized generalized gradient approximation plus U

The SGGA+ U band structure calculated with $U_{\text{Cu}} = 4.89$ eV is shown in Fig. 4. The antiferromagnetic ordered state is 0.57 eV/molecule lower in energy than the spin unpolarized state. As before, the energy difference with the ferromagnetic state is insignificant, i.e., smaller than 1 meV. Comparison to Fig. 3 shows that the inclusion of U_{Cu} causes the flat b_{1g} -derived Cu band below the Fermi level to shift downward in energy, and the empty b_{1g} to shift upward. Both the HOMO and LUMO derived bands in Fig. 4 are of Pc character. The LUMO derived valence bands are now precisely the bands that electrons are expected to end up in if we consider the electron doped system.

From the calculations, we find a valence band width of β -CuPc of 0.32 eV and a band gap of $\Delta_{\text{CuPc}}^{\text{band}} = 1.2$ eV. Since

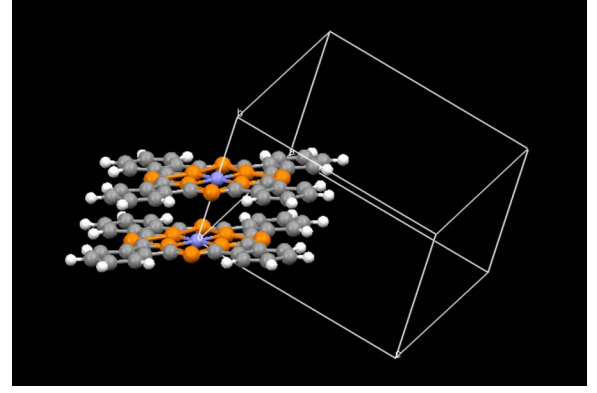


FIG. 5. (Color online) Schematic representation of the α -crystal structure of pristine CuPc. The unit cell is triclinic with $P\bar{1}$ space-group symmetry and contains two CuPc molecules: one in the origin of the cell and a second molecule at $(0, b/2, 0)$ (Ref. 43). The unit cell parameters are $a = 12.886$ Å, $b = 7.538$ Å, $c = 12.061$ Å, and $\alpha = 96.22^\circ$, $\beta = 90.62^\circ$, $\gamma = 90.32^\circ$.

we have only accounted for the on-site Coulomb interaction between Cu electrons by U_{Cu} , the band gap is basically a DFT gap, which does not represent the charge transport gap. For the present system, we can still estimate the latter, however, by taking into account the intramolecular Coulomb interaction U_{Pc} between electrons on the Pc ring. We then estimate a charge transport gap $\Delta_{\text{CuPc}}^{\text{solid}} \approx \Delta_{\text{CuPc}}^{\text{band}} + U_{\text{Pc}} = 2.5 \pm 0.1$ eV. This value compares well with the estimate of 2.6 eV based on molecular calculations, discussed in the previous section. So, within the error bars, the two estimates of the gap agree. They are also consistent with the reported experimental values from photoemission spectroscopy [2.3 ± 0.4 eV (Ref. 45)] from transport properties [2.1 ± 0.1 eV (Ref. 8)] and the lower bound on the gap of 2.1 eV (Ref. 8) determined by electron energy loss spectroscopy.

D. Pristine α -CuPc: Spin-polarized generalized gradient approximation plus U

To study the effect of the crystal structure on the electronic structure, we have also performed calculations on α -CuPc using SGGA+ U . The crystal structure of pristine α -CuPc (Ref. 43) is shown in Fig. 5. We use a unit cell that is doubled along the b direction in order to study the possibility of antiferromagnetic order. Indeed, we find the antiferromagnetic order to be stable with a magnetic moment on each molecule close to $1\mu_B$. As before, the energy difference with respect to the ferromagnetic ordering is vanishingly small, i.e., less than 1 meV. The band structure and density of states of α -CuPc are shown in Fig. 6.

From the dispersion of the bands, one easily recognizes the one-dimensional character of the electronic structure along the b direction (Γ - Y in the BZ). The bands of α -CuPc are arranged as follows. The occupied states just below the Fermi level are bands coming from the a_{1u} molecular states, which are derived from the Pc rings. At lower energy, we find flat bands resulting from the b_{1g} states of the Cu ions. Above the Fermi level, the unoccupied Pc derived e_g bands

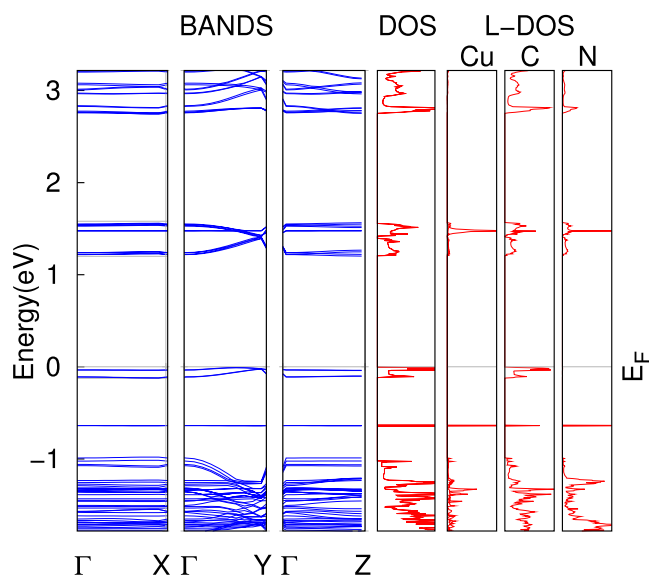


FIG. 6. (Color online) Pristine α -CuPc: band structure, density of states, and projected density of states, calculated with SGGA+ U . The points in the Brillouin zone are the same as in Fig. 3.

and the Cu derived b_{1g} bands are positioned, which are overlapping. Comparison to the band structure of β -CuPc (see Fig. 4) shows that the widths of the Pc derived bands of α -CuPc are slightly larger. In the α -CuPc structure, the molecules are more closely packed along the b direction, which increases the interaction between the molecules along this direction and increases the bandwidths.

The effect of the crystal field in α -CuPc is smaller than in the β polymorph. The CuPc molecules preserve their D_{4h} symmetry; e.g., all nearest neighbor Cu-N bond distances are 1.930 Å. This means that the unoccupied Pc derived e_g bands in α -CuPc are not split like in β -CuPc, but remain (nearly) degenerate (compare Figs. 4 and 6). The valence band width of α -CuPc is calculated to be 0.38 eV and the SGGA+ U band gap is 1.2 eV. When the electron correlations of the Pc ring are taken into account, as we did for β -CuPc, the charge transport gap becomes 2.5 ± 0.1 eV, which is the same value we found for β -CuPc.

The total energy of α -CuPc is 184 meV/unit cell higher than that of β -CuPc, which confirms the experimental observation that β -CuPc is the more stable structure.

IV. INTERCALATED CU PHTHALOCYANINE

Potassium intercalated CuPc has a monoclinic unit cell containing two CuPc molecules.³ The structure is quite different from that of pristine CuPc because it has one molecule at the corner and the other one in the *center* of the unit cell, i.e., at $(a/2, b/2, c/2)$ (see Fig. 7).⁵ In the experimental structure of $K_{2.75}$ CuPc, two inequivalent positions of the potassium ions are present, which are both partially occupied. In our calculations, we occupy only one of the two inequivalent K positions, so that we have 4 potassium ions/unit cell, i.e., we start by analyzing K_2 CuPc before looking at the electronic properties of $K_{2.75}$ CuPc. There are two reasons for doing that. First, when investigating the electronic structure

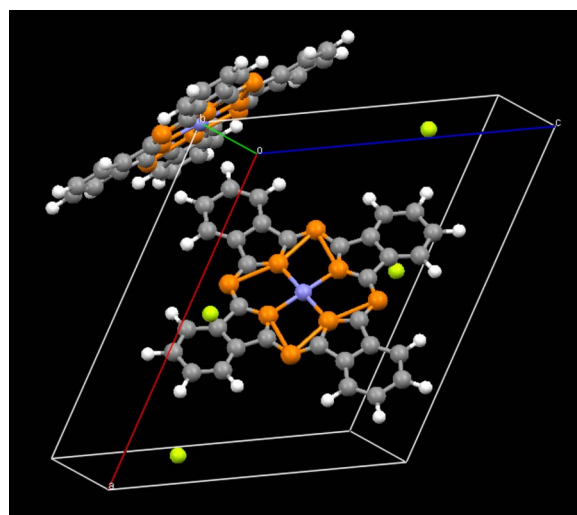


FIG. 7. (Color online) Schematic representation of the crystal structure of K_2 CuPc. The unit cell is monoclinic with $P2_1/n$ space-group symmetry and contains two CuPc molecules: one in the origin of the cell and a second molecule in the *center* of the unit cell $(a/2, b/2, c/2)$ (Ref. 3 and 5). The unit cell parameters are $a=16.2534$ Å, $b=6.1297$ Å, $c=14.4579$ Å, and $\beta=115.32^\circ$.

of our material, we want to separate its intrinsic electronic properties from the ones induced by disorder on the K sites. Second, the present unit cell is already very large (118 atoms) and the additional inclusion of disorder (by using a supercell or a coherent potential approximation) is numerically too demanding. We will see, moreover, that the band structure of K_2 CuPc forms the proper starting point to understand the electronic structure of the higher doped compound.

A. Electronic structure of K_2 CuPc

We minimize the total energy of K_2 CuPc by allowing the positions of the potassium atoms to relax. We observe that the K ions move to positions in the unit cell that are directly above the center of a phenyl ring of the phthalocyanine molecules. The K ions per CuPc are positioned at a distance of 3.0 Å from the molecular plane and are approximately connected by inversion symmetry through the center of the CuPc molecule.

The SGGA+ U band structure of antiferromagnetic K_2 CuPc and the corresponding density of states are shown in Fig. 8. As before, for the intercalated compound, the difference in energy between the antiferromagnetic and ferromagnetic couplings of Cu ions is too small to determine the exact magnetic ground state. We observe that the valence and conduction bands do not have any K character and thus conclude that each potassium atom donates a full electron to the CuPc rings, so that CuPc $CuPc^{2-}$ is formed. Other than this, K's do not play a role for the electronic properties of K_2 CuPc. This observation implies that for a qualitative understanding of the electronic structure of potassium doped CuPc, the electronic structure of CuPc is a reasonable starting point.

With this in mind, we now focus in Fig. 8 on the five bands around the Fermi level: the two that make up the valence band below it and the three of the conduction band

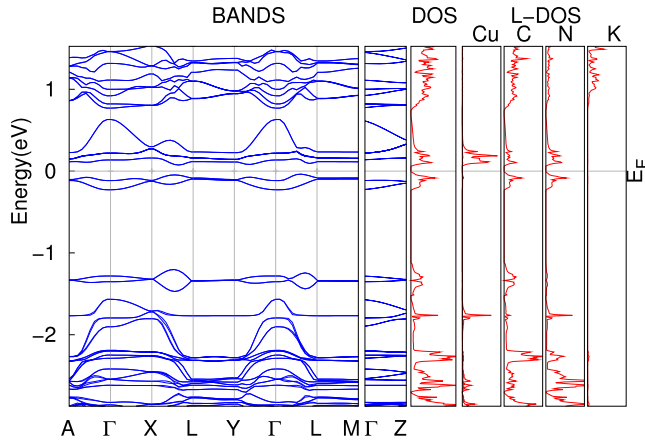


FIG. 8. (Color online) $(\text{K}_2\text{CuPc})_2$: band structure, density of states, and projected density of states, calculated with SGGA+ U . The points in the Brillouin zone are the same as in Fig. 3.

above. Compared to pristine CuPc the valence band has taken up two additional electrons per molecule. This valence band is entirely derived from molecular e_g orbitals, i.e., states that are localized on the Pc ring. The e_g orbitals of a neutral CuPc molecule can absorb up to four electrons because these states are twofold degenerate (and assuming spin degeneracy). So in K_2CuPc each CuPc molecule has two electrons in the e_g orbital. Since there are two CuPc molecules per unit cell, the e_g derived bands are doubled. Two of them are filled and form the valence bands just below the Fermi level, the empty states form two out of the three conduction bands. The third conduction band is derived from the empty molecular b_{1g} states—copper states with very little dispersion. We observe that this b_{1g} Cu band and the Pc-derived e_g conduction band cross but that there is very little hybridization between them.

From Fig. 8, we see that the valence and conduction bands, which are derived from the molecular e_g states, are separated by a small gap of 52 meV due to a splitting of the e_g bands. The splitting is related to the fact that a doubly charged CuPc molecule in the low-spin state is Jahn-Teller active. The molecular Jahn-Teller distortion lifts the degeneracy of the e_g states and causes an energy gain. The Jahn-Teller energy gain of low-spin state of CuPc apparently overcomes the opposing Hund's rule exchange energy that favors a high-spin state (but does not allow for a Jahn-Teller distortion). In the free molecule, the Jahn-Teller distortion is expected to be dynamical, but in K_2CuPc , the distortion freezes and becomes static due to the ionic and covalent molecular crystal fields from the surrounding ions and molecules. Between the central Cu ion and its four neighboring N atoms, there are two shorter bonds with $d_1=1.980$ Å and two longer ones with $d_2=2.003$ Å. Around the Cu ion, the short and long bonds alternate.

The 52 meV band splitting between the Pc-derived valence and conduction bands is expected to be only a fraction of the factual charge gap of K_2CuPc . If we take the Coulomb interactions between electrons on the Pc ring ($U_{\text{Pc}}=1.3$ eV) into account as for the pristine system, we estimate a charge transport gap of $\Delta_{\text{K}_2\text{CuPc}}^{\text{solid}}=1.4 \pm 0.1$ eV.

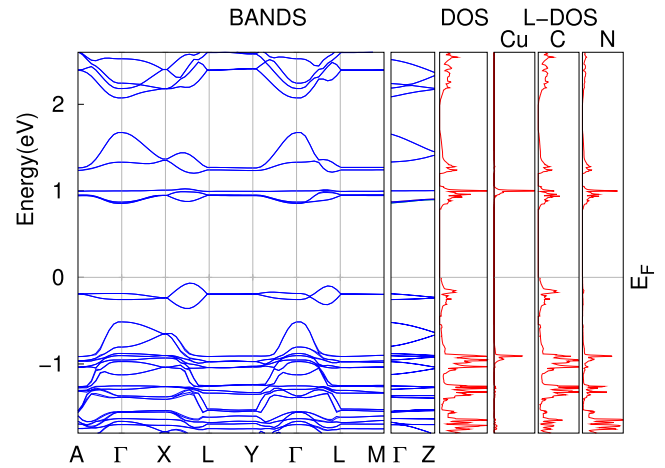


FIG. 9. (Color online) $(\text{K}_0\text{CuPc})_2$: band structure, density of states, and projected density of states, calculated with SGGA+ U . The points in the Brillouin zone are the same as in Fig. 3.

B. Comparison to K_0CuPc

In order to check the robustness of our result on K_2CuPc , we have performed the same calculations and analysis for an identical crystal structure, but with all the potassium atoms (including their electrons) removed. We refer to this as the K_0CuPc structure. In this case, we find a very similar band structure to the one of K_2CuPc , only with the Fermi level shifted (see Fig. 9). Apart from this shift, the only appreciable change in the band structure is that doping induces a small shift of 188 meV of the almost dispersionless Cu b_{1g} band to higher energy. We thus conclude that potassium intercalation basically gives rise to a simple band filling of the CuPc-related electronic states.

We notice from a comparison between K_0CuPc (or pristine CuPc) and K_2CuPc that the e_g bands are filled upon doping, and that the b_{1g} bands are just shifted upward in energy. This corresponds to the filling of levels for the isolated molecule (see Table I). For an isolated triply CuPc charged molecule, it costs almost 0.45 eV to put an electron in its b_{1g} state instead of e_g state.³¹ The behavior is important when considering further intercalation, as in $\text{K}_{2.75}\text{CuPc}$. This compound has compared to K_2CuPc an extra of 0.75 electrons/CuPc molecule. We can assume that these electrons start to fill the e_g Pc-derived conduction band in Fig. 8, and that the Cu-derived b_{1g} band stays empty. On the basis of rigid band filling, we then find that the extra 0.75 electrons shift up the Fermi level by 188 meV. The electronic transport properties of $(\text{K}_{2.75}\text{CuPc})_2$ are then fully determined by its Pc-derived e_g bands.

V. CONCLUSIONS

We find that pristine CuPc is a magnetic insulator with strong electronic correlations, a charge gap of 2.5 ± 0.1 eV and a Pc-derived valence band with a width of 0.38/0.32 eV for the α/β structure. K_2CuPc is also a magnetic insulator, with a gap of 1.4 ± 0.1 eV that is almost completely due to intramolecular Coulomb interactions. An important result is the bandwidth of the conduction band of K_2CuPc : 0.56 eV,

which is large for a molecular solid. As, due to the rigid band behavior, in $K_{2.75}CuPc$ the additional 0.75 electron/CuPc molecule fill the e_g Pc-derived conduction band, this wide and partially filled band entirely determines the electronic transport properties of the compound. Thus, on the basis of the band structure calculations, one expects that this material is metallic. In general, however, polaronic effects and disorder, not included in our analysis, are substantial in molecular crystals. These tend to localize charge carriers, especially in the low doping regime. However, in $K_{2.75}CuPc$, the large amount of doped charge carriers enables an effective screening of disorder, and the unusually large bandwidth makes polaron formation less likely, so that delocalization of the carriers is strongly promoted.

ACKNOWLEDGMENTS

We thank Monica Craciun, Serena Margadonna, and Alberto Morpurgo for stimulating discussions. We thank Meng-Sheng Liao for fruitful discussions on the technical aspects of the molecular computations. This work was financially supported by “NanoNed,” a nanotechnology program of the Dutch Ministry of Economic Affairs, by the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)” and by the “Stichting voor Fundamenteel Onderzoek der Materie (FOM).” Our calculations were performed with a grant of computer time from the “Stichting Nationale Computerfaciliteiten (NCF).” This paper was supported in part by the National Science Foundation under Grant No. PHY05-51164.

-
- ¹T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors*, 2nd ed. (Springer, Berlin, 1998).
- ²L. Forro and L. Mihaly, *Rep. Prog. Phys.* **64**, 649 (2001).
- ³M. F. Craciun, S. Rogge, M. J. L. den Boer, S. Margadonna, K. Prassides, Y. Iwasa, and A. F. Morpurgo, *Adv. Mater. (Weinheim, Ger.)* **18**, 320 (2006); M. F. Craciun, S. Rogge, D. A. Wismeijer, M. J. L. den Boer, T. M. Klapwijk, and A. F. Morpurgo, *AIP Conf. Proc. No. 696* (AIP, Melville, NY, 2003), p. 489.
- ⁴M. F. Craciun *et al.*, *J. Am. Chem. Soc.* **127**, 12210 (2005).
- ⁵M. F. Craciun, Ph.D. thesis, Delft University of Technology, 2006.
- ⁶For a review, see, for example, *Colossal Magnetoresistive Manganites*, edited by T. Chatterji (Kluwer Academic, Dordrecht, 2004) and references therein; J. van den Brink, *New J. Phys.* **6**, 201 (2004).
- ⁷E. Tosatti, M. Fabrizio, J. Tobik, and G. E. Santoro, *Phys. Rev. Lett.* **93**, 117002 (2004).
- ⁸J. van den Brink and A. F. Morpurgo, *Nature (London)* **450**, 177 (2007).
- ⁹S. Heutz *et al.*, *Adv. Mater. (Weinheim, Ger.)* **19**, 3618 (2007).
- ¹⁰T. Schwieger, H. Peisert, M. S. Golden, M. Knupfer, and J. Fink, *Phys. Rev. B* **66**, 155207 (2002).
- ¹¹T. Schwieger, M. Knupfer, W. Gao, and A. Kahn, *Appl. Phys. Lett.* **83**, 500 (2003).
- ¹²O. V. Molodtsova, V. M. Zhilin, D. V. Vyalikh, V. Y. Aristov, and M. Knupfer, *J. Appl. Phys.* **98**, 093702 (2005).
- ¹³K. Flatz, M. Grobosch, and M. Knupfer, *J. Chem. Phys.* **126**, 214702 (2007).
- ¹⁴Y. L. Gao and L. Yan, *Chem. Phys. Lett.* **380**, 451 (2003).
- ¹⁵M. F. Craciun, S. Rogge, and A. F. Morpurgo, *J. Am. Chem. Soc.* **127**, 12210 (2005).
- ¹⁶Y. Taguchi *et al.*, *J. Am. Chem. Soc.* **128**, 3313 (2006).
- ¹⁷L. Giovanelli, P. Vilmercati, C. Castellarin-Cudia, J. M. Themlin, L. Porte, and A. Goldoni, *J. Chem. Phys.* **126**, 044709 (2007).
- ¹⁸P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ¹⁹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ²⁰G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); *Comput. Mater. Sci.* **6**, 15 (1996).
- ²¹J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ²²P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ²³G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ²⁴A. Rohrbach, J. Hafner, and G. Kresse, *Phys. Rev. B* **69**, 075413 (2004).
- ²⁵P. E. Blöchl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
- ²⁶A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B* **52**, R5467 (1995).
- ²⁷G. Brocks, J. van den Brink, and A. F. Morpurgo, *Phys. Rev. Lett.* **93**, 146405 (2004); J. van den Brink, G. Brocks, and A. F. Morpurgo, *J. Magn. Magn. Mater.* **290**, 294 (2005); J. van den Brink and G. A. Sawatzky, *Europhys. Lett.* **50**, 447 (2000).
- ²⁸V. I. Anisimov and O. Gunnarsson, *Phys. Rev. B* **43**, 7570 (1991).
- ²⁹O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, *Phys. Rev. B* **39**, 1708 (1989).
- ³⁰A. Rosa and E. J. Baerends, *Inorg. Chem.* **33**, 584 (1994).
- ³¹M.-S. Liao and S. Scheiner, *J. Chem. Phys.* **114**, 9780 (2001).
- ³²M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1983).
- ³³A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ³⁴C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ³⁵J. van den Brink, M. B. J. Meinders, J. Lorenzana, R. Eder, and G. A. Sawatzky, *Phys. Rev. Lett.* **75**, 4658 (1995); R. Eder, J. van den Brink, and G. A. Sawatzky, *Phys. Rev. B* **54**, R732 (1996).
- ³⁶M. B. J. Meinders, J. van den Brink, J. Lorenzana, and G. A. Sawatzky, *Phys. Rev. B* **52**, 2484 (1995); J. van den Brink, R. Eder, and G. A. Sawatzky, *Europhys. Lett.* **37**, 471 (1997).
- ³⁷D. M. Chipman, *J. Chem. Phys.* **112**, 5558 (2000).
- ³⁸G. Brocks, *J. Chem. Phys.* **112**, 5353 (2000).
- ³⁹C. J. Brown, *J. Chem. Soc. A* **1968**, 2488.
- ⁴⁰L. Lozzi, S. Santucci, S. La Rosa, B. Delley, and S. Picozzi, *J. Chem. Phys.* **121**, 1883 (2004).

- ⁴¹M. Knupfer, T. Schwieger, H. Peisert, and J. Fink, *Phys. Rev. B* **69**, 165210 (2004).
- ⁴²N. Shi and R. Ramprasad, *Phys. Rev. B* **75**, 155429 (2007).
- ⁴³A. Hoshino, Y. Takenaka, and H. Miyaji, *Acta Crystallogr., Sect. B: Struct. Sci.* **59**, 393 (2003).

- ⁴⁴Actually, one observes two pairs of bands. The smallest splitting is caused by the fact that the unit cell contains two CuPc molecules.
- ⁴⁵I. G. Hill, A. Kahn, Z. G. Soos, and R. A. Pascal, *Chem. Phys. Lett.* **327**, 181 (2000).