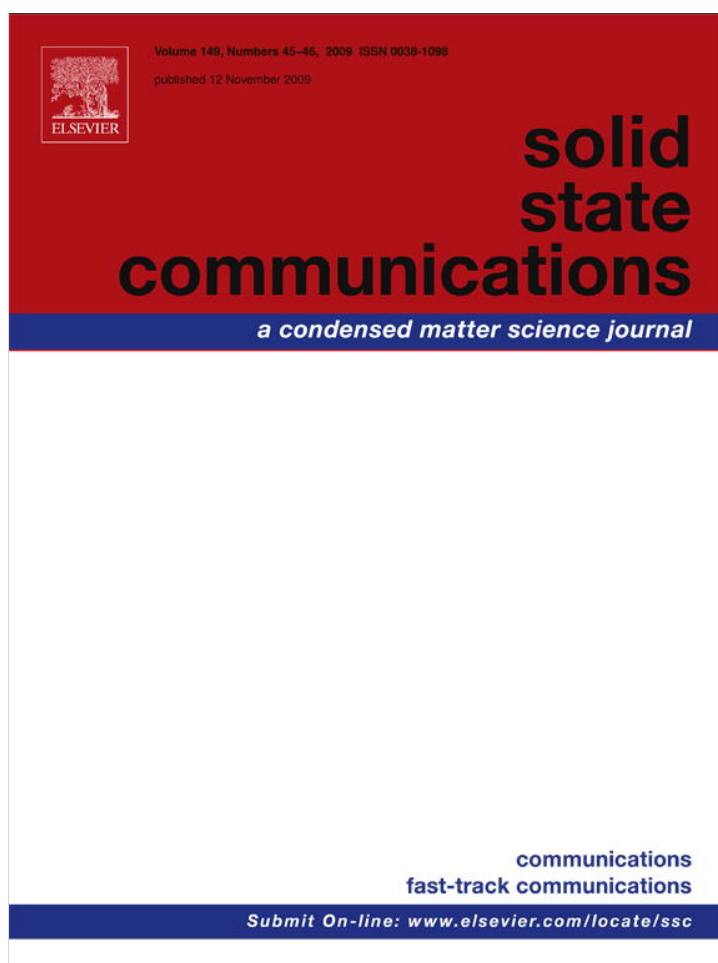


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Structure and magnetism of small Gd and Fe nanoclusters: LDA + U calculations

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ABSTRACT

We investigate the structure and magnetic characteristics of small metal nanoclusters consisting of Gd and/or Fe within the LDA + U density-functional approach. Pure Gd and Fe nanoclusters have larger ferromagnetic moments than their respective bulk counterparts. Among binary Fe–Gd nanoclusters of dimers, trimers, and tetramers, the Fe-rich nanoclusters are energetically favored with relatively small ferromagnetic moments and the Gd-rich nanoclusters prefer antiferromagnetic spin configurations, where Gd sites are spin up and Fe sites are spin down.

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1. Introduction

As a noninvasive diagnostic technique in clinical medicine, magnetic resonance imaging (MRI) visualizes the anatomical structure of the human body, based on the precession response of mainly hydrogen nuclei in water molecules to an applied magnetic field. To improve the contrast of the MRI images, contrast agents have been used [1,2]. Most of the promising MRI contrast agents are based on organic gadolinium (Gd) complexes [3–5], since Gd has the highest magnetic moment for positive contrast imaging. Another contrast agent is the superparamagnetic iron oxide nanoparticle for negative contrast imaging, which has become available recently [6]. So far, organic Gd-complexes have been used for the MRI technique but a large amount is necessary for diagnosis. On the other hand, bulk Gd has a smaller magnetic moment. To make things worse, it has less abundant surface atoms to attach to hydrogen nuclei compared to clusters. Therefore, the number of Gd (or Fe) atoms at the nanoscale needs to be optimized to enhance their contrast signal intensity. Searching for a promising agent with a higher magnetic moment will require a detailed understanding of

the structural properties and magnetic interaction of the magnetic clusters.

From the theoretical point of view, the magnetic properties of metal clusters have been limited to mainly 3d transition metals such as Fe and Co [7–11]. In spite of the recent experimental research into Gd nanoclusters for using an MRI contrast agent [12,13], no theoretical analysis for Gd nanoclusters has been reported yet. Furthermore, it is expected that the binding energy of Gd nanoclusters is structurally so weak that they might be dissociated easily in severe circumstances. On the other hand, Fe is known to be energetically stable. In the search for an MRI contrast agent with large magnetic moment and stability, we have considered nanoclusters of a Gd and Fe mixture. The alloy forms of Gd and Fe may sustain the high magnetic moments of Gd atoms while maintaining stable structures due to the presence of the Fe atoms. In this paper, we present the results of our density functional calculations for these stable structures of Gd and/or Fe clusters and their magnetic properties.

2. Calculation methods

Since the magnetic properties of the clusters depend closely on the optimization of the cluster structure, a theoretical understanding of the cluster magnetism depends on an accurate treatment of electron correlations. However, the state-of-the-art

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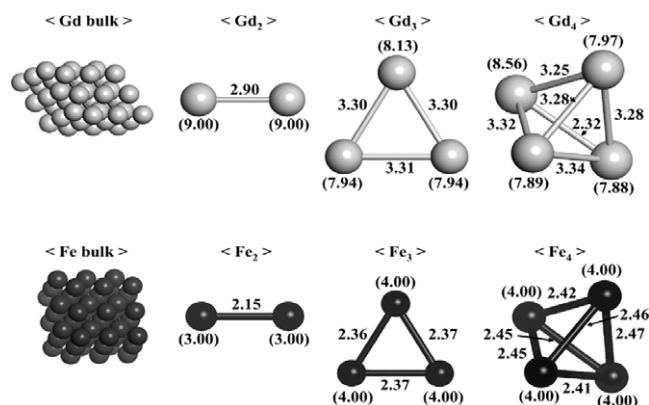


Fig. 1. Model structures of the optimized bulk, dimer, trimer and tetramer structures of Fe and Gd. The numbers in parentheses are the atomic magnetic moments in units of μ_B . The minus sign means the opposite spin direction to the plus sign. Bond lengths are also shown in the figures, in units of Å.

theoretical calculations of the structural and magnetic properties of transition metal clusters have been hampered by the abundance of low-lying electronic states and the possibility of multiple configuration due to the open d-shell nature of transition metal clusters. Owing to the vast size of the configuration space, there are severe computational restrictions for a full optimization of transition metal clusters [14]. In this work, to obtain the electronic structure and optimized geometry of transition metal clusters, we carried out first-principles calculations based on the density functional theory (DFT) within the local density approximation plus Hubbard U (LDA + U) [15] implemented in the OpenMX code [16]. Since the electron correlations in the localized d and f orbitals are crucial in the understanding of cluster magnetism [17], we employed the LDA + U method for the treatment of the Gd 4f, 5d and Fe 3d states. The effective on-site Coulomb parameter $U_{4f} = 6$ eV for Gd 4f electrons is found to be reasonable to describe the hcp Gd bulk [18] and the dimer structure, Gd₂ [19]. Considering the effect of the reduced coordination numbers and energy level widths, we also used $U_{5d} = 3$ eV for the Gd 5d orbitals and $U_{3d} = 4$ eV for the Fe 3d orbitals. For the Fe 3d orbitals, $U_{3d} = 4$ eV was used, which compares well with previous studies of iron oxides [20,21] and Fe clusters [22,23]. Kulik et al. compared the GGA + U and MRCI methods for the calculations of Fe₂ [23]. Their GGA + U results shows a consistent agreement with the MRCI results [24]. We believe that the general features which our model systems show within the LDA + U calculations would also occur in other calculational methods.

For the DFT calculations, we used the Ceperley–Alder-type exchange–correlation functional with the Troullier–Martins-type norm-conserving pseudopotentials [25] with a partial correction [26] by employing a linear-combination-of-localized-pseudo-atomic orbitals (LCPAO) method [27]. Double valence orbitals were used with a cutoff radius of 8.0 a.u. for Gd and 5.5 a.u. for Fe (1 a.u. is the Bohr radius). The relativistic effect, which could be important in heavy elements, was taken into account within the scalar relativistic formalism [28]. Real space grid techniques were used with an energy cutoff up to 400 Ry. The structures were relaxed until the Hellmann–Feynman forces were less than 0.03 eV/Å. In searching for the ground-state magnetic configurations of the nanoclusters, we considered small clusters ($n = 1-4$). For isomers, we determined the one with the lowest energy.

3. Results and discussion

Fig. 1 shows the fully relaxed geometries and magnetic moments of pure Gd and Fe clusters. In the calculation of bulk hcp Gd,

Table 1

Magnetic moments (μ_B /atom) and binding energies (eV/atom) of bulk, dimer, trimer and tetramer structures of Fe and Gd. Minus signs for binding energies represent exothermic processes.

Structure	Magnetic moment	Binding energy	Spin configuration
Bulk Gd	7.66	–	Ferro
Gd ₂	9.00	–0.285	Ferro
Gd ₃	8.00	–0.627	Ferro
Gd ₄	8.00	–0.928	Ferro
Bulk Fe	2.96	–	Ferro
Fe ₂	3.00	–1.185	Ferro
Fe ₃	4.00	–1.423	Ferro
Fe ₄	4.00	–1.648	Ferro

Table 2

Magnetic moments (μ_B /atom) and binding energies (eV/atom) of bulk, dimer, trimer and tetramer binary Fe–Gd cluster structures.

Structure	Magnetic moment	Binding energy	Spin configuration
FeGd	2.50	–0.610	^a Antiferromagnetic
FeGd ₂	5.33	–0.655	Antiferromagnetic
Fe ₂ Gd	4.67	–0.843	Ferrimagnetic
FeGd ₃	5.00	–0.355	Antiferromagnetic
Fe ₂ Gd ₂	2.00	–0.663	Antiferromagnetic
Fe ₃ Gd	4.50	–0.963	Ferrimagnetic

^a The antiferromagnetic configuration has antiparallel spins with different magnitudes.

the experimental lattice parameters ($a = 3.636$ Å, $c = 5.783$ Å) were used. Our LDA + U calculations show that the magnetic moment of bulk hcp Gd is 7.66 μ_B /atom, in good agreement with the experimental result (7.63 μ_B /atom) [29]. Among pure Gd clusters, Gd₂ has been attractive because of its highest magnetic moment. The electron spin resonance measurement revealed [30] that a Gd dimer has the magnetic moment of 9.0 μ_B /atom. For Gd₂ in our calculations, the bond length is 2.9 Å and the magnetic moment is 9.00 μ_B /atom, as listed in Table 1. According to the orbital-decomposed analysis, the moment of 9.00 μ_B /atom is mainly attributed to the increase of the 5d electron contributions as well as the 4f moment. This suggests that the ferromagnetic (FM) configuration is the ground state. In fact, the antiferromagnetic (AFM) configuration is less stable by ~ 0.6 eV [19]. On the other hand, the bond lengths in Gd₃ and Gd₄ are all about 3.3 Å. Their total magnetic moments are 18.0 and 32.0 μ_B , respectively, corresponding to 8.00 μ_B /atom on average (FM). Gd₄ prefers to form a tetrahedral structure rather than a planar structure.

Values for small Fe clusters have also been calculated. For bulk bcc Fe, the experimental lattice parameter ($a = 2.867$ Å) was used. A magnetic moment of 2.95 μ_B /atom ($U_{3d} = 4$ eV) was obtained for bulk bcc Fe, which is somewhat larger than the experimental result (2.2 μ_B /atom). For $U_{3d} = 0$, the calculated moment (2.26 μ_B /atom) of bulk bcc Fe is closer to the experimental value. Using $U_{3d} = 4$ eV, Fe₂ has a bond length of 2.15 Å, comparable with the experimental value of 2.02 Å [31], and a binding energy of 1.18 eV, which is in good agreement with an experimental value of 1.18 eV [32]. The rest of the calculations were done with $U_{3d} = 4$ eV. The lowest-energy configuration has a magnetic moment of 3.00 μ_B /atom (FM). In the cases of Fe₃ and Fe₄, their bond lengths are 2.37 and 2.45 Å, and their total magnetic moments are 12.00 and 16.0 μ_B , respectively, corresponding to 4.00 μ_B /atom. Similar to the case of Gd₄, the tetrahedral structure of iron tetramer (Fe₄) is lower in energy than the planar structure by ~ 0.3 eV.

Finally, we turn to small binary clusters consisting of both Gd and Fe atoms. In the case of an FeGd dimer, the bond length is 2.69 Å (see Fig. 2), with a binding energy of 0.61 eV (see Table 2). Interestingly, the spin configuration is antiferromagnetic (antiparallel spins with different magnitudes), yielding a small magnetic moment (spin down in the Fe atom and spin up in

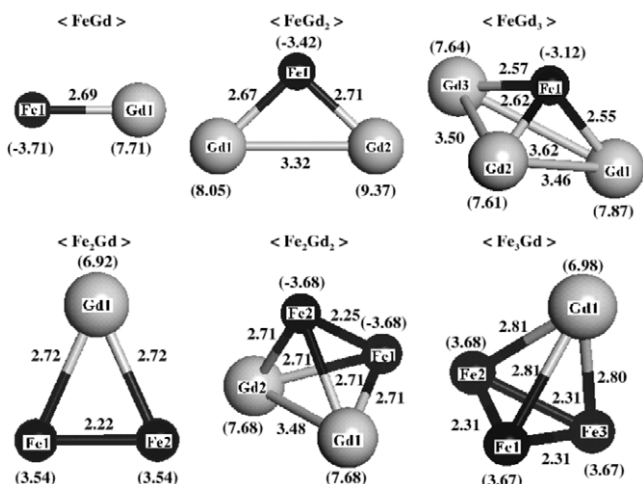


Fig. 2. Model structures of the optimized binary clusters consisting of Fe and Gd. The numbers in parentheses are atomic magnetic moments in units of μ_B . The minus sign means the opposite spin direction to the plus sign. Bond lengths are also shown in the figures, in units of Å.

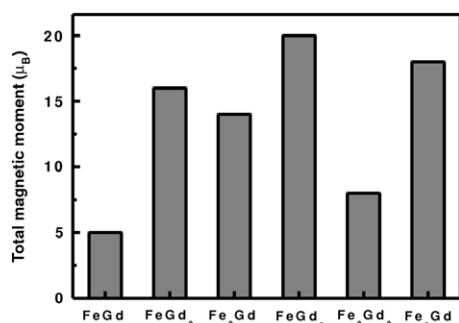


Fig. 3. Total magnetic moments (μ_B) of binary Fe–Gd nanoclusters. Gd-rich clusters possess higher magnetic moments.

the Gd atom). For binary clusters, the spin configuration varies depending on the binary type. When the number of Fe atoms is the same or less than that of Gd atoms, all spin configurations are antiferromagnetic: the spin moments of the Fe atoms are always antiparallel to those of the Gd atoms. Otherwise, they are ferrimagnetic (parallel spins with different magnitudes). This theoretical prediction may corroborate experimental evidence that antiferromagnetic and ferrimagnetic configurations occurred at interfaces of Gd/Fe multilayers due to the exchange interaction between Gd 4f and Fe 3d electrons, depending on the layer thickness [33]. Higher magnetic moments are found in Gd-rich clusters, as displayed in Fig. 3. Regarding the binding energy of the binary clusters, as listed in Table 2, Fe atoms tend to bind more tightly than Gd atoms, which is attributed to the Fe 3d electrons participating in the metallic bonding. This trend of the binding energy is also related to the fact that the experimental value of the cohesive energy of Fe (4.28 eV) is twice as high as that of Gd (2.08 eV). It is also reflected in the bond lengths in the clusters, as shown in Fig. 2.

4. Conclusion

In summary, we have investigated the geometric structures and magnetic properties of small Gd, Fe, and binary Fe–Gd nanoclusters using *ab initio* calculations based on the LDA + *U* method. Gd_{*n*} and Fe_{*n*} nanoclusters (*n* = 1–4) have slightly larger magnetic moments than bulk Gd and Fe. For various binary Fe–Gd nanoclusters, the magnetic moments of all atoms are parallel when there are

fewer Fe atoms than Gd atoms. Otherwise, the spin moments of the Fe atoms are antiparallel to those of the Gd atoms. As described above, the binding energy of Gd nanoclusters is weaker than that of Fe nanoclusters. Our calculations suggest that in order to design stable nanoclusters with high magnetic moments, Gd-rich nanoclusters must be produced with a small number of Fe atoms. If these nanoclusters are covered with graphene layers or organic molecules, they can act as MRI contrast agents. In particular, the Fe–Gd binary cluster could be a positive or negative contrast agent, depending on the MRI protocol, since Gd(III) is used for positive contrast imaging and Fe(III) is used for negative contrast imaging. This could be another advantage of the use of Fe–Gd heteroclusters. So far, experimental studies on FeGd binary nanoclusters have been lacking. We believe that our work will lead to useful applications of these small binary Fe–Gd clusters.

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References

- [1] J.V. Frangioni, Nat. Biotechnol. 24 (2006) 909.
- [2] M. Woods, D.E. Woessner, A.D. Sherry, Chem. Soc. Rev. 35 (2006) 500.
- [3] R.B. Lauffer, Chem. Rev. 87 (1987) 901.
- [4] P. Caravan, J.J. Ellison, T.J. McMurry, R.B. Lauffer, Chem. Rev. 99 (1999) 2293.
- [5] S. Aime, A. Barge, C. Cabella, S.G. Crich, E. Gianolio, Curr. Pharm. Biotechnol. 5 (2004) 509.
- [6] R. Weissleder, M. Papisov, Rev. Magn. Reson. Med. 4 (1992) 1.
- [7] G. Rollmann, H.C. Herper, P. Entel, J. Phys. Chem. A 110 (2006) 10799.
- [8] K. Lee, J. Callaway, S. Dhar, Phys. Rev. B 30 (1984) 1724.
- [9] M. Castro, D.R. Salahub, Phys. Rev. B 47 (1993) 10955.
- [10] J.L. Chen, C.S. Wang, K.A. Jackson, M.R. Pederson, Phys. Rev. B 44 (1991) 6558.
- [11] T. Oda, A. Pasquarello, R. Car, Phys. Rev. Lett. 80 (1998) 3622.
- [12] A. Hashimoto, H. Yorimitsu, K. Ajima, K. Suenaga, H. Isobe, J. Miyawaki, M. Yudasaka, S. Iijima, E. Nakamura, Proc. Natl. Acad. Sci. USA 101 (2004) 8527.
- [13] H. Hifumi, S. Yamaoka, A. Tanimoto, D. Citterio, K. Suzuki, J. Am. Chem. Soc. 128 (2006) 15090.
- [14] C.J. Barden, J.C. Rienstra-Kiracofe, H.F. Schaefer III, J. Chem. Phys. 113 (2000) 690.
- [15] V.I. Anisimov, F. Aryasetiawan, A.I. Liechtenstein, J. Phys.: Condens. Matter 9 (1997) 767.
- [16] M.J. Han, T. Ozaki, J. Yu, Phys. Rev. B 73 (2006) 045110.
- [17] G.M. Pastor, R. Hirsch, B. Mühlischlegel, Phys. Rev. Lett. 72 (1994) 3879.
- [18] B.N. Harmon, V.P. Antropov, A.I. Liechtenstein, I.V. Solov'yev, V.I. Anisimov, J. Phys. Chem. Solids 56 (1995) 1521.
- [19] M.J. Han, T. Ozaki, J. Yu, (unpublished).
- [20] M.P.J. Punkkinen, K. Kokko, W. Hergert, I.J. Vayrynen, J. Phys.: Condens. Matter 11 (1999) 2341.
- [21] A. Bandyopadhyay, J. Velez, W.H. Butler, S.K. Sarker, O. Bengone, Phys. Rev. B 69 (2004) 174429.
- [22] G.M. Pastor, J. Dorantes-Dávila, K.H. Bennemann, Phys. Rev. B 40 (1989) 7642.
- [23] H.J. Kulik, M. Cococcioni, D.A. Scherlis, N. Marzari, Phys. Rev. Lett. 97 (2006) 103001.
- [24] O. Hubner, J. Sauer, Chem. Phys. Lett. 358 (2002) 442.
- [25] N. Troullier, J.L. Martins, Phys. Rev. B 43 (1991) 1993.
- [26] S.G. Louie, S. Froyen, M.L. Cohen, Phys. Rev. B 26 (1982) 1738.
- [27] T. Ozaki, Phys. Rev. B 67 (2003) 155108.
- [28] D.D. Koelling, B.N. Harmon, J. Phys. C: Solid State Phys. 10 (1977) 3107.
- [29] L.W. Roeland, G.J. Cock, F.A. Muller, A.C. Moleman, K.A. McEwen, R.G. Jordan, D.W. Jones, J. Phys. F: Met. Phys. 5 (1975) L233.
- [30] R.J. Van Zee, S. Lee, W. Weltner Jr., J. Chem. Phys. 100 (1994) 4010.
- [31] H. Purdum, P.A. Montano, G.K. Shenoy, Phys. Rev. B 25 (1982) 4412.
- [32] L. Lian, C.-X. Su, P.B. Armentrout, J. Chem. Phys. 97 (1992) 4072.
- [33] D. Haskel, G. Sraber, J.C. Lang, J. Pollmann, C.S. Nelson, J.S. Jiang, S.D. Bader, Phys. Rev. Lett. 87 (2001) 207201.