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Density-functional study of the Cr_8 antiferromagnetic ring

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We present the results of an *ab initio* characterization of the electronic and magnetic properties of the Cr_8 molecular ring. The original molecule with formula $[\mathrm{Cr}_8\mathrm{F}_8\mathrm{Piv}_{16}]$(HPiv=pivalic acid, trimethyl acetic acid) has been approximated by replacing the disordered methyl groups by H atoms, obtaining *de facto* the formula $[\mathrm{Cr}_8\mathrm{F}_8(\mathrm{O}_2\mathrm{CH})_{16}]$. We find in agreement with experiments that the Cr atoms attain a local spin moment of $\frac{3}{2}$, and that the preferred arrangement of Cr atoms in the ground state is antiferromagnetic. By the total energy difference we calculate the value of the isotropic Heisenberg exchange parameter and we show that only after the inclusion of on-site correlation effects in the Cr *d* orbitals the value deduced by specific heat and torque measurements is recovered.

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I. INTRODUCTION

Single-molecule magnets have recently attracted much interest since they are collections of identical nanomagnets in which quantum phenomena such as steplike hysteresis curves of magnetization are observed.[1,2] Beyond being the actors of fundamental quantum phenomena, molecular magnets are widely studied because various present and future specialized applications of magnets require nanoscale, monodisperse, small magnetic particles.

We focus in the following on the magnetic molecule $[\mathrm{Cr}_8\mathrm{F}_8\mathrm{Piv}_{16}]$ (HPiv=pivalic acid, trimethyl acetic acid),[3] Cr_8 in short, which belongs to the class of antiferromagnetic rings, a subclass of molecular nanomagnets characterized by a cyclic shape and antiferromagnetic exchange coupling between nearest neighboring ions. As it has been pointed out by recent works,[4–6] such molecular rings are very promising candidates for the implementation of quantum logic devices.

While the discrete pattern of magnetic energy levels, with the singlet ground state and excited multiplets, has been deeply investigated in terms of effective spin model Hamiltonians,[7–10] a full first-principle description of electronic and magnetic properties of this molecular magnet is still missing. Several methods have been used to investigate other molecular magnets from first principles with different levels of accuracy depending on the size of the systems under interest: to name a few, Cr_1,[11] Cr_2,[12] V_{15},[13,14] Mn_2,[15,16] Mn_4 monomer[17,18] and dimer,[17,19] Mn_{10},[20] Mn_{12},[18,21–25] Fe_2 and Fe_3,[26] Fe_4,[11,15,27] Fe_6,[28] Fe_8,[29] Fe_{10},[30,31] Fe_{11},[22,32] Fe_{19},[33] Co_4,[11] Ni_2,[34] Ni_4,[35,36] Cu_2,[34,37–42] and Cu_4[43,44] have been analyzed (for recent reviews see Refs. 35, 45, and 46). Except for some Cu dimeric complexes which form the building block of three-dimensional (3D) solid crystals studied in Refs. 37, 41, and 42, and the Cr dimeric model complexes studied in Ref. 12, which are of pure molecular nature, the other systems cited above belong to the class of SMM's, for which the organic ligands determine the mutual arrangement of the single molecules in a molecular crystal, while not playing a role in the magnetic properties, being determined only by the intramolecular exchange interactions between the transition metal's magnetic moments.

In this paper we present results of an all-electron density-functional investigation of the Cr_8 antiferromagnetic molecular ring, and discuss its electronic and magnetic properties. Particular emphasis is given to the evaluation of the Cr-Cr exchange interaction from total energy calculations, pinpointing the importance of the inclusion of correlation effects beyond standard exchange-correlation functionals. The paper is organized as follows. In Sec. II we give the details on the computational method and describe how the Cr_8 molecule is approximated in order to perform the calculations. In Sec. III we discuss its electronic and magnetic properties focusing in Sec. IV on the extraction of the exchange parameters. We conclude by summarizing our results in Sec. V.

II. COMPUTATIONAL DETAILS

In its real synthesized structure, the asymmetric unit of Cr_8 consists in two chromium atoms in and two fluorine atoms, bonded to four (disordered) pivalic groups. These molecular units pack into a crystal with a unit cell of volume 6783 Å^3 and space group $P42_12$, with two formula units per unit cell.[47] The Cr atoms arrange in an octagon with almost perfect planarity, and are connected to each other via two independent carboxylate (-O-C-O-) bridges, and a F bridge, leaving them at an average distance of $\simeq 3.38$ Å. Would the whole ligand's structure be considered, a total number of 68 inequivalent atoms should be taken into account, not to mention the disorder in the pivalic groups? In order to tackle the system with *ab initio* techniques, we have "pruned" the building block by approximating the organic matrix. More specifically the pivalic groups can be approximated taking into account that they are composed of several methyl subgroups. In Fig. 1(a) one of the carboxylate bridges between two neighboring Cr atoms is sketched, together with an ordered form of the pivalic block. By replacing each methyl molecule CH_3 with an isovalent H atom, i.e., substituting C-$(\mathrm{CH}_3)_3$ with C-H_3 (a procedure also known as "hydrogen saturation") the pivalic group resizes, see panel (b) of Fig. 1, to a methyl group on which we can apply further the substitution described above. Thus it turns out that each pivalic group can be substituted by a single H atom, without chang-

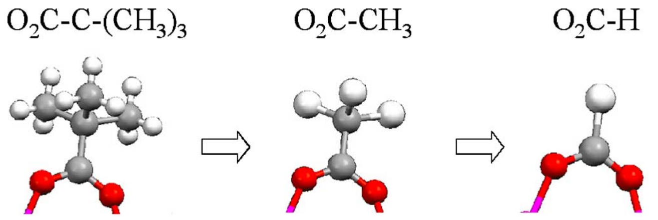

FIG. 1. (Color online) Schematic representation of the pruning procedure adopted to approximate the Cr_8 molecule (see text for details)[figure by XCrySDen (Ref. 74)].

ing the valence of the C in the carboxylate bridge. After this "pruning" the molecule, shown from a top and side view in Figs. 2(a) and 2(b), respectively, retains the formula $Cr_8F_8(O_2CH)_{16}$. The inequivalent atoms are reduced to 20, with a total number of 160 atoms in the cell. It is important to stress that this approximation keeps the magnetic core unaltered and preserves the D_4 point symmetry of the molecule. Moreover the role of the organic ligands in separating the molecules and characterizing them as noninteracting units in the original structure, is played equally well by vacuum space in the "pruned" structure.

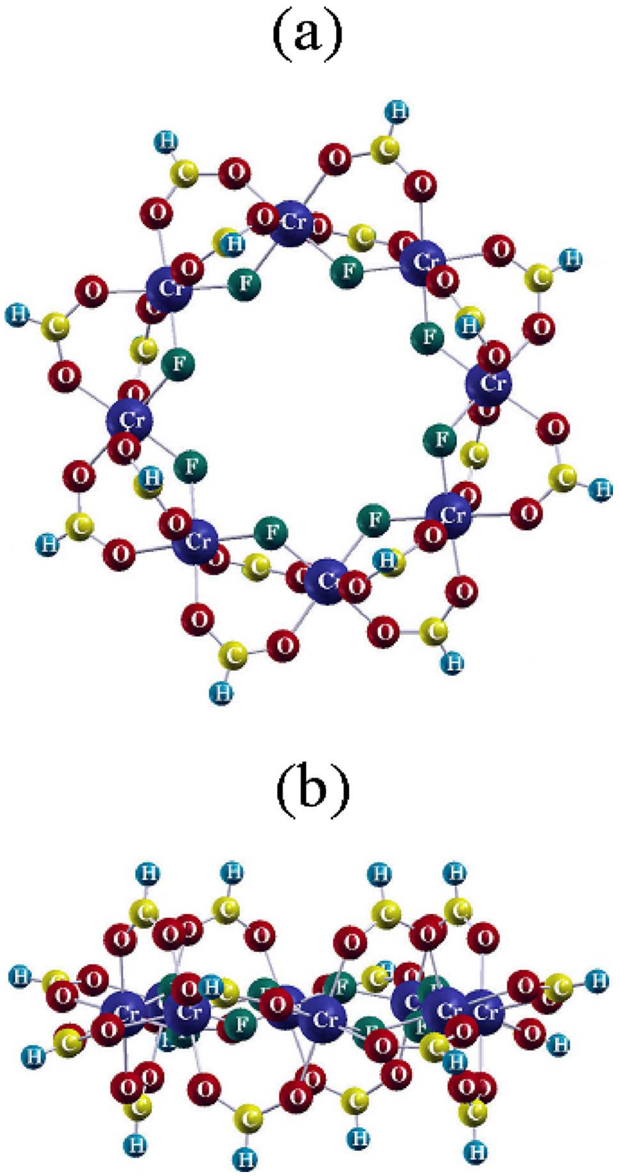

FIG. 2. (Color online) Top (a) and side (b) view of the a single Cr_8 molecular unit, after the H substitution (see text for details) [figure by XCrySDen (Ref. 74)].

We use the augmented plane wave method (APW) (Refs. 48 and 49) developed within the density-functional theory (DFT),[50,51] implemented in its most recent version (APW +local orbitals[52,53]) in the WIEN2k code.[54] Because of the hybrid nature of the employed basis set, this method turns out to be well suited to treat with high accuracy systems composed of both vacuum space and close-packed regions such as molecular crystals. Exchange and correlation effects are accounted for by the generalized gradient local approximation (GGA) in the version proposed by Perdew *et al.*[55] The muffin-tin radii, which define the atom-centered spheres where the plane waves are augmented by a linear combination of products of radial functions and spherical harmonics, have been chosen to be 2.40, 1.20, 1.24, 1.00, and 0.83 bohrs, respectively, for Cr, F, O, C, and H atoms. In order to have a converged basis set, up to 90–100 APW's per atom have been taken into account, resulting in more than 14 500 APW's in the basis set (equivalent to a cutoff of circa 7 Ry in a plane wave analog). Since the single Cr_8 molecules are well separated in the crystal (≥ 6.4 Å), a discrete molecular energy level spectrum with no dispersion is observed, so that only one k point, i.e., the Γ point, is considered for Brillouin-zone (BZ) integrations. The *ab initio* characterization by means of the WIEN2k program of the H-terminated Cr_8 molecule represents still a rather challenging task and thus no optimization of the atomic coordinates has been attempted, considering instead the experimentally determined x-ray structure.[47] We have performed accurate tests in order to assess the accuracy of our calculations; by increasing the number of APW's the exchange coupling constants and/or parameters between the Cr centers varies of around one-tenth of meV. Concerning the other quantities, such as the magnetic moments, or the energy gaps in the density of states, the precision might be estimated, respectively, of the order of $\pm 0.005\mu_B$ and ± 0.01 eV.

III. ELECTRONIC AND MAGNETIC PROPERTIES

In the query of the magnetic ground state of this molecule within a collinear description we have to assume either ferromagnetic (FM) and antiferromagnetic (AFM) coupling between the magnetic moments of the two inequivalent Cr atoms. Comparing *ab initio* total energy calculated for the two magnetic arrangements we obtain, in agreement with experiments, that the AFM configuration is the ground state, while the FM configuration is 0.42 eV/formula unit higher in energy (see Table I). Table I reports also the magnetic moments of Cr atoms, derived by integrating the charge and spin densities inside the muffin-tin regions; a very small induced magnetic moment of $0.01-0.02\mu_B$ is found for the oxygen atoms and for the fluorine atoms in either the AFM or FM configuration, while for all the other atoms no magnetic moment is observed. Within the uncertainties induced by the

TABLE I. Calculated GGA total energy (relative to the ground state), HOMO-LUMO majority and minority gaps, Cr magnetic moments, and the total magnetic moment per formula unit for the Cr_8 molecule are reported for the AFM and FM configurations

	AFM	FM
ΔE_{TOT} (eV)	0	+0.209
$E_{H-L}^{maj.}$ (eV)	2.36	2.15
$E_{H-L}^{min.}$ (eV)	2.36	4.08
m_{Cr} (μ_B)	+2.72,–2.71	+2.78,+2.77
m_{Tot} (μ_B)	0	24

finite spatial integration the values for Cr atoms $(2.71-2.78\mu_B)$ are compatible with a spin $S=\frac{3}{2}$ that would result from Hund's rule assuming a charge 3+ at each Cr atom. This is also corroborated by the fact the total magnetic moment per formula unit (see Table I) in the FM configuration is $24\mu_B$, resulting in a magnetic moment associated with each of the eight Cr atom of $3\mu_B$.

The spin polarization of Cr *d* orbitals which contribute to the formation of slightly covalent bonding with oxygen *p* states is shown in Fig. 3 as a three-dimensional isosurface plot for the AFM ground state. A significant spin polarization of the charge density is found only close to the Cr atoms supporting a localized picture of the Cr magnetic moments. Due to the local arrangement of nearest neighbor oxygen and fluorine atoms which sit at the vertices of a weakly distorted octahedron around each chromium (see Fig. 2), the Cr *d* states are split in two *T*2*g*- and *Eg*-like levels of degeneracy three and two, respectively; the triple degenerate level lies lower in energy and hosts three parallel spin electrons that are responsible for the cubic shaped spin isosurfaces shown in Fig. 3.[56]

The calculated total density of states (DOS) of Cr_8 in the AFM ground state configuration is shown in Fig. 4, as well as the partial DOS obtained by the projections onto the F($2p$), C($2s/2p$), and O($2p$) orbitals. The two crystallographically inequivalent Cr atoms are almost identical due to their local chemical environment; this holds also for the two F, eight O, and four C atoms. Consequently we can plot the DOS for only one representative atom per atomic species. Because of the zero spin polarization for all the atoms in the cell except Cr, we have plotted only the DOS of one spin channel. The analysis of Fig. 4 shows that the DOS in a region just below and above the Fermi level is mainly due to the Cr *d* orbitals, while the region between −10 eV and 2 eV is governed by the *p* orbitals of the F and C and O atoms; hybridization results into the formation of Cr($3d$)-C/O($2p$), as well as C($2s$)-C/O($2p$) orbitals, a sign of the bonding nature of the carboxylate bridges, which interconnect the Cr atoms. Between the Cr($3d$) and the F($2p$) states we can observe a similar hybridization in the energy window −4 eV/−2 eV, leading to a molecular bonding orbital between Cr and F atoms; the character of this bonding is more ionic than the Cr-O ones, because of higher electronegativity of fluorine with respect to oxygen.

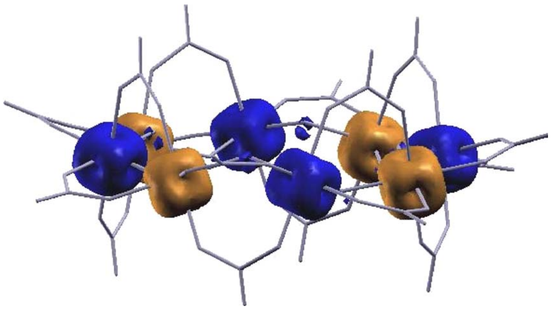

FIG. 3. (Color online) 3D plot of the spin polarization of the charge density; dark (blue) and light (yellow) shades are positive (negative) isosurfaces for the value of ±0.01 electrons/(a.u.)^3 [figure by XCrySDen (Ref. 74)].

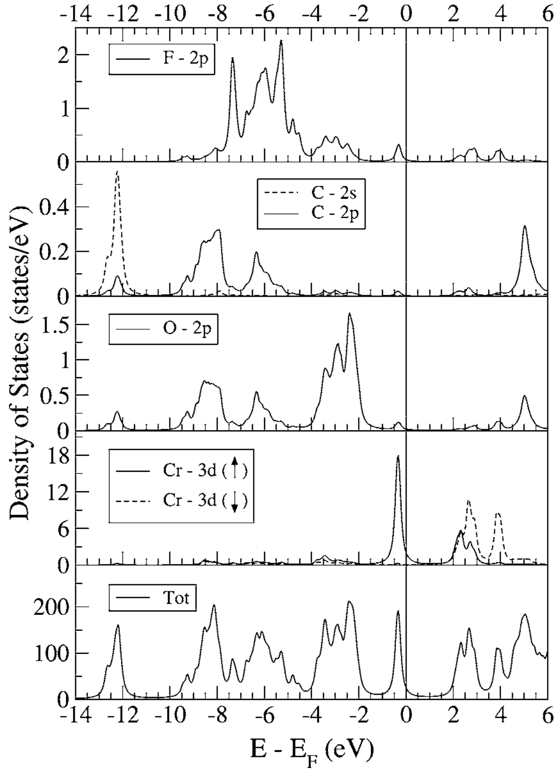

FIG. 4. Total and atom and/or orbital projected DOS of Cr_8 in the AFM ground state for one spin channel within the GGA approach (see text for details)].

The highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) gap (hereafter H-L gap) are also reported in Table I. In the AFM ground state, as discussed above, the majority states for one Cr atom are minority states for the other, which means that the same H-L gap is found for both spin channels, and attains a value of 2.36 eV. In the FM state two clear spin channels exist, and one can identify a majority H-L gap and a minority H-L gap, respectively, of 2.15 and 4.08 eV. Experimentally, the lowest excited states of the molecules, characterized by finite values of the total spin, can be probed in the presence of an external magnetic field. The above analysis suggests that a magnetic characterization of the molecule by a transport experiment is feasible, since an asymmetry in the electronic gaps, i.e., a different efficiency in the transport channels, can be established, depending on the relative orientation between the spins of the molecule and of the injected electrons.

IV. EXCHANGE INTERACTION PARAMETER

The adoption of *ab initio* methods for the investigation of magnetic molecules offers a unique opportunity to calculate exchange parameters otherwise inferred from fitting the eigenvalue spectrum of an appropriate spin interaction Hamiltonian to magnetization, specific heat, and neutron scattering measurements. There are several ways to extract exchange parameters from the calculations, for instance, by exploiting the concept of the magnetic transition state,[22,57] by the local-force method,[58] or by total energy difference methods. We adopt this last method, which in the case of a single exchange parameter, has a simple implementation and has been successfully applied to several magnetic molecules, e.g., Mn_{12},[23,24] V_{15},[13,14] or Fe_6.[28] This method relies on a mapping of the *ab initio* Hamiltonian onto a spin model Hamiltonian that in our case is the Heisenberg Hamiltonian. A fundamental prerequisite for the direct application of the Heisenberg model is the localization of the magnetic moments; we see from Table I that the absolute values of the magnetic moments in the AFM and FM configurations are very similar, with a difference of the order of 2%. This is a clear sign that the spin degrees of freedom are decoupled from the charge degrees of freedom, and that a localized moment picture can be envisaged.

Considering only nearest neighbor Heisenberg exchange interaction between the Cr magnetic moments, and in absence of anisotropy terms (we did not include in the calculations spin-orbit coupling, neither dipolar terms), the Hamiltonian is simply

$$E^{TOT} = J\sum_{i=1}^{7} S_i \cdot S_{i+1} + JS_8 \cdot S_1, \tag{1}$$

where $S_i = S = \frac{3}{2}$ for $i = 1, \ldots, 8$, is the spin moment in unit of bohr magneton of the Cr atoms. After straightforward algebra, we end up with the formula

$$J = \frac{4}{9}\frac{[E^{TOT}_{FM} - E^{\mathrm{TOT}}_{AFM}]}{16}, \tag{2}$$

where $\Delta E_{TOT} = E^{TOT}_{FM} - E^{TOT}_{AFM}$ is the calculated total energy difference per formula unit between the FM and AFM configurations. We obtain the value $J_{GGA} = 5.8$ meV, while the value inferred by the experiments is $J_{Exp} = 1.5$ meV, with an overestimate of the coupling strength by almost a factor 4.

The Cr-Cr magnetic interaction is not direct (we recall that the average Cr-Cr distance is as large as 3.38 Å), but follows superexchange paths through the carboxylate and fluorine bridges, as evident from the crosscut of the charge density in the plane of the Cr atoms shown in Fig. 5. It is interesting to note in passing that Cr_8 rings have been synthesized in a number of different molecular crystals, one of them (referred to as Cr_8-OH hereafter) being the hydroxide analog of Cr_8 (which might be relabeled as Cr_8-F). In this compound, with formula $Cr_8(OH)_8(O_2CPh)_{16}$,[59] the F bridges are replaced with O-H bridges, where the O-H unit points toward the center of the molecule. The exchange coupling constants that have been extracted in Cr_8-OH,[3] differ very little from the one extracted in Cr_8-F, which testify the stability of the Cr-Cr interactions in this cyclic compounds; as shown in the paper of Christian *et al.*,[12] this holds on condition that we do not change the valencies of the bridges. The carboxylate bridges imply direct Cr-O bondings, as much as it happens in Cr oxide bulk compounds. The overestimation of J discussed above is, therefore, not much surprising if we consider that GGA or local density, i.e., LDA, approximations of the exchange and correlation potential are known to underestimate the electron-electron correlation among d orbitals of transition metals, and not to reproduce properly the superexchange mechanism responsible for the magnetic interactions in transition metal oxides. Several methods exist that include some of the correlation effects missing in LDA and GGA. Among them the LDA(GGA) $+U$ method,[58] which includes explicitly an on-site Hubbard correlation term albeit within a mean-field picture, is able to enhance electron localization thus reducing exchange interactions in a better agreement with experiments. This holds for most transition metal oxides and it has been shown to apply also to the case of single-molecule magnets such as Mn_{12} (Refs. 18 and 23) and V_{15}.[60]

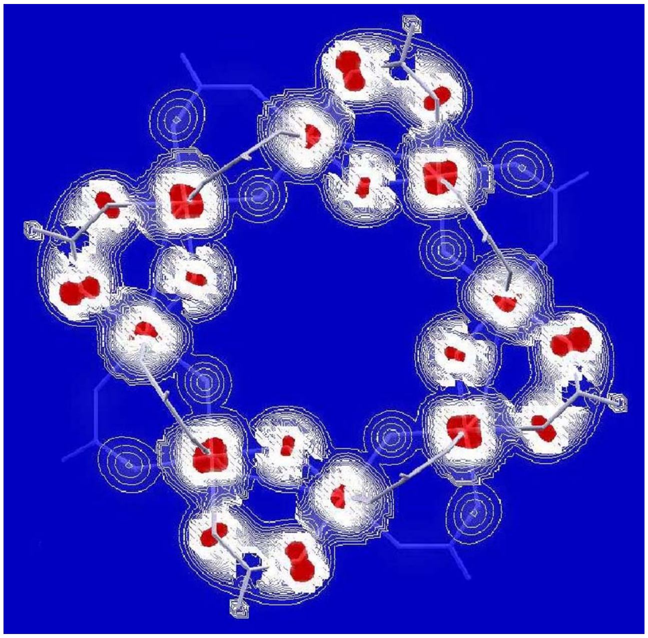

FIG. 5. (Color online) 2D contour plot of the charge density across the plane identified by the Cr atoms [figure by XCrySDen (Ref. 74)].

In the following we present GGA$+U$ calculations by using the self-interaction corrections (SIC) method[61] implemented in the rotationally invariant way.[62] In order to minimize the fluctuation of the orbital polarization induced by the additional orbital dependent potential, we have included in our calculations spin-orbit interactions within a second variational technique.[49] The magnetization axis has been fixed to lie along the z axis of the molecule, perpendicular to the plane identified by the Cr ring. The orbital moment at the Cr atoms is very small as expected, $\simeq 0.03$ and antiparallel to the local Cr spin moment, consistently with the Hund's rule for a $3d$ shell less than half-filled.

Before proceeding with the results we comment on the reliability of this approach as compared to hybrid functional methods, which are known to give good estimates of the exchange coupling constants. Recent calculations performed on a dinuclear Cr model complexes within hybrid B3LYP functional and Gaussian basis sets[12] substantiate the concept of the importance of the inclusion of correlation effects beyond standard local functionals in Cr based molecular magnets. Standard B3LYP, within the broken symmetry spin projected method as suggested originally by the seminal work of Noodleman,[63] has been found to give generally an overestimation of a factor of 2 with respect to the exact (as calculated by configuration interactions techniques) or experimental data. The inclusion of self-interaction corrections (see the recent paper of Ruiz *et al.*[64] on this issue) helps in recovering good agreement, since it adjusts the nondynamical correlation contributions which are present in a nonspecified way in standard local or nonlocal functionals. A different approach is to use nonspin projected states, and this assumption results in an automatic amendment to this "error" without the need of self-interaction corrections. The $+U$ approach can be thought as an analog method to tune, within mean field and with the help of the Hubbard parameter U, these nondynamical correlation terms. The choice of U is done under the same logic as the choice of the percentage with which the Hartree-Fock nonlocal exchange is mixed with standard local exchange terms employed in DFT. It may be calculated by, e.g., constrained DFT method,[65] or it may be simply fixed to reproduce the available experimental data. For the two examples cited above, namely Mn_{12} and V_{15}, values of $U = 8$ eV and $U=4-5$ eV have been used, respectively, being these values are very similar to the ones used in the case of manganese- and vanadium-oxide crystals. In order to choose a proper value of U for Cr, we exploit the experience maturated by other authors on Cr bulk oxides.

For CrO_2, the literature is somewhat controversial and arguments in favor[66–68] or against[69,70] the importance of correlation effects in this compound have been published. Instead, for chromia, i.e., Cr_2O_3 it has been shown[71] that electron-correlation effects lead to an improved description of its electronic and magnetic properties. Values of $U = 3$ eV $[U=5$ eV$]$ and $J=0.87$ eV $[J=1$ eV$]$ have been used, respectively, for CrO_2 $[Cr_2O_3]$. In both these oxides the Cr atoms are at the center of a distorted octahedra with oxygen atoms at the vertices, and have a different formal charge of +4 and +3, respectively, for CrO_2 and Cr_2O_3. In the Cr_8 ring, the Cr atoms have a formal charge of +3 but two fluorine atoms replace two of the oxygen atoms; moreover the Cr atoms are not simply bridged by oxygen, but by -O-C-O-, so that it is not clear how this interaction is affected by d electron localization as compared to standard superexchange interactions. We have not carried out systematic calculations varying U but we have simply chosen the value of $U = 2.7$ eV, which is somehow in between the values for the two Cr oxide compounds cited above.[72]

TABLE II. Same as in Table I, but obtained within the GGA $+U$ method; for Cr atoms the orbital magnetic moments are also reported.

	AFM	FM
ΔE_{TOT} (eV)	0	+0.075
E_{H-L} (eV)	3.85	3.49
m_{Cr} Tot. (μ_B)	+2.78,−2.78	+2.80,+2.80
Spin (μ_B)	+2.81,−2.81	+2.83,+2.83
Orb. (μ_B)	−0.03,+0.03	−0.03,−0.03
m_{Tot} (μ_B)	0	24

The results of the GGA$+U$ calculations are shown in Table II and Fig. 6 to be compared with their GGA counterparts of Table I and Fig. 4. Spin magnetic moments are enhanced by $0.03-0.05\mu_B$ with respect to GGA, as well as the spin-independent H-L gaps[73] which now attain values of 3.85 and 3.49 eV for the AFM and FM configurations, respectively. The further localization in the Cr $3d$ electrons leads to a shift in the occupied states towards higher binding energies, and, therefore, to a reduction in the DOS of the separation between the Cr d and O p/F p states. Applying Eq. (2) to the total energy calculated by the GGA$+U$ method we obtain a value of $J_{GGA+U}=2.1$ meV, which is now in much better agreement with the experimental value of $\simeq 1.5$ meV. This result clearly indicates that by taking into account on-site correlation terms it is possible to correct the LDA (GGA) total energies and improve sensibly the agreement with the experimental data. This work further supports the conclusion already inferred for other molecular magnets such as Mn_{12}

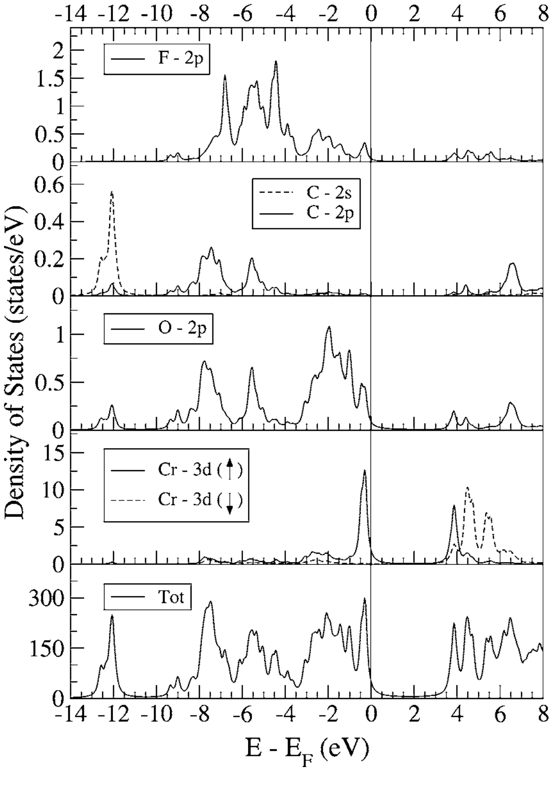

FIG. 6. Total and atom and/or orbital projected DOS of Cr_8 in the AFM ground state within the GGA$+U$ approach ($U=2.7$ eV).

and V_{15}, that the LDA (GGA)+U method, under proper choice of the parameter U, gives a description of the magnetic properties of these systems at a level of accuracy comparable to hybrid functional approaches.

V. CONCLUSIONS

To summarize, we have performed *ab initio* calculations of the Cr_8 antiferromagnetic molecular ring, by using state of the art DFT methods. We find that the spin polarization of the charge density is localized almost exclusively at the Cr atoms. Such localized moment pictures allowed us to extract, for the first time from first-principle calculations, the exchange interaction energy parameter in this molecule, by mapping the total energies obtained in the FM and AFM configuration states onto a classical Heisenberg Hamiltonian. We find that the GGA gives an overestimation of a factor of 4 with respect to the value inferred from experiments, and that, as expected, the inclusion of an additional on-site electron-electron correlation term among the electrons in Cr d orbitals, by means of the GGA+U method, improves notably the agreement with the experiments.

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