

OXYGEN ADSORPTION INDUCED DEMAGNETISATION OF COPPER PHTHALOCYANINE MONOLAYER: A FIRST PRINCIPLES STUDY

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Semiconducting transition metal phthalocyanines (MPcs) are widely used in industry for their interesting physico-chemical properties [1]. It was shown that conductivity of MPcs is influenced by gas adsorption. It is still important to know what changes in the electronic structure of the materials are induced by adsorption of ambient gases on their surfaces. One of the macrocycle compound often applied in various fields of industry is copper phthalocyanine (CuPc). Recently, we have done much effort to reveal the electronic structure and magnetic properties of some transition MPcs model monolayers [2] with the use of full-potential linearized augmented plane-wave (FLAPW) method [3]. The method was for the first time used to investigate such an organic system as CuPc. We found that the central Cu atom of the molecule consisted the monolayer has a considerable magnetic moment (MM) of 0.56 μ_B , the nearest nitrogen atoms of the inner ring are weakly polarized, while the other atoms of the molecule have negligible MM. We confirmed that conduction properties of CuPc thin films are strongly associated with the electron states within the Cu d and ligand orbitals.

Here, we present the preliminary results derived from first principles study of the electronic structure of the CuPc monolayer affected by oxygen adsorption. The geometry of the system was chosen in such a way that an O_2 was put perpendicularly to the CuPc plane just above the Cu atom. For symmetry reasons we attached the O_2 on both sides of CuPc (Fig. 1). The distance between Cu atom and the nearer O atom was set to 2.0 \AA , accordingly to quantum chemical calculation results on O_2 interaction with CuPc molecule [4], and the O_2 bond length was set to 1.21 \AA .

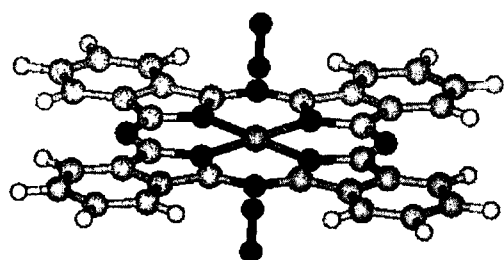


Fig. 1. Schematic view of a unit cell of the investigated monolayer.

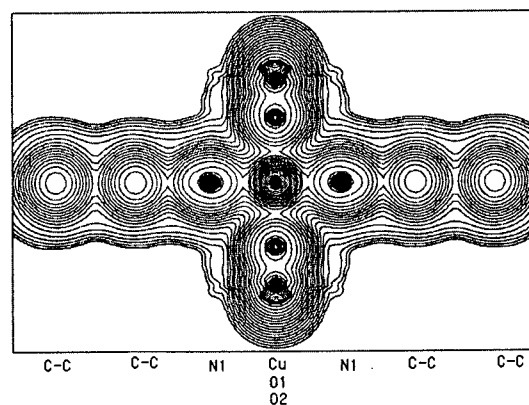


Fig. 2. Charge density within CuPc- O_2 monolayer unit cell drawn in the plane vertical to CuPc led along Cu-N1 bonds.

The spin-polarized calculations were performed within generalized-gradient approximation (GGA) with the PW92 exchange-correlation potential. We have found that O₂ adsorption causes that density of states coming from majority- and minority-spin electrons are nearly symmetrical in the whole energy range. This demonstrates that Cu atom loses its magnetic character under the influence of oxygen. Its magnetic moment changes from 0.56_B (in bare monolayer) to 0.03_B in oxygen-covered layer. The origin of this phenomenon may be the charge transfer between O₂ and CuPc molecule, which can be analyzed on the base of charge distribution shown in Fig. 2. and the data collected in Table 1.

Table 1. l-like charges within Cu and O atoms muffin tin for O₂-covered CuPc monolayer (for comparison we present the charges of Cu in bare monolayer in parentheses).

atom	spin-up	spin-down
	s; p; d; total	s; p; d; total
Cu	0.21; 0.24; 4.73; 5.24 (0.22; 0.26; 4.86; 5.39)	0.21; 0.24; 4.70; 5.20 (0.23; 0.26; 4.30; 4.84)
O1	0.48; 0.38; 0.00; 0.86	0.48; 0.38; 0.00; 0.86
O2	0.41; 0.84; 0.17; 1.44	0.41; 0.84; 0.17; 1.44

As it is seen, the central Cu atom of the system loses majority d electrons that most likely are transferred to the CuPc ring. At the same time O₂ donates electrons to CuPc, first of all through Cu central atom filling its d states, and also directly to the system of π -electrons of the CuPc inner ring (Fig. 2). Such a gain of electrons from adsorbed molecule is known as back-donation.

The finding that there is a direct transfer of charge between adsorbed oxygen and CuPc ring through the inner-ring carbon atoms and nitrogen atoms linking the four Pc units may have substantial meaning for explanation of charge transport and conductivity mechanism of CuPc thin films used in organic electronics.

References

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