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Mark R. Pederson
Naval Research Laboratory

Jens Kortus
Max-Planck-Institut für Festkörperforschung

S. N. Khanna
Virginia Commonwealth University

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Mark R. Pederson[a]
Center for Computational Materials Science, Code 6390, Naval Research Laboratory, Washington, DC 20375-5000

Jens Kortus
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

S. N. Khanna
Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284-2000

We have performed density-functional-based electronic structure calculations on a single Fe_8 molecular nanomagnet. Our calculated total moments and local moments are in excellent agreement with experiment. By including spin–orbit coupling we determine the easy, medium, and hard axes and find the ordering of the principle axes also agrees with experiment. From our calculated anisotropy Hamiltonian, we calculate the oscillations in the tunnel splittings and compare to the experimental results. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1450786]

Recent experiments on molecular magnetic clusters[1–7] have revealed the phenomena of quantum tunneling of magnetization. For systems with a second-order anisotropy Hamiltonian [e.g., $W = -DS_z^2 + E(S_x^2 - S_y^2)$] there are two types of experiments that can be performed. In the first experiment, which is primarily applicable to systems that are exactly or approximately uniaxial (e.g., $D \gg E$) with an easy axis ($D > 0$), a magnetic field is applied parallel to the easy axis (B_z) and states of different M_s on opposite sides of the barrier are brought into resonance allowing for tunneling mechanisms. This experiment allows for the direct measurement of D since the resonance conditions correspond to magnetic fields which are an integer multiplied by D and fundamental constants. For nonuniaxial systems, which can always be described by $D > 0$ and E non-negligible, Garg has shown that a second experiment allows for the measurement of $[2E(D+E)]^{1/2}$.[8] In this experiment, the anisotropy Hamiltonian splits the $2S+1$ states into S two-fold and one non-degenerate states. Upon application of a magnetic field along the hard axis (B_x) the pairs of two-fold states cross with a frequency proportional to $[2E(D+E)]^{1/2}$ which again allows for tunneling mechanisms to occur when the resonance condition is satisfied. The Mn_{12}–acetate molecule with a molecular formula $Mn_{12}O_{12}(OOCCH_3)_{16}(H_2O)_4$ is a well studied system which fits into the first category (e.g., $D > 0$ and $E = 0$).[1–3] The octanuclear iron (III) oxo-hydroxo cluster (Fe_8)[4–6] is another molecular magnet which allows for the observation of the second type of tunneling mechanism.

As pointed out earlier by van Vleck,[9] the magnetic anisotropy Hamiltonian, which ultimately controls the afore-mentioned tunneling resonances, arises because of spin–orbit coupling and other relativistic terms. For over a decade, it has been recognized that the calculation of magnetic anisotropies are, in principle, possible within density-functional theory (DFT)[10] and many researchers have performed such calculations on solids and films.[11] Problems associated with the accurate density-functional-based determination of MAE in the solid state have been identified and the role of incomplete orbital polarization has been shown to be one issue related to inaccuracies in the solid.

The electronic and magnetic structure of the Mn_{12}–acetate molecule has recently been determined within the framework of DFT.[12,13] The resulting electronic structure showed an insulating behavior and all magnetic properties were in reasonable agreement with experiment. In particular, the total moment, ferrimagnetic ordering, and second-order anisotropy parameter matched the experimental data quite well. The good agreement for the case of Mn_{12} may be relatively unsurprising since the on-site filling of $Mn(3d)$ states is determined entirely by strong covalent bonding to neighboring ligands or to strong Jahn–Teller distortions. In this work, we describe recent efforts at deriving the same properties for the Fe_8 molecule and compare our results to experiment.

The DFT calculations[14] discussed herein were performed with the all-electron Gaussian-orbital-based NRLMOL program.[15] All calculations employed the Perdew–Burke–Ernzerhof generalized-gradient approximation for the density functional.[16] NRLMOL combines large Gaussian-orbital-basis sets, numerically precise variational integration, and an analytic solution of Poisson's equation in order to accurately determine the self-consistent potentials, secular matrix, total energies, and Hellmann–Feynman–Pulay forces.[17] The ex-

[a]Author to whom all correspondence should be addressed; electronic mail: pederson@dave.nrl.navy.mil
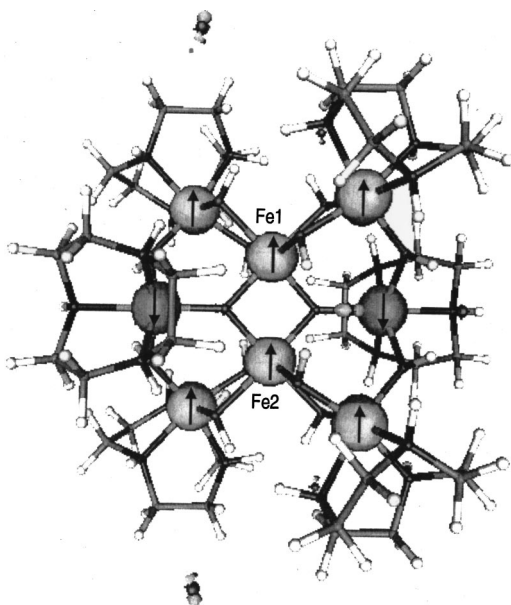
FIG. 1. Optimized geometry and spin configuration of the Fe_8 cluster. The large balls show isosurfaces of the spin density at $\pm 0.08 e/a.u.^3$. Arrows represent the ferrimagnetic spin ordering in the cluster. On top and bottom, a fluorine atom can be seen, which also has small spin polarization.
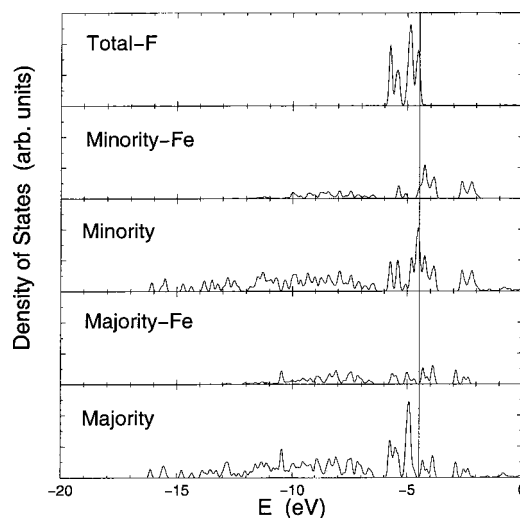

FIG. 2. Total and projected density of states for the fluorinated Fe_8 complex near the Fermi level as calculated within GGA. The halide p states appear at the Fermi level.

ponents for the single Gaussians have been fully optimized for DFT calculations.[18] The basis set for the fluorinated cluster consisted of a total of 1466 contracted orbitals while the basis set for the brominated cluster consisted of a total of 1562 contracted orbitals. Basis sets are available upon request. Using x-ray data deposited at the Cambridge Crystallographic Data Center[19] we generated the Fe_8 cluster. For these calculations, we follow the same method used in Ref. 12 to start our calculations with overlapping atomic potentials. To further allow for the possibility of spin ordering, we add to this potential an empirical starting potential which favors the spin ordering shown in Fig. 1. After the first iteration, this potential is removed and all the electronic and spin degrees of freedom are optimized variationally.

The structure of the Fe_8 cluster is shown in Fig. 1. The approximate D_2 symmetry observed in the molecule,[19] is formally broken by the presence of halide atoms and waters of crystallization. The central iron atoms are connected by oxo-hydroxo bridges to the four outer iron ions. The large spheres show the iron Fe(III) ions with a d^5 electron configuration. The ferrimagnetic coupling of spins between the eight Fe atoms results in an $S = 10$ spin ground state[20] and is illustrated by arrows inside the spheres in Fig. 1. The organic *tacn* rings are very important for stabilizing the magnetic core of the molecule because the three pairs of nitrogen dangling bonds complete a quasi-six-fold environment for the Fe atoms. Further, the *tacn* rings separate the Fe_8 clusters in the crystal, resulting in negligible intermolecular dipole fields which are typically on the order of 0.05 T.[6] The resulting formal charge states are nominally Fe^{3+}, $(OH)^{-1} O^{-2}$, and $tacn^0$ leading to a molecule with an overall formal charge state of $+8$ which may then be compensated by the eight negatively charged halide ions

In order to make the problem computationally tractable, we have adopted an isolated Fe_8 geometry with the D_2 symmetry plus inversion, and replaced the Br anions by F anions. This leads to a 186 atom Fe_8 complex with 50 inequivalent atoms. In the actual crystal, the halide ions break this symmetry. The magnetic core with iron and the oxo-hydroxo bridges is unchanged by our chosen symmetry operations.

The results of our calculations (Fig. 1) confirm that there are two minority spin iron atoms and six majority spin iron atoms, all of which carry a local moments of approximate $5 \mu_B$. We find a total spin moment of $20 \mu_B$. The density of states for the Fe_8 complex is summarized in Fig. 2. We have used a Fermi function with an electronic temperature of 0.001 a.u. for the occupation of states near the Fermi level.

The larger spheres in Fig. 1 are isosurfaces of the spin density showing that we indeed obtain the same magnetic ordering observed in experiment by Pontillon *et al.*[21] However some degree of spin polarization is visible in the region of the nominally closed-shell fluorine atoms. The minor polarization of the halide anions may be quenched in the solid by a variety of interactions which include additional Madelung stabilization or polarization due to the inclusion of the waters of solvation. Alternatively, additional interactions which may be improperly accounted for within the existing approximations to the DFT could be needed. A more detailed discussion will appear elsewhere. The recent experiments by Pontillon *et al.*[21] confirm not only the ferrimagnetic ordering but find smaller local moments on the two minority-spin iron atoms than on the six majority-spin iron atoms. In order to ascertain changes in the local moments as a function of atom type, we placed a sphere of 1.32 Å around each iron, and calculated the net moment inside each sphere. For the two iron atoms with minority spins, we obtain a moment of $-3.6 \mu_B$, whereas the majority-spin irons have moments $3.8 \mu_B$ and $3.9 \mu_B$ which is in qualitative accord with experiment. The plot of the spin density also confirms the correct spin polarization of the irons by showing a spherical spin

density around the Fe as expected for a closed-shell d^5 electron configuration.

To further address the experiments on this molecule, we have used a variant of the methodology discussed in Ref. 12 to determine the spin–orbit energy as a function of different magnetization directions which yields an anisotropy Hamiltonian with the general form $H = \Sigma_{x,y} \gamma_{xy} S_x S_y$. Diagonalizing this particular anisotropy Hamiltonian defines the set of principal axes and in the most general case identifies the easy, medium, and hard axes. We obtain the following eigenvalues for the diagonal anisotropy Hamiltonian: $\gamma_{xx} = -6.325$ K, $\gamma_{yy} = -6.2165$ K, and $\gamma_{zz} = -6.8045$ K. The medium axis is aligned along the two central iron atoms (Fe1–Fe2) in the middle of Fig. 1. All axes are in very good agreement with experiment.[22] From the eigenvalues of the spin Hamiltonian, we obtain a classical barrier of 59 K between the easy and hard axis, and 48 K between the easy and medium axis. Translating these results into the form proposed by Barra *et al.*[4,22] (e.g., $W = -DS_z^2 + E(S_x^2 - S_y^2)$) would correspond to $D = -0.53$ K and $E = 0.054$ K, with the anisotropy D parameter too large by a factor of 2, whereas E agrees very well with experiment.

Although our D does not quantitatively agree with experimental findings,[4,3,20,22] we point out that our D and E anisotropy parameters give a better agreement with the measured period of oscillations for the tunnel splitting which only depends on D and E. The period of oscillation has been given by Garg[8] to be $\Delta H = (2k_B/g\mu_B)\sqrt{2E(E+D)}$, and we have numerically verified this analytic result by direct diagonalization of the anisotropy Hamiltonian. Experiment observes $\Delta H \sim 0.4$ T,[7] whereas we obtain a value of 0.37 T, in better agreement than the previous value of 0.26 T deduced from the experimentally determined D and E parameters.[7] However, as discussed in Ref. 7, higher-order terms in the anisotropy Hamiltonian, which have also been experimentally determined, also increase the tunnel oscillation to the experimental value.

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