

Strong Correlations in Electron Doped Phthalocyanine Conductors Near Half Filling

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We propose that electron doped nontransition metal phthalocyanines such as ZnPc and MgPc, similar to those very recently reported, should constitute novel strongly correlated metals. Because of orbital degeneracy, Jahn-Teller coupling, and Hund's rule exchange, and with a large on-site Coulomb repulsion, these molecular conductors should display, particularly near half filling at two electrons/molecule, very unconventional properties, including Mott insulators, strongly correlated superconductivity, and other intriguing phases.

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Building novel metals by doping molecular crystals such as polyacetylene, fullerenes, TTF-TCNQ, (TMTSF)₂X, (TMTTF)₂X, and (BEDT-TTF)₂X salts, etc., is a well trodden route [1,2], but remains an exciting and ever moving front. Very recently the Delft group showed that thin films of transition metal phthalocyanines (MPcs) FePc, CoPc, NiPc, CuPc, initially insulating, can be turned genuinely metallic through potassium doping [3]. Electron doping appears to take place largely in the twofold degenerate lowest unoccupied e_g molecular orbital (LUMO) [4,5] of the molecules. The simplest rigid band model naturally explains, according to [3], why the MPcs, initially insulating when pristine ($n = 0$) [6], become metallic upon increasing doping ($0 < n < 4$), ending up again as insulators at full doping ($n = 4$). It is not yet clear whether stoichiometric compound phases may exist here as they do in alkali doped fullerenes, but there is an otherwise striking overall analogy, to the point that even the conductance values reported at optimal metallic doping are close in magnitude and temperature (in)dependence to those of K_xC_{60} films.

While the pursuit of metallicity cum magnetism in the transition metal doped MPcs [5] will in the future constitute an interesting goal in itself, the scope of this Letter is to point out newer directions and possibilities that can make slightly different metallic doped MPcs, yet to be realized, potentially even more exciting. Doped MPcs are not, we claim, regular metals, but constitute strongly correlated electron systems, akin to doped two-band Mott insulators. Characterized by a strong on-site electron repulsion by the e_g orbital degeneracy and by intra-site Jahn-Teller and electron-electron multiplet couplings, the doped MPc molecular system should approach near $n = 2$, as foreshadowed by recent studies [7–9], a novel unstable fixed point heralding a wealth of possible low-temperature phenomena and phases. We conduct in this Letter a preliminary exploration of this scenario by addressing theoretically—and thus proposing the experimental realization of—new metals ob-

tained through electron doping of ZnPc, MgPc, and other such nontransition metal MPcs. The extra electrons should flow into the MPc $2e_g$ lowest unoccupied molecular orbital (LUMO) [4] to form a two-band metal. The LUMO states are ligand shell orbitals loosely surrounding the central metal ion, with a large intramolecular Coulomb repulsion U in comparison with the narrow electron bandwidth W expected from weak intermolecular electron hopping. In the neighborhood of half filling, $n = 2$, a doubly degenerate e_g orbital also has a molecular Hund's rule exchange J (lowering the triplet state by $4|J|$ relative to the singlet), and a Jahn-Teller (JT) coupling of the electronic state to B_{1g} and B_{2g} MPc molecular vibrations, lowering the singlet state energy by an amount E_{JT} . Thus, there will be some cancellation between the two couplings. These ingredients are similar in nature to those present in fullerenes, where orders of magnitude are $U = 1$ eV, $E_{JT} = 0.15$ eV, $J = 0.03$ eV, and $W = 0.5$ eV. Although the corresponding values in MPcs are not yet so accurately known, we obtain estimates that are surprisingly close. The similarity noted in Ref. [3] between alkali doped MPcs and fullerenes[2] may thus reach much deeper than just the dopability and the closeness of mobilities pointed out experimentally. As in fullerenes, the resulting phase diagram will depend upon the balance between low and high spin states of the molecular ion. Unlike fullerenes, however, the twofold degeneracy will reveal a potentially richer overall phase diagram.

The Hamiltonian for electrons in the e_g -orbitals of molecule i is

$$\hat{H}_{i,\text{mol}} = \frac{U}{2} \hat{n}_i^2 + \frac{J}{2} (\hat{\tau}_{i,x}^2 + \hat{\tau}_{i,y}^2) + g(q_{i,1} \hat{\tau}_{i,x} + q_{i,2} \hat{\tau}_{i,y}) + \frac{\hbar\omega_0}{2} (q_{i,1}^2 + p_{i,1}^2 + q_{i,2}^2 + p_{i,2}^2), \quad (1)$$

where \hat{n}_i is the overall occupation at site i ; $\hat{\tau}_{i,\alpha}$ with $\alpha = x, y, z$ are pseudospin operators spanning the twofold degeneracy $\hat{\tau}_{i,\alpha} = \sum_{a,b=1}^2 \sum_{\sigma} c_{i,a\sigma}^\dagger (\tau^\alpha)_{ab} c_{i,b\sigma}$, where τ^α

are Pauli matrices. Here, $c_{i,a\sigma}^\dagger$ denotes creation of electrons with spin σ at site i in orbital $a = 1, 2$ of the LUMO e_g doublet. The last two terms in (1) describe JT coupling of strength g to a doubly degenerate vibration with frequency $\hbar\omega_0$, coordinates $q_{i,1}$ and $q_{i,2}$ and momenta $p_{i,1}$ and $p_{i,2}$, where $E_{JT} = 8g^2/\hbar\omega_0$. A single but degenerate mode is assumed as a simplifying approximation, replacing the actual 14 pairs of nondegenerate JT modes B_{1g} and B_{2g} allowed by the MPC D_{4h} symmetry. As detailed in Ref. [10], an estimate of parameters appropriate to MPCs such as ZnPc, MgPc indicates $U \sim 1$ eV and, for $n = 2$, a singlet energy gain $E_{JT} - 4|J| \sim 0.06\text{--}0.07$ eV over Hund's rule triplet. This prevalence of singlet over triplet, the main ingredient potentially leading to s -wave superconductivity, could be mitigated or even reversed in a solid state compound; we shall therefore examine both possibilities in the rest of this Letter.

In the MPC molecular crystal, electrons can quantum mechanically hop between neighboring sites

$$\hat{H}_{\text{hop}} = \sum_{ij} \sum_{a,b=1}^2 \sum_{\sigma} t_{ij}^{ab} c_{i,a\sigma}^\dagger c_{i,b\sigma}. \quad (2)$$

Assuming first a generic three-dimensional structure with ν neighboring molecules and a weak isotropic first-neighbor hopping t , the LUMO e_g orbitals will give rise to a pair of narrow molecular bands of width $W = 2|t|\nu$. (We will discuss the additional signature of a quasi-one-dimensional structure of these compounds in the final part of the Letter.) Before doping we generally expect a narrow band $W \sim 0.3$ eV (see below), due to very weak van der Waals bonding between molecules. While W will eventually depend on the intermolecular geometry, including the way that may be altered by doping, we will assume W to remain of approximately the same magnitude after doping. In addition to Eqs. (1) and (2), we should in principle include additional terms such as the dispersion of vibrations (to account for the coupling between the JT distortion of a molecule and those of other molecules), intermolecular electron-electron interactions, and more. We will presently neglect them, concentrating on the basic Hamiltonian

$$\hat{H} = \hat{H}_{\text{hop}} + \sum_i \hat{H}_{i,\text{mol}}. \quad (3)$$

Because U/W is large, and for $n \sim 2$, this system is generally close to a Mott transition. There, the quasiparticle band is very narrow and it is a good approximation to neglect retardation, replacing (1) with

$$\hat{H}_{i,\text{mol}} \rightarrow \frac{U}{2} \hat{n}_i^2 + \frac{J_{\text{eff}}}{2} (\hat{\tau}_{i,x}^2 + \hat{\tau}_{y,i}^2), \quad (4)$$

where $J_{\text{eff}} = J - E_{JT}/4$.

The further simplifying assumption of nearest-neighbor hopping that are diagonal in the orbital indices

[15] brings this Hamiltonian to coincide with that recently studied by Dynamical Mean Field Theory (DMFT) [16] in Refs. [7,8]. Close to $n = 2$, it was shown to display a rich phase diagram including, besides the regular metal, a Mott insulator, a strongly correlated superconductor, and a pseudogap metal. Within DMFT, the lattice model in Eq. (3) is mapped onto an Anderson impurity self-consistently coupled to a conduction electron bath [16]. The many-body physics of the Anderson impurity and its fixed points foreshadow that of the infinite many-body system [9], as confirmed by the calculated DMFT phase diagram [7,8]. We exploit here these results to analyze the implications for the phase diagram of half filling doped MPCs considering both possibilities, namely: (i) singlet ground state or (ii) triplet ground state.

(i) $J_{\text{eff}} < 0$.—The $n = 2$ molecular ground state is a nondegenerate spin singlet accompanied by a dynamical Jahn-Teller effect. If, in the solid, U/W is larger than the critical Mott value (between 1 and 2, depending in detail on J and E_{JT}), the half-filled MPC will realize a non-magnetic, singlet Mott insulator [17]. For U just below that value, or for light doping away from $n = 2$, the MPC solid will be lightly metallic. In this ‘‘doped Mott insulator’’ regime, the Anderson impurity displays instabilities against symmetry-broken phases in both particle-particle and particle-hole channels; which instability will eventually win out depends on band structure and coupling details. If nesting or other band-structure singularities are absent or very weak, the particle-particle instability should dominate, leading to an s -wave superconductor with order parameter

$$\Delta_{SC} = \langle c_{11}^\dagger c_{21}^\dagger + c_{21}^\dagger c_{11}^\dagger \rangle \neq 0. \quad (5)$$

This state is a strongly correlated superconductor (SCS) of a kind first pointed out in Ref. [18], further confirmed in the two-band model in Refs. [7,8]. It was also suggested [7,18]—although without a calculation of T_c —that SCS is a ‘‘high temperature superconductor’’ in the sense that the SCS superconducting gap may reach values several orders of magnitudes greater than the corresponding BCS value (that would be attained for $U = 0$), $\Delta_{BCS} \sim \hbar\omega_0 e^{-1/\lambda}$, where $\lambda = 2\rho_0|J_{\text{eff}}|$ and ρ_0 is the density of states at the Fermi level per spin and band.

If, on the contrary, the particle-hole instability channel was favored by some detail of the band structure such as Fermi surface nesting, then one of two alternative symmetry-broken phases can be expected. The first is a trivial one, with order parameter

$$\Delta_{JT} = \cos\phi \langle \hat{\tau}_x \rangle + \sin\phi \langle \hat{\tau}_y \rangle \neq 0, \quad (6)$$

corresponding to a cooperative Jahn-Teller distorted state, either modulated or uniform, the angle ϕ reflecting U(1) orbital symmetry breaking. The model in fact possesses O(2) orbital symmetry, which naturally decomposes into $Z_2 \otimes U(1)$. Z_2 is the discrete symmetry

$\tau_z \rightarrow -\tau_z$, while $U(1)$ represents invariance under rotations around the pseudospin z -axis. As a consequence of the static cooperative Jahn-Teller distortion, a conventional insulating band gap or at least a strong lowering of metallic density of states should take place at the Fermi level. More interesting is the alternative instability, associated with a different order parameter in the particle-hole channel

$$\Delta_{PT} = \sum_{\alpha\beta} \langle c_{1\alpha}^\dagger \vec{\sigma}_{\alpha\beta} \cdot \vec{S}_{c_{1\beta}} \rangle - \langle c_{2\alpha}^\dagger \vec{\sigma}_{\alpha\beta} \cdot \vec{S}_{c_{2\beta}} \rangle \neq 0, \quad (7)$$

breaking both orbital Z_2 and spin $SU(2)$ symmetry, \vec{S} being the direction along which the spin $SU(2)$ symmetry is broken. We note that the LUMO e_g orbitals are mainly localized onto the MPc four N-atom ring and have odd parity with respect to the central metal ion. Therefore, the discrete Z_2 symmetry translates into parity in MPcs, whence $\Delta_{PT} \neq 0$ represents a spin current flowing on the Pc ring, a very intriguing possibility. This kind of phase should be either insulating or a poor metal like the cooperative JT phase. Unlike the latter, it should break both time reversal and parity, conserving only the product of the two. These properties are reminiscent of a phase discussed some time ago by Varma [19].

(ii) $J_{\text{eff}} > 0$.—In this case (less likely in MPcs than (i), as said above), the isolated $n = 2$ molecular ion is a spin triplet. The strongest instability here is towards bulk magnetism [9], ferro or antiferro depending on the band structure, a state which may or may not be accompanied by parity-symmetry breaking or by a Jahn-Teller distortion. If (depending on lattice structure) magnetism was sufficiently frustrated, then it would be possible for spin-triplet superconductivity to appear with order parameter

$$\Delta_{SC} = \langle c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger - c_{2\uparrow}^\dagger c_{1\downarrow}^\dagger \rangle \neq 0. \quad (8)$$

Since orbitals 1 and 2 have opposite parity, this translates into a p -wave spin-triplet superconducting order parameter. This is an interesting possibility since, at variance with conventional p -wave superconductors, the pairing function is nonzero on the molecule. According to the DMFT analysis of Ref. [8], where this kind of triplet superconductor was first discussed, this superconducting instability is also enhanced by the proximity of a Mott insulating phase, although not as dramatically as in case (i).

Much of the uncertainty in the above scenario depends on our ignorance of the doped MPc film crystal structure, so far treated generically. A second guess based on the crystal structure of pristine MPcs suggests that the alkali doped crystals could, similar to the undoped alpha-phase of the CuPc films [3], be made up of quasi-one-dimensional (1D) chains. We carried out density functional electronic structure calculations of MgPc assuming an alpha-phase structure with $n = 0$ [20], and found an intrachain e_g bandwidth $W \sim 0.3$ eV but an interchain

bandwidth between 1 and 2 orders of magnitude narrower (see Fig. 1). If doped MPcs were indeed this close to 1D, then our earlier DMFT-based analysis, valid for the opposite limit of large coordination lattices, should be replaced by another where the additional effect of quantum fluctuations and other 1D specific anomalies are properly treated.

We studied this 1D model by adapting the two-loop renormalization group (RG) equations derived by Ref. [21] to the two-band model. The fixed point Hamiltonian towards which the model flows under RG was analyzed by means of bosonization [21,22]. At strict half filling, we found a spin-gapped insulator for any value of U . However, for large U , this was a spin-liquid Mott insulator, i.e., a spin-gapped phase without any symmetry breaking. That corresponds either to the DMFT singlet Mott state found with $J_{\text{eff}} < 0$, or to a Haldane spin-1 chain for $J_{\text{eff}} > 0$. Here, the DMFT metallic phase at small U is replaced by a spontaneously dimerized insulator, i.e., a spin-gapped phase with broken translational symmetry, for either sign of J_{eff} . Away from half filling, the model turns metallic: nonetheless, we find that the spin gap survives. In particular, in the large U regime likely pertinent to the MPcs, the spin-liquid Mott insulator at $J_{\text{eff}} < 0$ turns at low doping into a spin-gapped metal with dominant fluctuations in the SC singlet channel (5) and subdominant fluctuations in the particle-hole $4k_F$ channels identified by Ref. [9]. The weakly-doped spin-1 chain at $J_{\text{eff}} > 0$ feels on the contrary more the effects of the reduced dimensionality which causes the spin gap to survive in the metallic phase, hence preventing long-range spin-triplet superconducting correlations. Indeed, in 1D the leading SC fluctuations appear

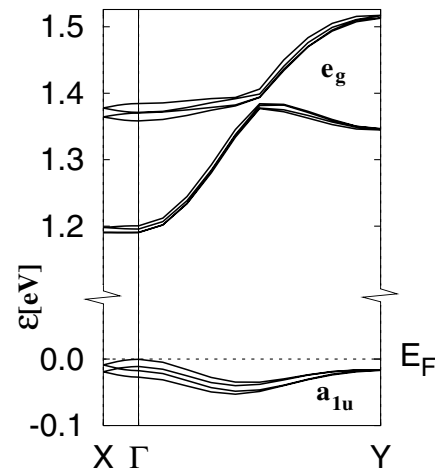


FIG. 1. Density functional electronic band structure of undoped α structure MgPc. The molecular stack direction is $\Gamma - Y$. The crystal structure was taken from Ref. [24]. The monoclinic cell ($a = 26.29$, $b = 3.818$, $c = 23.92$ Å, $\beta = 94.6$) contains four molecules and has symmetry $C2/n$.

in a spin-singlet orbital-singlet but space-odd particle-particle channel [23].

Weak but nonzero interchain interactions will in a hypothetical doped MPc with alpha-phases-like structure turn all these instabilities into properly long-range ordered phases at sufficiently low temperatures. While our present state of ignorance prevents further in-depth discussion, the expected emerging scenario is parallel to that obtained by DMFT, apart from those differences specific to 1D, like dimerization at $n = 2$ or the persistence of a spin gap away from half filling for regular Hund's rules.

Summarizing, we conclude first of all that stoichiometrically doped nontransition MPcs should display Mott insulating phases at all integer fillings, in particular, at half filling. Analysis of a simple model (1) revealed a stunning variety of phases in the immediate neighborhood of the Mott metal-insulator transition near half filling. The variety is greater than either that predicted for the three band case fullerides [18], or that experimentally known in fullerides [2] as well as in doped organics (with lower symmetry than MPcs) near half filling [1].

Many of the phases described above will individually merit an in-depth study. At the theoretical level, approximations will need to be improved, for example, by treating properly the nondegeneracy of the B_{1g} and B_{2g} molecular vibrations, the nondiagonal hopping, the dispersion of vibrations, etc. At the moment, nonetheless, it seems fair to say that more direct experimental input is urgent and essential. It will be important to dope and metallize nontransition MPcs, and to investigate whether they can be made at least locally stoichiometric. Subsequent examination by, e.g., scanning tunneling spectroscopy could search for the Mott insulating state and begin broaching in its neighborhood this fantastic scenario.

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- [1] See, e.g., T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors* (Springer, New York, 1998), 2nd ed.
- [2] L. Forro and L. Mihaly, *Rep. Prog. Phys.* **64**, 649 (2001).
- [3] M. F. Craciun, S. Rogge, D. A. Wismeijer, M. J. L. den Boer, T. M. Klapwijk, and A. F. Morpurgo, in *Proceedings of the 12th International Conference on Scanning and Tunneling Microscopy/Spectroscopy and Related Techniques*, edited by P. M. Koenraad and M. Kemerink, AIP Conference Proceedings **696**, 489 (2003); M. F. Craciun *et al.*, cond-mat/0401036.
- [4] M. S. Liao and S. Scheiner, *J. Chem. Phys.* **114**, 9780 (2001).
- [5] In most MPcs described in Ref. [3], there is a partly filled d -level. Strongly localized and with a large on-site Coulomb repulsion, that constitutes a nontrivial magnetic complication. The potentially interesting interplay of metallic conduction in the LUMO with these localized d electrons is beyond the scope of this work.
- [6] MnPc, FePc, CoPc, and CuPc are open shell molecules [4], so that the pristine parent insulators must themselves constitute (single-band) Mott-Hubbard insulators.
- [7] M. Capone, M. Fabrizio, C. Castellani, and E. Tosatti, *Phys. Rev. Lett.* **93**, 047001 (2004).
- [8] J. E. Han, *Phys. Rev. B* **70**, 054513 (2004).
- [9] M. Fabrizio, A. F. Ho, L. De Leo, and G. E. Santoro, *Phys. Rev. Lett.* **91**, 246402 (2003); L. De Leo and M. Fabrizio, *Phys. Rev. B* **69**, 245114 (2004).
- [10] An estimate of U is given by $U = (E_2 - E_3) - (E_1 - E_2) = A_1 - A_2$, where E_n is the total energy of the molecular ion with n electrons, and A_n its electron affinity. Calculations for isolated ZnPc(n^-) and MgPc(n^-) [4] find $A_1 \sim 3.7$ eV and $A_2 \sim 0.7$ eV, whence $U \sim 3$ eV, essentially identical to that of fullerene in vacuum [11]. In crystalline MPcs, the screening could be similar to that of fullerene [12], suggesting $U = 1-1.5$ eV as a crude estimate. Fits of the multiplet spectra of ZnPc [13] suggest that in the LUMO, eg., orbitals $4|J|$ could be $\approx 0.15 - 0.2$ eV. DFT calculations of ZnPc(2^-) and MgPc(2^-) yield singlet ground states, with $E_{JT} - 4|J| \sim 0.06$ and 0.07 eV, respectively [4]. Resonance studies on ZnPc(2^-) and MgPc(2^-) in solution [14] confirms that these dianions could indeed be singlets.
- [11] M. Lüders, A. Bordoni, N. Manini, A. Dal Corso, M. Fabrizio, and E. Tosatti, *Philos. Mag. B* **82**, 1611 (2002).
- [12] R. W. Lof, M. A. VanVeenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, *Phys. Rev. Lett.* **68**, 3924 (1992).
- [13] P. C. Minor, M. Gouterman, and A. B. P. Lever, *Inorg. Chem.* **24**, 1894 (1985).
- [14] D. W. Clack, N. S. Hush, and J. R. Yandle, *Chem. Phys. Lett.* **1**, 157 (1967).
- [15] While the diagonal hopping approximation is not particularly realistic in the present context, it does not change the nature of the problem, and provides useful physical understanding for application to the doped MPcs.
- [16] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996).
- [17] M. Fabrizio and E. Tosatti, *Phys. Rev. B* **55**, 13465 (1997).
- [18] M. Capone, M. Fabrizio, C. Castellani, and E. Tosatti, *Science* **296**, 2364 (2002).
- [19] C. M. Varma, *Phys. Rev. Lett.* **83**, 3538 (1999).
- [20] J. Tóbiš and E. Tosatti (to be published).
- [21] M. Fabrizio, *Phys. Rev. B* **48**, 15838 (1993).
- [22] See, for instance, A. O. Gogolin, A. A. Nersesyan and A. M. Tsvelik, *Bosonization and Strongly Correlated Systems* (Cambridge University Press, Cambridge, England, 1998).
- [23] M. Fabrizio and A. A. Nersesyan (to be published).
- [24] C. J. Brown, *J. Chem. Soc. A*, 2494, 1968.