Ferrimagnetism in 2D networks of porphyrin-X and -XO (X=Sc,...,Zn) with acetylene bridges.

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(Dated: February 23, 2015)

Magnetism in 2D networks of the acetylene-bridged porphyrins doped with transition metals (TM) and co-doped with oxygen is studied with the density functional theory (DFT) and the self-interaction corrected pseudopotential scheme (pSIC). The oxygen co-doping lowers magnetism for most of the first-half 3d-row TMs. In contrast, binding O with the second-half 3d-row TMs or Sc increases the magnetic moments. Ferrimagnetism is found for the porphyrin networks doped with the TMs from V to Co and also for co-doping them with O. This is a long-range effect, extended even to the acetylene bridges. Moreover, the analysis with the maximally-localized Wannier functions (MLWF) reveals the existence of the anisotropic local moments.

PACS numbers: 68.35.bm, 68.35.Dv, 68.65.Cd, 75.10.Lp, 75.25.Dk

I. INTRODUCTION

Porphyrins are popular molecules in living organisms. Their ability to bind the transition metals is utilized in biological processes significant for the human-blood functions - employing Fe in heme - and is responsible for the photosynthesis in plants - building a complex with Mg, namely chlorofl1. The oxygen doped metal-porphyrins, such as oxotitanium porphyrin, can be used for solar-activated water splitting - what has been proposed theoretically to occur due to low-lying ligand-to-metal intramolecular charge-transfer states2 and recently experimentally confirmed3.

Porphyrins or phthalocyanines can be assembled at metals4,5 and other surfaces6 forming 2D networks7. In turn, the surfaces or additional ligands change the charge state of the transition metal bound to porphyrins with respect to the bare 2D network. This is because different valence states of a metal, metal-oxygen moiety, or metal-Li complex lay closely in the energy8–11. Not only the single layers of the metal-organic networks exist, also the double- and triple-decker layers of metal-phthalocyanines have been grown, on both the ferro- and antiferromagnetic substrates12.

For catalytic reactions with the intramolecular charge transfer, such as the water splitting, the intermolecular connections must be very weakly conducting (non-covalent); for example the hydrogen bridges (O-H...O). For the spintronic applications, on the other hand, these connections should be conducting. Various choices of the intermolecular-bridging type were examined experimentally for the energy transfer rates13,14, and a role of the frontier molecular-orbitals was theoretically studied for the donor-acceptor dimers15.

A new branch of material science grows on potential utilization, in electronic devices, of the 2D organic layers16 and magnetic nanoparticles deposited on various substrates17. Selective incorporation of metal atoms into organic templates enables wide functionalization of the layers18, hence many applications are plausible. The 4-fold symmetry of porphyrins and phthalocyanines doped with the transition metals makes their networks similar to the Heusler compounds, which are very strong magnets19. There are review articles on the spintronic topics in 2D networks20,21. The photovoltaic thin films based on metal-phthalocyanine 2D networks, and organized in the AA-stacking order, conduct in columnar direction22. similar effect should be observed in metal-porphyrins. For the technological reasons, the conductive properties of single porphyrin molecules doped with a metal23 and 1D metal-porphyrin chains24 were also investigated. Recently, high-mobility field-effect transistors have been constructed building the ABAB-type stacking of the phthalocyanine-VO and -TiO layers25.

In this work, we focus on 2D networks of porphyrins doped with all 3d-row transition metals and TM-O, bridged with the acetylene moiety. The model structure of our systems is presented in Fig. 1. We want to obtain a material with strong and long-range magnetic-exchange interactions, thus the covalent intermolecular connection was chosen. It has been found that the covalent inorganic materials, as hosts for the magnetic impurities, are strongly coupled magnetically for long distances26,27.

FIG. 1. 2D network of porphyrin-MnO with acetylene bridges.

Interestingly, another molecular system - similar to
that studied in this work, but assembled at Cu and doped with Fe - was demonstrated to switch the easy magnetization-direction after oxygen co-doping.\textsuperscript{23} We report the ferimagnetism, similar to as it was theoretically predicted by other authors in porphyrins doped with Mn and connected by 4-bromophenyl to form 1D magnetic chains.\textsuperscript{20} This effect can be mapped on the atomic scale by the measurement of magnetic resonance spectra at gigahertz frequencies using x-ray magnetic circular dichroism (XMCD).\textsuperscript{34}

II. THEORETICAL DETAILS

We performed the density-functional theory (DFT) calculations using the QUANTUM ESPRESSO (QE) suit of codes\textsuperscript{31} which employs the plane-wave basis set and the pseudopotentials to describe the core electrons. The exchange-correlation functional was chosen for the gradient corrected Perdew-Burke-Ernzenhoff (PBE) parametrization.\textsuperscript{32} The ultrasoft pseudopotentials were used with the energy cutoffs 35 Ry and 400 Ry for the plane-waves and the density, respectively. The Monkhorst-Pack uniform k-mesh in the Brillouin zone (BZ) has been set to \(10 \times 10 \times 1\), and the Fermi-surface energy broadening parameter 0.02 Ry was chosen for a better convergence. The vacuum separation between the periodic slabs was 40 Å. The pseudopotentials for the atoms from Sc to Co were modeled with the semicore states (3s and 3p) included in the valence band, in contrast, the Cu and Zn valence shells were constructed without the deeper states.

We started with the geometry optimization of a single molecule - namely Ti doped porphyrin - using the B3LYP method which is equivalent to the DFT scheme of the BLYP-type with 20\% of the exact exchange (EXX).\textsuperscript{33–35} This step was done with the quantum chemistry package TURBOMOLE,\textsuperscript{37} which represents the wavefunctions in the gaussian basis set (the XX type was used). Obtained geometry and the lattice vectors, derived from the molecular size, were inserted as an input for the geometry optimization of the periodic structures, calculated by means of the generalized gradient approximation (GGA) scheme (with the PBE parametrization) using the QE tool. The above procedure is accurate enough, since the central ‘squares’ of porphyrin and phthalocyanine derivatives do not relax much after binding a metal.\textsuperscript{38}

It is known, that the DFT approach underestimates the energy gaps and the energetic positions under the Fermi level of the localized d- or f-shells. This fact has consequences in the description of magnetization. In order to improve a treatment with the lack of the exact exchange, we applied the pseudopotential self-interaction correction (pSIC) method proposed by Filippetti and Spaldin,\textsuperscript{38,39} and implemented by us in the QE package.\textsuperscript{40} The pSIC method is superior to the DFT+U approach\textsuperscript{40} for two reasons: (i) the correction is parameter free, unlike the DFT+U parameters: the Coulomb U and the exchange J, (ii) the correction is applied to all atomic shells, not only d- or f-shell of the transition metals or the rare earths. The pSIC-kernel includes the Hartree and the exchange-correlation potentials, \(V_{\text{HXC}}\), calculated on the orbital-density dependent on spin \(\sigma\), \(n_\sigma^r(r)\), and built using the atomic pseudopotential orbital, \(\varphi_i(r)\). The main equations are:

\[
V_{\text{SIC}}^\sigma = \sum_i \frac{|\varphi_i(r)\rangle\langle V_{\text{HXC}}^\sigma[n_\sigma^r(r)]|\varphi_i(r)\rangle}{\langle \varphi_i(r)\rangle V_{\text{HXC}}^\sigma[n_\sigma^r(r)]|\varphi_i(r)\rangle} \\
n_\sigma^r(r) = p_\sigma^r |\varphi_i(r)|^2 \\
p_\sigma^i = \sum_{nk} f_{nk}^\sigma \langle \psi_{nk}^\sigma | \varphi_i \rangle \langle \varphi_i | \psi_{nk}^\sigma \rangle
\]

The occupation numbers \(p_\sigma^r\) are obtained from the projection of the Kohn-Sham states \(\psi_{nk}^\sigma\) onto the pseudopotential atomic-orbitals \(\varphi_i(r)\) and \(f_{nk}^\sigma\) are the Fermi-Dirac occupations. Usefulness of this method has been demonstrated in a number of various applications.\textsuperscript{41–43} For this work, the most important are the relations between the energetic positions of the shells: 3d-3TM, 4s-4TM, 4p-O and 4p-N. Although, we included the SIC for all atomic shells, these corrections are ‘on-site’ - the same like in the DFT+U approach and contrary to the Nagaoaka model, which includes the ‘inter-site’ strong correlations on the parametric grounds.\textsuperscript{44,45}

We complete the description of our results with the Wannier-functions symmetry analysis. Characterization of the chemical bonds and their spin-polarization is performed with the maximally-localized Wannier functions (MLWF) obtained with the wannier90 code.\textsuperscript{46} The MLWFs were applied by many authors to a variety of physical and chemical problems.\textsuperscript{46,47} The Bloch functions used in the input to the wannier90 code do not need to be calculated on a very dense BZ mesh - in the following, we chose the \(5 \times 5 \times 1\) division. Other details of the Wannier calculations are described in the results section, where the MLWFs are applied.

III. RESULTS AND DISCUSSION

In this study, we focus our attention on magnetism, which is a phenomenon sensitive to the system geometry. As mentioned in the theoretical details section, the geometry was optimized for all studied cases. Positions of transition metal atoms above the plane of the nitrogen square and the oxygen-TM bond lengths are collected in the Table in the supporting information. Inspecting the atomic gradients varied during the geometry optimization and the corresponding magnetizations of the systems, we noticed that a tiny change of the TM-positions or the TM-O bond-lengths can influence magnetizations. This effect is similar to the phenomenon observed in the perovskites\textsuperscript{48} and also for metal atoms at graphene and graphite.\textsuperscript{50} In our cases, however, the geometric effect does not alter main trends in the results.
FIG. 2. Total and absolute magnetizations of doped porphyrins with acetylene bridges, obtained with the GGA and pSIC approaches, using the GGA-optimized geometry.

reported below.

A. Magnetizations

In Fig. 2, the total and absolute magnetizations in the elementary cells, obtained within the GGA and the pSIC frameworks, are presented for porphyrins with all TM and TM-O dopants. The total magnetization, defined via the up and down spin-densities, $n_\uparrow(r)$ and $n_\downarrow(r)$, as

$$M_{\text{total}} = \int n_\uparrow(r) \, dr - \int n_\downarrow(r) \, dr,$$

reflects the summed magnetization of the sample seen from a distance. In contrast, the absolute magnetization, defined as

$$M_{\text{absolute}} = \int | n_\uparrow(r) - n_\downarrow(r) | \, dr,$$

means a sum of the local magnetizations regardless their signum. Large difference between the total and the absolute magnetizations gives an information on the space separation of the altered magnetic moments, i.e. the ferrimagnetic character of the sample.

Ferrimagnetism is well pronounced in the doped cases from V to Co, and it is the strongest in the Mn, Fe and FeO cases for both calculation methods, GGA and pSIC, and additionally in the V and VO cases obtained with the pSIC scheme. The spin-density map for the Mn-doped porphyrin network is presented in Fig. 3 for the pSIC method. The vanadium spin-density map is similar and included in the supporting information. It is clear that the nitrogen atoms spin-polarize in the vicinity of TM.

The effect of oxygen co-doping on magnetization is very strong. In the case of the TM atoms from the first half of the 3d-row, the oxygen addition strongly reduces the magnetic moments; except the ScO-doped network. In contrast, for TM dopants from the second half of the 3d-row, co-doping with oxygen causes an increase of the magnetic moments. This is an interesting result - similar to the results for co-doping metal-phthalocyanines with Li\textsuperscript{11} - and might be utilized in spintronic devices.

FIG. 3. Spin-density map of the Mn-doped porphyrin, obtained with the pSIC approach.
We present the numbers obtained mainly with the pSIC scheme. C1 denotes carbons adjacent to N, C2 carbons terminated with H, C3 carbons adjacent to acetylene, and C4 carbons of acetylene. Corresponding GGA numbers are given in parenthesis.

To get further insight into the electronic structure and magnetism, it is useful to examine the Löwdin population analysis (LPA) and corresponding GGA numbers.

The pSIC method usually tends to localize the electrons and delocalize the holes. With the DFT method, the occupations of 3d-TM orbitals often increase and the sp-orbitals of TM-neighbours decrease, with respect to the DFT result. For the pSIC, the occupations of 3d-TM are usually the same as that of the coupling to sp-TM. Large spin-polarization of the sp-V orbitals overlap and couple ferromagnetically (FM) with the sp-N shells. The fact that the 4p-shell of V in porphyrins is substantially occupied can be compared to the similar effect observed in (GaAs,Mn) and Si:Mn. On the other hand, in the GGA approach, the sp-V shell couples ferromagnetically to 3d-V, since the strong SI error is not corrected for the sp-N orbitals.

For the porphyrin-VO, the sp-N is also AF-coupled with respect to 3d-V. With the difference that the strong coupling of sp-V with N-sp is replaced by the V interaction with oxygen, which is more strongly polarizable than nitrogen. The spin polarization of oxygen is around -1.6 \( \mu_B \) and antiferromagnetic with respect to 3d-V. The sp-N localized spin is -0.27 \( \mu_B \) - similar to that for porphyrin-VO. However, the largest spin polarization of the sp-N orbitals is in the case of porphyrin-Mn, around -0.47 \( \mu_B \). Interestingly, the coupling of sp-N with respect to 3d-TM is antiferromagnetic not for all studied 2D networks - the exceptions are: porphyrin-Co, -Cu, -FeO, -CoO, -NiO and -CuO. This is a consequence of the 4-fold crystal symmetry and electronic filling of the 3d-TM. Large spin polarization of the sp-O orbitals is very promising for tailoring spintronic devices. It is worth to notice that the orientation of the spin coupling at oxygen with respect to 3d-TM is usually the same as that of the coupling between sp-N and 3d-TM.

**TABLE I.** Löwdin spin-polarizations in the porphyrin networks doped with TM-O (upper part) and TM (lower part); calculated with the pSIC scheme. C1 denotes carbons adjacent to N, C2 carbons terminated with H, C3 carbons adjacent to acetylene, and C4 carbons of acetylene. Corresponding GGA numbers are given in parenthesis.

| shell | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|-------|----|----|---|----|----|----|----|----|----|----|
|       |    |    |   |    |    |    |    |    |    |    |
| O sp  | 0.720 | 0.0 | -1.570 | -0.215 | 0.043 | 1.670 | 2.265 | 1.546 | 1.636 | 1.491 |
|       | (0.577) | (0.0) | (-0.149) | (-0.062) | (0.577) | (0.728) | (1.392) | (1.403) | (1.435) | (1.389) |
| TM d  | 0.003 | 0.0 | 0.940 | 2.036 | 2.991 | 2.612 | 3.026 | 1.562 | 0.506 | 0.001 |
|       | (-0.016) | (0.0) | (1.154) | (1.684) | (2.424) | (1.128) | (1.579) | (1.749) | (0.677) | (0.025) |
| TM sp | 0.007 | 0.0 | 0.005; | 0.038 | 0.087 | 0.015 | 0.008 | -0.005 | -0.044 | -0.006 |
|       | (-0.001) | (0.0) | (0.020) | (0.021) | (0.024) | (0.006) | (0.013) | (-0.010) | (-0.043) | (-0.009) |
| N sp  | 0.000 | 0.0 | -0.270 | -0.047 | -0.036 | 0.051 | 0.057 | 0.101 | 0.158 | 0.008 |
|       | (0.004) | (0.0) | (-0.019) | (-0.032) | (-0.030) | (-0.007) | (0.003) | (0.135) | (0.164) | (0.011) |
| C1 sp | 0.000 | 0.0 | -0.120 | 0.024 | 0.006 | 0.109 | 0.117 | -0.005 | -0.007 | -0.001 |
|       | (0.000) | (0.0) | (0.002) | (0.003) | (0.004) | (0.005) | (0.006) | (0.007) | (0.008) | (0.009) |
| C2 sp | 0.000 | 0.0 | -0.057 | 0.007 | 0.001 | 0.056 | 0.047 | 0.007 | 0.007 | 0.001 |
|       | (0.000) | (0.0) | (0.001) | (0.002) | (0.003) | (0.004) | (0.005) | (0.006) | (0.007) | (0.008) |
| C3 sp | 0.003 | 0.0 | 0.052 | 0.003 | -0.005 | -0.051 | -0.057 | -0.004 | 0.007 | 0.001 |
|       | (0.001) | (0.0) | (0.003) | (0.004) | (0.005) | (0.006) | (0.007) | (0.008) | (0.009) | (0.010) |
| C4 sp | 0.001 | 0.0 | 0.006 | 0.003 | -0.001 | -0.006 | -0.003 | -0.003 | 0.001 | 0.001 |
|       | (0.000) | (0.0) | (0.002) | (0.003) | (0.004) | (0.005) | (0.006) | (0.007) | (0.008) | (0.009) |

1. 0.032(s), -0.27(p)
2. 0.006(s), -0.977(p)
3. 0.099(s), -0.334(p)
Let us have a look at carbons of the porphyrin molecules and bridges; these adjacent to nitrogens, denoted C1, and farther, denoted: C2, C3 and C4 - see the caption of Table 1. The carbon C1 bears a spin which couples AF to 3d-V (with local C1 moment of -0.12 µB) for the VO case, and FM (0.21 µB) for the porphyrin-V. The other spin polarizations at C1 - Fe (0.17 µB), Mn (0.09 µB), FeO and Co (0.11 µB), and CoO (0.12 µB) - also deserve our attention. The C2 carbon polarizes mostly in the case of porphyrin-Co (0.08 µB). Even far C3 is spin-polarized around 0.04-0.07 µB for porphyrin-Mn, -Fe, -FeO, -Co, -CoO. Remarkably, the carbon atom of the acetylenic-bridge, namely C4, couples antiferromagnetically to C1, and it is spin-polarized of about -0.1 µB in porphyrin-V.

The results presented in this subsection align with the experimental and theoretical conclusions of the work on porphyrin-Cr adsorbed at the Co surface. Namely, the local spin-moments induced at nitrogens are AF-coupled to Cr, and the spin of less than halfly-occupied 3d-shell of Cr is AF-coupled to the more than halfly-occupied 3d-shell of Co substrate - as in our case, it holds for the Cr and O localized magnetic moments.

B. Metallicity

The projected densities of states (PDOS) onto the 2p-N, 3d-TM and 2p-O states are presented in Fig. 4; for the results obtained with the pSIC approach. The spin-asymmetry of the PDOS is visible for the dopants: V, Cr, Mn, Fe, and Co without and with the oxygen co-doping. Similar figures for the 2D networks doped with the remaining atoms: Sc, Ti, Ni, Cu and Zn, obtained with the pSIC, and for all doped porphyrins calculated with the GGA, are included in the supporting information. The spin-asymmetry of the 2p-N PDOS is pronounced even for the cases where the Löwdin spin-polarizations are rather small.

Most of doped porphyrin 2D-networks are metallic. The Fermi levels of some cases - Cr, MnO, TiO, Ni, Zn - lay in a little energy gap. The half-metallicity is plausible in the cases: Ti, Cu, VO, CrO, FeO, CoO, where the more accurate GW-calculations would be necessary. It is very usual for the TM-doped metallic systems, that the Fermi level cuts the 3d-states. The effect of such methods like the DFT+U or the pSIC with respect to the GGA results moves the 3d-states away from the Fermi level, if these states are not pinned to it. In our systems, however, some cases calculated with the GGA approach show clearly the TM-based metallicity, while in the pSIC approach, the 3d states disappear from the Fermi level - e.g. for the Mn-, Fe-, VO-, MnO-, CoO- and Ni-doped porphyrins. Purely carbon-based metallicities in such magnetic systems like VO-, Mn- and FeO-doped networks seem to be promising for spintronic devices, because the magnetic couplings in these cases might be long range. Interestingly, there are also the metallic states dominated by the oxygen states, and they are almost half metallic, for instance in NiO-, CuO- and ZnO-doped porphyrins (please see figures in the supporting information).

C. MLWFs: symmetry, localization and spin-polarization

Further insight into the nature of the spin polarization can be obtained from the analysis of the maximally-localized Wannier functions. The 4-fold symmetry of porphyrins suggests a choice of the trial Wannier functions listed in Table 2. The symmetry of the porphyrins network is the origin of the spin-polarization localized at oxygen, since six valence electrons occupy four 'molecular' orbitals centred at O and oriented towards nitrogens and the p_2 orbital on the TM-O bond. Hund's rules and
TABLE II. Choice of the trial Wannier functions at atoms and bonds. The set of functions localized at the transition metal is of sp3d2 type, and given in the wannier90 users-guide.

| center       | Wannier type                                      |
|--------------|---------------------------------------------------|
| oxygen       | $p_z +$ four sp-type ($\pm x$, $\pm y$ lobes)      |
| metal        | $1/\sqrt{6}s - 1/\sqrt{2}p_x - 1/\sqrt{2}d_{x^2} + 1/2d_{x^2-y^2}$  |
|              | $1/\sqrt{6}s + 1/\sqrt{2}p_x - 1/\sqrt{2}d_{x^2} - 1/2d_{x^2-y^2}$  |
|              | $1/\sqrt{6}s - 1/2p_y - 1/\sqrt{2}d_{x^2} - 1/2d_{x^2-y^2}$  |
|              | $1/\sqrt{6}s + 1/\sqrt{2}p_y - 1/\sqrt{2}d_{x^2} - 1/2d_{x^2-y^2}$  |
|              | $1/\sqrt{6}s - 1/2p_x + 1/\sqrt{3}d_{x^2}$  |
|              | $1/\sqrt{6}s + 1/\sqrt{2}p_x + 1/\sqrt{3}d_{x^2}$  |
| nitrogen     | s-type close to N, and shifted towards the porphyrin center |
| N-C1, C1-C2  | two s-type.                                       |
| C2-C2, C1-C3 | shifted from the molecular plane                  |
| C2-H, C3-C4  | s-type                                           |
| C4-C4        | s-type + two p-type $\perp$ bond-axis            |

the relative electron affinities of O, with respect to chosen TM, govern the portions of valence electrons with the spin up and down at oxygen.

Shapes of the MLWFs obtained for the TM and TM-O doped porphyrins are similar. In Fig. 5, we plot some chosen MLWFs for porphyrin-VO: oxygen-centered (one of the 4-fold and $p_z$), TM-centered (one of the 4-fold and two z-axis oriented) and TM-N bond centred, for the both spin polarizations. Other porphyrin-centered MLWFs for the VO-doped case are printed in the supporting information. The spin-asymmetries of the MLWFs are visible for the functions centred close to the C1 atoms (e.g. C1-C3, C2-C1-C3) and C3-C4 bond. These results align with further analysis by means of the MLWFs parameters, and confirm that the spin polarization in the studied systems is long range, extending to the acetylene bridges.

The TM-centered MLWFs are very asymmetric for the ScO-doped porphyrin. The Wanniers centred at the Sc-O bond and oriented along the z-axis are printed in Fig. 6 for both spins. Diversity of shapes is well pronounced and additionally confirms the results obtained for magnetization at the oxygen atom.

MLWFs are characterized by two parameters: the spreads and the occupation numbers. Minimization of the total spread, defined as

$$\Omega_{tot} = \sum_n \Omega_n = \sum_n [(r^2)_n - \bar{r}^2_n],$$

is a criterion of the MLWFs finding procedure. The expectation values of the real-space position operator $r$ are: $\bar{r}^2_n = \langle 0n|\hat{r}|0n\rangle^2 = \langle r_n^2 \rangle^2$ and $\langle r^2 \rangle_n = \langle 0n|\hat{r}^2|0n\rangle$, and $|0n\rangle$ is the Wannier function with number $n$ and

FIG. 5. MLWFs of the porphyrin-VO network, obtained with the pSIC approach. The atomic indeces are introduced in Table. 1. Arrows indicate the spin polarization.

centred in the original cell with the direct-lattice vector $\mathbf{R} = 0$.

The occupation numbers are constructed from two unitary transformations $U_{pq}^{\text{dis}}$ and $U_{ij}$ - where the first acts in the disentangling procedure to obtain the optimal subspace of Bloch-like functions possessing proper symmetries and the second is obtained during the MLWFs optimization process - as follows

$$f_{nm}^{\text{MLWF}} = \sum_{k \in BZ} \sum_p \sum_s \sum_r U_{nm}^k U_{pr}^{\text{dis}} U_{sn}^{k*} U_{ps}^{\text{dis}} U_{rs}.$$  

'win' runs over all states in the 'outer' window (including
some unoccupied states) and 'occ' runs over states up to the Fermi level. Since the off-diagonal elements sum to zero in the whole system, we use only the diagonal occupations ($f_n = f_{nn}$) in the discussion. The numbers $f_{nn}^{MLWF}$ bear a similar information to the orbital occupations used in the DFT+U method and the Löwdin occupations. But in contrast to the atomic-orbital occupations used in the DFT+U method and the Löwdin occupations, the MLWFs can be centred wherever - on atoms, bonds, in the middle of the ring etc. - and they represent rather the molecular than the atomic orbitals.

For most of the studied here cases, the spreads of TM-centred MLWFs are smaller for the spin down. The occupations of the z-axial functions are higher than the 4-fold ones for the spin up, and the reversed situation is for the spin down; with total spin down occupations smaller since it is the minority spin. For the TM-O centred MLWFs, the spreads are about 0.2 Å² larger in the minority-spin case, and this holds for both couplings, for example for the AF-coupled porphyrin-VO and FM-coupled CoO-doped porphyrin.

Diversities of the spreads and the occupations for the MLWFs in two spin polarizations do not surprise for the functions centred around oxygen, transition metal, and nitrogens. We are interested, however, in the 2D materials which are promising as strong-coupling magnets - such systems should additionally exhibit a spin-asymmetry also for the MLWFs centred on the bridges between porphyrins. Examining our results, for the V- and VO-doped cases, the occupations of the C3-C4 bond centred MLWFs are about 0.25 smaller in the majority spin than in the minority-spin case. The spreads of the minority-spin functions are about 0.38 Å² smaller than of the majority-spin Wanniers. It means that in the above cases, the local spin at the bridge is AF-coupled to that of the TM and TM-O localized MLWFs. Similar spin-asymmetry of spreads is observed in the Cr-doped case, but not for the CrO. However for Cr, the spin-asymmetry of the occupation numbers is much less pronounced than in the vanadium doped cases. The spin-asymmetry of the MLWFs centred at the bridge can be seen also for manganese, iron and cobalt doped porphyrins, although weaker than for the V and Cr doped cases, and this asymmetry is not observed in nickel, copper and zinc cases. Therefore, the less than half-filled 3d-row elements seem to be more promising dopants for the high-Tc magnets than the more than half-filled 3d-row TM.

**D. Outlook**

As a continuation of this work, it would be interesting to investigate the elastic properties of the ferrimagnetic porphyrin networks, because the auxetic materials might be found in this class. The photo-magnetism is a phenomenon worth our attention in these systems, since the Jahn-Teller symmetry-lowering has been found for the triplet state in zinc complexes of porphyrin and phthalocyanine. Another open-issue is to replace the acetylenic bridge by some other connections, for example containing nitrogens; it has been shown for the rare earth dimer-complexes that the N₂ 'perpendicular bridge' leads to exceptionally strong magnetic exchange. As follows, studies of the spininterface-formation at the bridge or sub-
strate - depending on the chosen molecular connections - would be an extension of our studies and the experimental and theoretical work on phthalocyanine-Mn at the Co surface. Additionally, the effect of the choice of a bridge on the charge state of the transition metal or TM-O moiety, and the range of these interactions, still remain open questions.

IV. CONCLUSIONS

2D organic networks are promising for spintronic applications. In this work, we searched for magnets among porphyrins connected with acetylene bridges and doped with transition metals, with and without oxygen co-doping. For magnetism, the relative energetic positions of the transition-metal states, 3d, 4s and 4p, with respect to the 2p-states of the neighbouring atoms are very important. Therefore, we used the self-interaction corrected pseudopotential scheme (pSIC), within the DFT framework, for calculations of the electronic structure, and the maximally-localized Wannier functions tool for the analysis of the properties.

Most of the porphyrin networks doped with TM and TM-O are magnetic; except the Sc, TiO, Ni and Zn cases. The co-doping with oxygen increases the magnetizations for the second-half 3d-row TMs and the ScO case. The rest of cases: Ti, V, Cr and Mn decrease magnetizations after the oxygen addition.

Difference between the total and absolute magnetizations indicate ferromagnetism, which is the strongest for V-, VO- and Mn-doped porphyrins. Further examination of the systems with the Löwdin populations tool shows the AF-coupling of the oxygen spin with respect to the TM local moment for the VO- and CrO-doped cases, and FM-coupling for the FeO-, CoO-, NiO-, CuO- and ZnO-doped porphyrins. Interestingly, in the ScO-doped case, the magnetic moment is localized at oxygen and not at TM, and in the MnO case the situation is opposite. The strongest spin-polarization localized at nitrogens, and AF-coupled to the 3d-TM local moment, was found for the Mn+, V-, VO- and Fe-doped cases. The same couplings are ferromagnetic for the NiO-, Cu- and CuO-doped cases. The spin-polarization effects are very long range for the porphyrin networks with the TMs from V to Co: the spin-asymmetry of the atomic shells was found very far from the TM, even on the acetylenic bridges.

The MLWFs analysis enabled finding another important phenomenon: the anisotropic properties of the TM, O- and acetylene-localized magnetic moments. This effect shows up as the MLWF-occupation numbers ‘exchange’ between the spin up and down functions of the z-axial and 4-fold symmetry. In total, those atomic-centred functions are almost equally occupied for both spins, and this is what the Löwdin analysis shows since it is spherically averaged.

In summary, the ferrimagnetic cases found in our studies are characterized by the induced long-range spin-polarizations - in addition, they are anisotropic. These systems certainly would be good candidates for the high-Tc magnets and will show up new properties when are deposited at the surfaces of other materials.

Acknowledgements

This work has been supported by the the National Science Center in Poland (the Project No. 2013/11/B/ST3/04041). Calculations have been performed in the Interdisciplinary Centre of Mathematical and Computer Modeling (ICM) of the University of Warsaw within the grant G59-16.

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