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Optimized Geometry of the Cluster Gd_2O_3 and Proposed Antiferromagnetic Alignment of f-Electron Magnetic Moment

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There is currently experimental interest in assemblies of Gd_2O_3 clusters. This has motivated the present study in which a single such cluster in free space is examined quantitatively by spin-density functional theory, with appropriate relativistic corrections incorporated for Gd. First, the nuclear geometry of the cluster is optimized, and it is found to be such that the two Gd atoms lie in a symmetry axis perpendicular to the isosceles triangle formed by the O atoms. Then, a careful study is made of the magnetic arrangement of the localized f-electron moments on the two Gd atoms. The prediction of the present treatment is that the localized spins are aligned antiferromagnetically. An alternative picture using superexchange ideas leads to the same conclusion.

I. Introduction

This work is motivated by the recent interest in Gd_2O_3 clusters.[1] In this work, the Gd_2O_3 clusters show quantum confinement effects, and the electronic energy gap was found to evolve with size, showing a trend similar to other more covalent materials. The authors also speculated about the sensitivity to stress, because the particles are very small, but little sensitivity was found. However, the changes induced in the electronic structure by ionic effects or by the magnetic coupling of the Gd atoms were not considered.

Gadolinium oxide is a rather ionic material. One of us, in earlier work with Alonso,[2−5] addressed aspects of clusters with typically ionic bonding that can be ionized;[6,7] and also, with Kunz,[8] addressed the evolution of electronic properties with size in some clusters with partially ionic bonding, such as MgO.[9] Later, we made theoretical studies of rare-earth metals in combination with covalent bonds[10] (La−C systems) or magnetic impurities in some covalent semiconductors with highly ionic character, such GaAs and GaN.[11−13] These subjects are brought together in this work. The study of Gd−O bonding combines high ionicity (of a rare-earth material, Gd) with magnetic behavior involving local spin-polarization (due to half-full f-electronic shells).

Here, we restrict our attention to the smaller tridimensional Gd_2O_3 cluster viewable as a nanocrystal. The geometry of this unit (see Figure 1) is rationalized in a manner similar to that of the structure of the ionic and the ionized clusters of alkalide-halides,[6,7] whereas the method is the same as in ref 10. Sections II and III describe the computational details and the geometrical results, respectively. We study the magnetic coupling as well as the magnetic impurities in our previous works.[11−13] Section IV includes our discussion about the magnetic alignment of f electrons in Gd. A summary and some proposal for future directions constitute Section V.

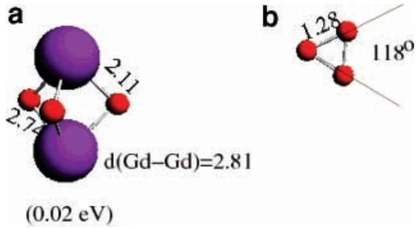

Figure 1. (a) Geometry of a Gd_2O_3 cluster. Gd atoms are large (violet) spheres, and oxygen ones are small (red) spheres. For comparison purposes, the triangular O_3 is also shown in panel b. Distances (in Å) and angles (°) are written in the plot. In parenthesis, under panel a, we give the energy difference Δ_{FM-AFM} between FM and AFM configurations of Gd atoms.

II. Methods

To analyze the effect of geometry on the energy, we have relaxed all atomic coordinates for the geometry of Figure 1a, assuming a tridimensional geometry as was earlier found for these nanocrystals.[1] We use density functional theory (DFT) with the generalized gradient approximation (GGA) for exchange and correlation effects. The calculations were performed with the Amsterdam density functional (ADF) code[14] using the GGA exchange−correlation functional[15] and including relativistic effects in the zero-order regular approximation (ZORA).[16] The basis set is designated TZ2P: it is a triple-ζ quality and has been augmented with two sets of polarization functions on each atom. To accelerate convergence, the orbitals of atomic cores were frozen, O.1s for O and Gd.5p for Gd.

There are not that many local minima in the global landscape taken into account that the Gd has a positive charge and prefers to be close to the negative oxygen to minimize Coulomb interactions, as we will see later. Anyhow other arrangements of the atoms were also tested, such as planar and linear configurations. They were found lying with more than 1 eV

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from the ground-state, which is the one given in Figure 1. Additionally, spin states other than those presented here were also calculated. However, they were not the ground-state, and these were not shown in this work because the spin promotion induces one-electron levels that do not follow aufbau occupations, with empty levels below the highest occupied molecular orbital (HOMO).

III. Nuclear Geometry of Isolated Gd_2O_3 Cluster in Free Space

The results are given in Figure 1 with a summary of the corresponding bond lengths. For the ferromagnetic (FM) case the point group is D_{3h}, with irreducible representations A_1', A_2', E', A_1'', A_2'', and E'', and they can label the electronic levels of Figure 1a. The antiferromagnetic (AFM) case has less symmetry, and the point-group changes to C_{3v}, with irreducible representations A_1, E_1, and A_2. Our distances are slightly smaller for the AFM configuration, but they are the same up to the second digit. Thus, a single geometry is shown in Figure 1a, even when we choose their respective relaxed configurations for the following plots. The Gd−O distance is 2.81 Å, whereas the Gd−Gd one is 2.11 Å. These values mean that the O−O distance is 2.74 Å, which is clearly larger than in the ozone O_3 triangular cluster by more that one Angström. This finding indicates a dramatic reorganization of the electrons around the oxygen, presumably because of charge transfer to make the oxygen centers 2− ions (as indeed we argue in more detail in the next section).

IV. Magnetic Alignment of Localized f-Electron Moments on Gd Atom

A. Results of Spin-Density Full Theory. The ground-state configuration corresponds to the AFM case with an energy gain of 0.02 eV, which is not negligible as a “magnetic” energy. For example, we can recall that for clusters of magnetic transition metals such as Fe, Co, and Ni, the energy cost to flip an atom is on the order of few meV.[17]

We now address the question concerning the bonding, starting with an examination of the orbital electronic levels. The calculated levels are plotted in Figure 2 for the (a) FM and (b) AFM spin alignments. On the left side of Figure 2a we have also indicated the main character of the atomic contributions. The low-lying levels come from the oxygen 2s-level, which sum up to three electronic levels with double occupations. Next, the 4f-levels of Gd are situated slightly lower in energy than the oxygen 2p-levels. Although mainly on Gd, the f-levels are broader for the FM cases than for the AFM one, and they are strongly influenced by the oxygen p-levels; for instance, one notes the strong hybridization of the middle orbital in Figure 2a. The global AFM magnetization is also zero, as it is in the paramagnetic calculation. The small inset in Figure 2b allows us to check that the Gd−Gd interaction is, in effect, AFM, because the up (down) orbitals only participate in the first (second) Gd atom.

In principle, the naive picture concerning charge redistribution that we have in mind is as follows. There is full charge transfer of six Gd electrons (two s and one d for each Gd atom) to the three oxygens. Each O atom accommodates two such transferred electrons. This extra charge is one of the implicit problems of allowing convergence in these calculations. Although some free ions such as O^{-2} are not well described by standard DFT codes, there is much less of a problem when in the field of nearby positive counter-ions.

Our levels seem to follow the previous charge-transfer picture, but in actuality, the situation is more complex because of the strong level mixing already seen in the hybridization of the orbitals in Figure 2. Thus, we have checked the charge transfer by several methods. The Mulliken analysis is already well-known and described in text books. With respect to each neutral paramagnetic fragment (atom in this work), the Hirshfeld charge analysis is given by the numerical integral of $\rho_{SCF}(r)q_{atom}/q_{sum}$, where the nuclear charges are included and electrons are counted as negative. The charge transfer out of Gd atoms is 1.22 electrons in the Mulliken sense and is 0.7 electrons in the Hirshfeld one. These values are clearly smaller than the charges ascribed previously in our naive picture, namely, three electrons from Gd. We also justify a posteriori the resemblance of this structure with the one found in a previous ionized cluster with typical ionic bonding.[6,7]

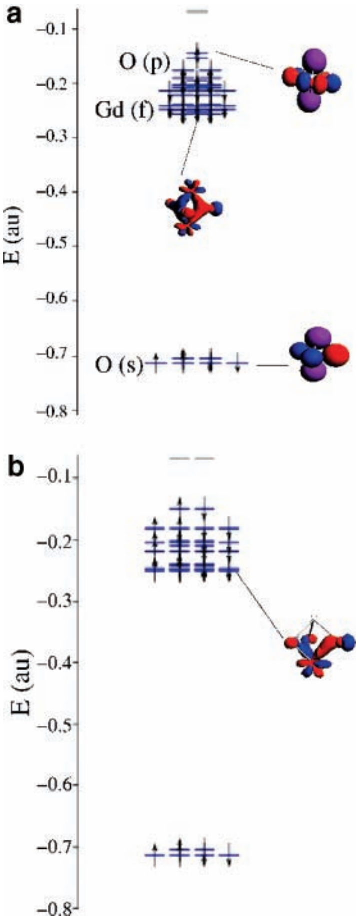

Figure 2. Energetic levels of the (a) ferromagnetic and (b) antiferromagnetic Gd_2O_3 cluster in atomic units. Their main atomic contribution is indicated in the left side, whereas on the right side some orbitals are plotted as examples to see their spatial distribution. In order to see the f-like orbitals, the Gd ions have been omitted.

The ferromagnetic configuration has a total spin of 14 μ_B. Following a Mulliken decomposition, this magnetic moment is distributed mainly on Gd^{3+} ions with a value of 7.029 μ_B, of course due to the f electrons. The local magnetic moment per O atom is −0.047 μ_B. The minus sign indicates that the small induced magnetic moment on O atoms is coupled antiferromagnetically to the Gd ones. This moment coupling follows the trends found in magnetic semiconductors.[11−13]

For the FM configuration, we have done further work to (perturbatively) include a magnetic field and the spin−orbit term. Then, use is made of the double group of D_{3h}, with additional symmetries (irreducible representations) $E_{1/2}$, $E_{3/2}$, $E_{5/2}$ and $E_{7/2}$. We align the magnetic field along symmetry-determined principal axes: first, along an axis that contains the

Gd atoms; and second, along another axis lying in the plane of the oxygens, symmetrically bisecting their triangular arrangement. The energetic difference for these two directions defines the so-called magnetic anisotropy energy (MAE). Our MAE is only 0.7 meV, which is, as usual, notably smaller than the magnetic FM−AFM differences. The easy axis, which gives the lower energy for the alignment of the field, is the one in the oxygen plane.

In a simple way, we know that Gd^{3+} with its half-filled 4f shell has orbital angular momentum $L = 0$, so the effects of the 1s term can be reasonably neglected. In fact, the magnetic anisotropy of bulk Gd provided by the spin−orbit splitting is very small, and comparable to traditional 3d ferromagnets (Fe, Co, and Ni), on the order of μeV. The magnetic anisotropy of bulk Gd metal is due to the 5d conduction electrons that transfer, via exchange interactions, the magnetic anisotropy to the 4f electrons.[18] When applying a magnetic field, which couples mainly with the f electrons, it would appear to be a magnetic anisotropy of the localized 4f states. However, our MAE for the Gd_2O_3 cluster is much larger and is very close to the values of Ni surface[19] and transition metal clusters,[20] with magnitudes on the order of meV. In comparison with bulk Gd, the large MAE of Gd_2O_3 is due to a different mechanism because the d-levels of Gd are nearly empty. The reason is again grounded in the strong f−p hybridization between Gd and O, as indicated by our charge-transfer analysis.

In addition, Figure 2 allows us to make some inferences concerning the gaps of nanoparticles. The HOMO−LUMO gaps are 2.03 and 2.25 eV in the panels (a) and (b), respectively, of Figure 2. The gap is larger in the AFM configuration as the f-levels become less strongly split. The FM−AFM gap difference (0.23 eV) is comparable to the variation of the gap of nanocrystals with a size range between 1 and 50 nm (0.27 eV from Figure 6 in ref 1). However, our gap value (2.25 eV) is around half the value found experimentally for the nanocrystals. This might convievably be due to an enhacement of ionicity in the larger experimental nanocrystals. But in any case, such an underestimation is a well-known consequence of the usual density approximation (GGA) used for the exchange and correlation functional in our work.

B. Superexchange. Elemental Gd is a Ruderman−Kittel−Kasuya−Yosida (RKKY) metallic ferromagnet par excellence. In particular, localized moments of 7 μ_B/atom from the Gd 4f-electrons are aligned parallel by RKKY oscillatory exchange interactions[21−23] mediated by the conduction electrons, which themselves are partially spin-polarized in parallel alignment to the f-electron moments. The overall measured magnetic moment per Gd atom is 7.55 μ_B.[24]

However, Gadolinium oxides have a different spin-coupling mechanism based on superexchange, sometimes called "kinetic" exchange. This mechanism may be viewed[25,26] in a perturbation-theoretical framework with a localized determinantal product of atomic-like orbitals of zero-order and is considered an effect of configuration mixing involving electron transfers between Gd and O centers. That is, the ground-state configuration involving two Gd centers and one of the bridging O centers is $Gd^{3+}O^{2-}Gd^{3+}$, with the O^{2-} closed shell ($2p^6$) and the Gd^{3+} exactly half-filled ($4f^7$). The relevant excited configurations involve just the lower energy configurations reachable via 1-electron transfers, such as the following;

$$Gd^{3+}O^{2-}Gd^{3+} \leftrightarrow Gd^{3+}O^{-}Gd^{2+} \leftrightarrow Gd^{4+}O^{2-}Gd^{2+}$$

and there is a symmetrically related chain (connecting to $Gd^{2+}O^{-}Gd^{3+}$ and $Gd^{2+}O^{2-}Gd^{4+}$). However, for the indicated triplet, one sees that for the first transfer, starting with ↿⇂ on the O^{2-}, this transfer to the f^7 Gd^{3+} on the right is facilitated if the transferred electron is oriented spin-opposite to that of this f^7 Gd^{3+} (because at half-filling the only low-energy orbitals available are those that already are singly occupied, so that the remaining unpaired electron on O^{-} is parallel to those of the f^7 Gd^{3+}). And for the second transfer from the Gd^{3+} on the left (to the O^{-}), the transfer must involve an electron of opposite spin to that of this remnant O^{-} electron. That is, the right-hand Gd^{3+} is favored to have spins antiparallel to that of the remnant O^{-} electron, whereas the left-hand Gd^{3+} is favored to have spins parallel to that of this same remnant O^{-} electron. Clearly, in the framework of the zero-order $Gd^{3+}O^{2-}Gd^{3+}$ space, energy lowering is favored when the two Gd^{3+} atoms have opposite spins, or equivalently, the coupling is of an AFM sign.

But there are other ways to phrase[27] this AFM result without recourse to such a perturbation-theoretical picture. For example, for parallel spins on the two Gd centers, the orbitals on these two centers delocalize (through f−p hybridization) onto the O center under a constraint of orthogonality enforced within coordinate space; whereas for antiparallel spins on the two Gd centers, the delocalation onto the O center is not subject to this constraint. Therefore, the resultant orbitals can adopt a lower-energy form; or said slightly differently, granted spatially non-orthogonal orbitals localized on the two centers, the problem parallels somewhat $H_{2,}$ which, of course, displays antiferromagnetically signed coupling.

Overall, we then anticipate an antiferromagnetically signed effective exchange coupling ($J > 0$), most simply described by a Heisenberg spin Hamiltonian (eq 1);

$$H = JS_AS_B \tag{1}$$

where A and B label the two Gd^{3+} ions, with spins S_A and S_B, respectively, each having spins of 7/2. With the constraint of the two centers being either fully parallel or fully antiparallel, one then obtains two energies, $E_{\uparrow\uparrow} = J(7/2)^2$ and $E_{\uparrow\downarrow} = -J(7/2),^2$ and taking their difference to correspond to our ab initio computed difference of 0.02 eV, one has $J = 2(0.02\ \mathrm{eV})/49 = 0.001$ eV. Of course, without the constraint of full alignment or counter-alignment between the two centers, the two-center Heisenberg model is trivially solved to give eq 2,

$$E(S) = \left\{S(S+1) - \frac{63}{2}\right\}J/2 \tag{2}$$

for each net spin $S = 0, 1, ..., 7$. Also, each level has a degeneracy of $2S + 1$.

V. Summary and Future Directions

The present study was motivated by the experimental study[1] of the nanoscaled insulating material Gd_2O_3 by means of vacuum ultraviolet excitation spectra of dopant Eu^{3+}. Although the principal results obtained here, using spin-density functional theory, are for the equilibrium structure and the magnetism of a single Gd_2O_3 cluster, we have been able, via Figure 2, to draw some inferences concerning the gaps of nanoparticles, which was a focal study in ref 1.

In a little more detail, the equilibrium geometry of the Gd_2O_3 cluster predicted by the present spin-density functional calculations is such that the two Gd atoms lie on a symmetry axis perpendicular to the plane of the three O atoms. However, the proximity of the Gd atoms is found to completely alter the chemistry of the isosceles triangular ozone molecule shown in Figure 1b, and the O−O distances change by more than 1 Å.

Furthermore, we anticipated, via qualitative arguments based on the mechanism of superexchange (see also Section IV B), that the Gd f-electron magnetic moments would align antiferromagnetically, and this conclusion is supported by the spin-density functional calculations presented here.

As for future directions, methods now exist to improve the DFT theory of energy gaps. It would clearly be of interest to apply these in the present context, to larger nanocrystals, and in the more general area of quantum confinement. Experiments on clusters in an inert matrix embracing the area of the present study would, of course, be important in testing the theoretical predictions made here for both equilibrium geometry and magnetic properties, should such observations prove feasible in the laboratory.

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References and Notes

(1) Mercier, B.; Ledoux, G.; Dujardin, C.; Nicolas, D.; Masenelli, B.; Mélinon, P.; Bergerel, G. *J. Chem. Phys.* **2007**, *126*, 044507.

(2) Aguado, A.; Ayuela, A.; Lopez, J. M.; Alonso, J. A. *Phys. Rev. B* **1997**, *56*, 15353.

(3) Ayuela, A.; Lopez, J. M.; Alonso, J. A.; Luaña, V. *Phys. B* **1995**, *212*, 329.

(4) Ayuela, A.; Lopez, J. M.; Alonso, J. A.; Luaña, V. *Z. Phys. D* **1993**, *26*, S213.

(5) Aguado, A.; Ayuela, A.; Lopez, J. M.; Alonso, J. A. *J. Phys. Chem. B* **1997**, *101*, 5944.

(6) Aguado, A.; Ayuela, A.; Lopez, J. M.; Alonso, J. A. *Phys. Rev. B* **1998**, *58*, 9972.

(7) Ayuela, A.; Lopez, J. M.; Alonso, J. A.; Luaa, V. *Can. J. Phys.* **1998**, *76*, 311.

(8) Recio, J. M.; Pandey, R.; Ayuela, A.; Kunz, A. B. *J. Chem. Phys.* **1993**, *98*, 4783.

(9) delaPuente, E.; Aguado, A.; Ayuela, A. A.; Lopez, J. M. *Phys. Rev. B* **1997**, *56*, 7607.

(10) Ayuela, A.; Seifert, G.; Schmidt, R. *Z. Phys. D* **1997**, *41*, 69.

(11) Hynninen, T.; Raebiger, H.; J. von Boehm, J.; Ayuela, A. *App. Phys. Lett.* **2006**, *88*, 122501.

(12) Raebiger, H.; Ayuela, A.; Nieminen, R. M. *J. Phys. Cond. Matter*. **2004**, *16*, L457.

(13) Raebiger, H.; Ayuela, A.; von Boehm, J. *Phys. Rev. B* **2005**, *72*, 014465.

(14) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comp. Chem.* **2001**, *22*, 931.

(15) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(16) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

(17) Pastor, G. M.; Dorantes-Dávila, J.; Bennemann, K. H. *Phys. Rev. B* **1989**, *40*, 7642.

(18) Colarieti-Tosti, M.; Burkert, T.; Eriksson, O.; Nordström, L.; Brooks, M. S. S. *Phys. Rev. B* **2005**, *72*, 094423.

(19) Burket, T.; Eriksson, O.; James, P.; Simak, S. I.; Johansson, B.; Norström, L. *Phys. Rev. B* **2004**, *69*, 104426.

(20) Nicolas, G.; Dorantes-Dávila, J.; Pastor, G. M. *Phys. Rev. B* **2006**, *74*, 014415.

(21) Ruderman, M. A.; Kittel, C. *Phys. Rev.* **1954**, *96*, 99.

(22) Kasuya, T. *Progr. Theoret. Phys.* **1956**, *16*, 45.

(23) Yosida, K. *Phys. Rev.* **1957**, 106.

(24) See for example, Chapter 7 In *Magnetism: Materials and Applications* du Trémolet de Lacheisserie, E., Gignoux, D., Schlenker, M., Eds.; Springer Science and Bussiness Media Inc.: New York, 2005; p 269.

(25) Anderson, P. W. *Phys. Rev.* **1959**, *106*, 893.

(26) Kefer, F.; Oguchi, T. *Phys. Rev.* **1959**, *115*, 1428.

(27) Waite, T. R. *J. Chem. Phys.* **1960**, *33*, 256.