

Correlation effects in the electronic structure of the Mn_4 molecular magnet

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We present joint theoretical-experimental study of correlation effects in the electronic structure of $(pyH)_3[Mn_4O_3Cl_7(OAc)_3] \cdot 2MeCN$ molecular magnet (Mn_4). Describing the many-body effects by cluster dynamical mean-field theory, we find that Mn_4 is predominantly a Hubbard insulator with strong electron correlations. The calculated electron gap (1.8 eV) agrees well with the results of optical conductivity measurements, while other methods, which neglect many-body effects or treat them in a simplified manner, do not provide such an agreement. Strong electron correlations in Mn_4 may have important implications for possible future applications.

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Single molecule magnets (SMMs), made of exchange-coupled magnetic ions surrounded by large organic ligands, represent a novel and interesting class of magnetic materials. They are of fundamental interest as test systems for studying magnetism at nanoscale and interplay between the structural, electronic, and magnetic properties. SMMs demonstrate a fascinating mixture of classical and quantum properties: as classical superparamagnets, they possess large anisotropy and magnetic moment and also exhibit interesting mesoscopic quantum spin effects.¹⁻³ Moreover, recent experiments on the electron transport through SMMs,⁴ and predicted connection between the transport and spin tunneling,⁵ make SMMs good candidates for interesting spintronics studies. Progress in this area—synthesis of novel SMMs with optimized properties, design, and analysis of the transport experiments and possible uses in information processing—demands detailed theoretical investigations of the magnetic and electronic structures of SMMs.⁶⁻¹⁰ Among other factors, the many-body correlations caused by the Coulomb repulsion between electrons may be important. For example, in transition metal-oxide systems,¹¹ which share many similarities with SMMs, strong correlations may form the Mott-Hubbard insulating state,¹² where the nature of the charge and spin excitations is drastically different from the predictions of standard band-insulator theory. This affects the basic properties of the system (e.g., exchange interactions) and drastically changes charge and spin transport.

In this joint experimental-theoretical work, we present a detailed study of the many-body effects in electronic structure of SMMs $(pyH)_3[Mn_4O_3Cl_7(OAc)_3] \cdot 2MeCN$ (denoted below as Mn_4 for brevity).¹⁹ We use the cluster local density approximation (LDA)+dynamical mean-field theory (DMFT) method¹³ that combines the realistic *ab initio* calculations based on the LDA and the accurate description of the correlation effects within the cluster dynamical mean field theory (CDMFT). By using the electron gap as a most convenient benchmark, we show that the gap value (1.8 eV) calculated within LDA+CDMFT is in good agreement with

the optical conductivity measurements (showing the peak that corresponds to vertical transitions at ~ 1.8 eV). The approaches that neglect the electron correlations (LDA), or treat these correlations in a simplified manner [LDA+U (Ref. 15)], do not provide such agreement. Based on LDA+CDMFT calculations, we establish that Mn_4 is a predominantly Mott-Hubbard insulator with strong electron correlations. These correlations are important for description of ground-state properties of Mn_4 (intramolecule exchange interactions, spin ground state, etc.) and may be crucial for future studies of transport through Mn_4 molecules.

It is important to note that DMFT currently provides the most advanced description of the correlation effects and is actively used to describe correlations in many materials.¹⁴ However, its use so far has been restricted to the systems containing only a few atoms per unit cell.^{14,16-18} The present work is an example of applying the LDA+CDMFT method to large systems with very low molecular symmetry, containing 80 atoms per unit cell, establishing feasibility of such calculations and reliability of results. Moreover, the LDA+CDMFT method allows studies of the electronic structure of Mn_4 at finite temperatures.

The family of Mn_4 SMMs^{3,19-21} includes different compounds that have structurally similar cores made of four Mn ions located in the corners of distorted tetrahedron, but possess different ligands, and exhibit different magnetic and electronic properties. Here, the $(pyH)_3[Mn_4O_3Cl_7(OAc)_3] \cdot 2MeCN$ molecules studied contain three ferromagnetically coupled Mn^{3+} ions (spin 2) which antiferromagnetically interact with the fourth Mn^{4+} ion (spin 3/2), thus leading to the total ground-state spin $S=9/2$.

Electronic structure of many SMMs, including dimers of the Mn_4 family, has been previously studied by using the density functional theory within generalized gradient approximation.^{9,10} These methods describe well the magnetic moments of individual ions and magnetic anisotropy energy, but do not take into account the correlation effects, which are

important for many transition metal-oxide systems¹¹ and for SMMs (where the transition metal ions are coupled via oxygens).^{6–8,22} As a result, the value of the electronic gap is underestimated, while the magnitude of the superexchange coupling between magnetic ions is seriously overestimated (by a factor of 3 for V_{15} SMMs and for Mn_4 dimers). The electron correlations can be treated in a simplified way by using the LDA+ U approach,¹⁵ which takes into account the on-site Coulomb repulsion between the electrons (quantified by the energy U) and the intra-atomic Hund exchange (quantified by the parameter J). The LDA+ U calculations^{6–8,22} have shown that even a simplified account of many-body effects in SMMs leads to much better agreement between theory and experiment: e.g., for V_{15} , the electronic gap, positions of the bands, as well as the exchange interaction parameters agree with experiment within 20%–30%.

For electronic structure of Mn_4 , we first used the single-electron LDA and LDA+ U methods. The calculations have been performed by using the atomic sphere approximation—linear muffin-tin orbitals (LMTO) method,²³ as reported in our earlier works.^{6–8,22,24} Based on the agreement with experiments achieved in Refs. 7 and 24, we used the values $U=4$ eV and $J=0.9$ eV for Mn atoms. The experimentally determined structure was employed. The resulting densities of states (DOSs) are given in Fig. 1 with small additional broadening to make a simpler comparison with LDA+CDMFT results. The LDA results, giving finite electron density at the Fermi energy, cannot reproduce the correct insulating states of SMMs and are not discussed.

The LDA+ U calculations give a finite gap of 0.9 eV, thus demonstrating the importance of the Coulomb interaction effects.²⁶ However, the calculated gap is much smaller than the experimentally measured one (~ 1.8 eV for vertical excitations; see below). Also, LDA+ U calculations give no information about the dependence of the gap on temperature, and the nature of the gap is unclear: it may be of band origin, magnetic origin, or the Hubbard origin (caused by the Coulomb repulsion between electrons). Furthermore, the LDA+ U scheme predicts correct values for the magnetic moments, $3.20\mu_B$ on Mn^{4+} and $4.32\mu_B$ on Mn^{3+} ions. Also, we calculated the exchange parameters J_{ij} in the Heisenberg spin Hamiltonian $H=\sum_{i,j}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$ (where \mathbf{S}_i are the spins of Mn ions), assuming spin configuration where Mn^{3+} spins are directed up and the Mn^{4+} spin is directed down. The calculated couplings between Mn^{4+} and Mn^{3+} are -29 , -14 , and -12 K, and the couplings within the Mn^{3+} triangle are about 75 K, which is in qualitative agreement with the previously reported exchanges.^{19,20} The exact diagonalization of the Heisenberg exchange Hamiltonian yields the correct $S=9/2$ ground state of Mn_4 , but the excited spin states are not correctly reproduced. Also, the exchange parameters strongly depend on the spin configuration: for ferromagnetic arrangement of all Mn spins (i.e., with reversed spin of Mn^{4+}), the Mn^{3+} - Mn^{4+} exchanges increase by a factor of 2. Therefore, the LDA+ U scheme provides only a qualitative description of electronic and magnetic properties of Mn_4 . This is in striking contrast to the V_{15} SMM, where the LDA+ U results are in very good quantitative agreement with a wide range of experiments from x-ray spectroscopy to magnetic susceptibility measurements.^{6,8} The difference is due to the limited

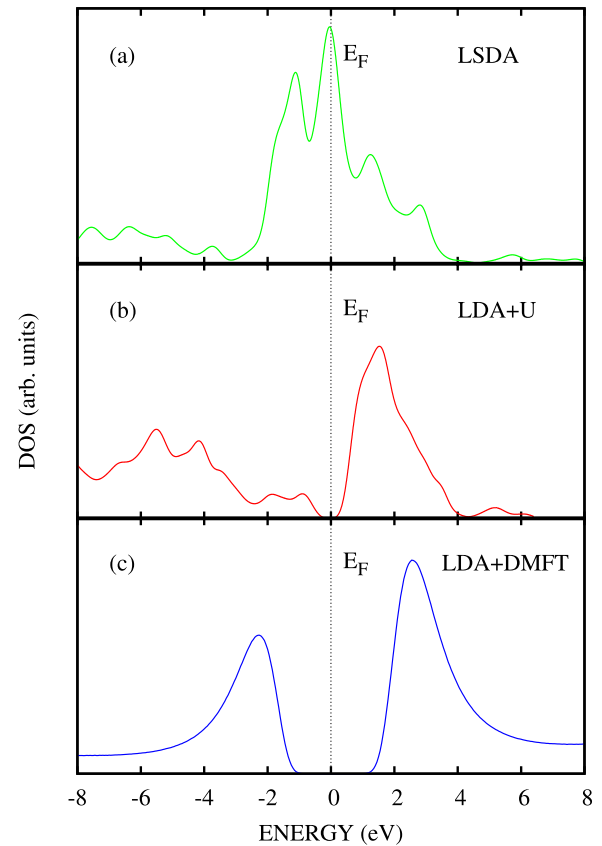


FIG. 1. (Color online) Densities of states (DOSs) for Mn 3d orbitals of Mn_4 calculated using (a) local spin density approximation; (b) local density approximation taking into account one-site Coulomb repulsion (LDA+ U) for $U=4$ eV, $J=0.9$ eV; (c) LDA+CDMFT approach for $U=4$ eV, $J=0.9$ eV, $\beta=8$ eV⁻¹.

account of the correlation effects by the LDA+ U scheme: for V_{15} , where many-body effects are moderate, LDA+ U is adequate, while in Mn_4 , where the many-body effects are very strong, this is not so.

A detailed account of the electron correlations for Mn_4 is achieved by using the DMFT within the cluster LDA+DMFT scheme.^{13,16,17} Unlike density functional approaches, DMFT considers the total energy of the system (more accurately, the thermodynamic potential) as a functional of the Green's function instead of the density matrix. The analytical properties of the Green's function guarantee that the knowledge of the spectral density is equivalent to the knowledge of the time-dependent Green's function, whereas the density matrix is only static value of the latter. The CDMFT approach maps the many-body crystal system onto an effective self-consistent multiorbital quantum impurity-cluster problem.¹³ The Green's function matrix is calculated via the Brillouin zone integration. We downfolded the full LMTO Hamiltonian to the basis of four Mn d orbitals in the unit cell and performed CDMFT calculations with the four Mn atoms. We found that hybridization to neighboring Mn atoms in SMM crystal is negligible, and already the first CDMFT iteration gives a reasonable solution of the LDA+CDMFT scheme. The only important quantity that needs to be self-consistently found is the value of the many-body

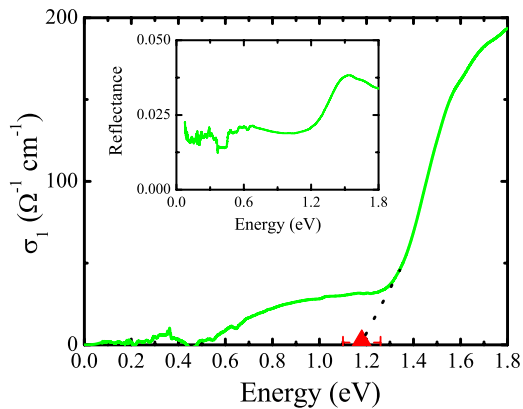


FIG. 2. (Color online) Optical conductivity of Mn_4 at 300 K, which is obtained from a Kramers–Kronig analysis of the measured reflectance (inset) on the $[2\bar{2}1]$ crystal face. The red triangle shows the onset of optical absorption due to Mn charge transfer excitations with the corresponding error bar (1.18 ± 0.08 eV). The peak (~ 1.8 eV) corresponds to the vertical excitations. The residual ac conductivity between 0.6 and 1.2 eV is attributable to the organic constituents.

chemical potential, which gives the number of d electrons in the Mn_4 cluster.

The cluster impurity solution within LDA+CDMFT method was carried out by using the multiorbital quantum Monte Carlo (QMC) simulations¹⁷ for four Mn atoms with full d -shell basis with the same Coulomb interaction parameters ($U=4$ eV), starting from high temperature $\beta=8$ eV⁻¹ (corresponding to the temperature $T=1450$ K) down to the actual experimental temperature $T=305$ K ($\beta=38$ eV⁻¹). The value of the gap given by the LDA+CDMFT method is 1.80 eV, which is two times higher than the gap given by the LDA+ U method, and is practically independent of temperature. The DOSs were calculated by using the maximum-entropy continuation from the imaginary time axis; the results are given in Fig. 1(c) for $T=1450$ K.²⁸ One can see the formation of the broad Hubbard bands due to strong interactions between four Mn atoms in the cluster. Note that similar broad Hubbard bands exist in theoretical description and x-ray spectroscopy of manganite compounds.²⁹

In order to check our LDA+CDMFT calculations, in particular, the value of the gap (which can clearly differentiate between the LDA, LDA+ U , and LDA+CDMFT results), we measured the optical properties of Mn_4 . Figure 2 displays the optical conductivity of Mn_4 measured on the $[2\bar{2}1]$ crystal face.³⁰ Based upon the electronic structure results and comparison with chemically similar model materials, we assign the 1.8 eV peak to a superposition of Mn^{3+} to Mn^{4+} charge transfer excitations of the distorted $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$ core and (much lower intensity) d -to- d on-site excitations of the Mn centers. The interest in microscopic conduction pathways in

molecular magnets has motivated several combined transport, optical, and theoretical studies.^{4,7,21,31–33} These investigations showed that exact gap values depend on the nature of the experimental probe and its associated length scale, although overall trends for chemically similar materials are consistent. While the optical gap in Mn_4 is experimentally determined by extrapolation of the leading edge of the 1.8 eV band to zero conductivity (1.18 ± 0.08 eV), the peak of this excitation marks the $\Delta k=0$ transitions and the maximum in the joint density of states. The peak value (~ 1.8 eV) should thus be compared to theoretical predictions. The weaker feature between 0.6 and 1.2 eV derives from the organic constituents, which is consistent with the data from the $[3\bar{2}\bar{1}]$ crystal face that has increased sensitivity to these structures.

The agreement between experiment and the LDA+CDMFT predictions, and lack of such agreement for LDA and LDA+ U methods, clearly demonstrates the importance of the correlation effects in Mn_4 SMMs. These correlations may persist in functionalized Mn_4 SMMs: deposition of SMMs on the metal substrates may have little effect on their electronic structure (unless charging effects or mechanical deformations occur).^{24,25} The correlation effects may also be crucial for transport through Mn_4 , due to peculiar nature of carriers in the Hubbard bands, and for intramolecular exchanges (which are still too complex for LDA+CDMFT). Our work presents only the first step in this interesting direction, and further studies are required.

Summarizing, we have investigated the correlation effects in electronic structure of Mn_4 SMMs. Theoretical studies employed (i) the LDA that neglects the electron correlations, (ii) LDA+ U method that describes correlations in a simplified way, and (iii) LDA+CDMFT method that provides a detailed account of the many-electron effects within the cluster dynamical mean-field theory. The measurements of the optical conductivity have been used to determine the electronic gap in $(\text{pyH})_3[\text{Mn}_4\text{O}_3\text{Cl}_7(\text{OAc})_3] \cdot 2\text{MeCN}$. Among the three theoretical approaches, only LDA+CDMFT predicts a gap consistent with experimental measurements, clearly demonstrating importance of the electron correlations. The LDA+CDMFT calculations evidence the predominantly Hubbard insulator state of Mn_4 . Based on similarities with other Mn-oxide strongly correlated systems,^{34,35} one may expect the correlations to be important for magnetic and transport properties of Mn_4 .

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