

Electronic and Magnetic Structure of L1₀-FePt Nanoparticle Embedded in FePt Random Alloy

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Nanocomposite permanent magnets made of hard and soft magnetic nanoparticles are important nanostructured materials. They, however, present substantial theoretical challenges due to the need to treat the electronic interactions quantum-mechanically whilst dealing with a large number of atoms. In this presentation, we show a direct quantum mechanical simulation of magnetic nano-structures made of spherical L1₀-FePt nanoparticles, with diameter within 2.5–5 nm, embedded in an fct-FePt random alloy. The calculation is performed using the locally self-consistent multiple scattering (LSMS) method, a linear scaling *ab initio* method capable of treating tens of thousands of atoms. We found that there exists a screening region below the surface of each nanoparticle. This screening region essentially screens out the effect of the external random alloy to keep the physical properties of the interior region unchanged from the bulk of L1₀-FePt. Interestingly, the depth of this screening region is around 4 Å and is independent of the size of the nanoparticles we have investigated. We will discuss the formation of this screening region and the effect of the external random alloy on the electronic and magnetic structure of the nanoparticles.

Index Terms—*Ab initio*, FePt, LSMS method, nanoparticle.

I. INTRODUCTION

MAGNETIC nanoparticles and their composites are of great interest to us because of their potential applications in future high density data storage devices and high performance permanent magnets [1]–[3]. Over the past few years, we have witnessed tremendous increase in the data storage density of magnetic disk drives, an increase at a rate of greater than 100% annually achieved by reducing the critical physical dimensions. However, experiments and theory indicate that there is a so-called superparamagnetic limit to the recording density that will be reached within just a few years. It is clear that overcoming this superparamagnetic limit requires major scientific and technological breakthroughs. One possibility for such breakthroughs relies on a radical new design, in which magnetic nanoparticle composite forms a patterned media and each bit (0 or 1) is stored in a single magnetic nanoparticle. Of critical importance for such magnetic storage design is the length of time for which magnetic orientation of individual nanoparticles, once written, is stable at operating (room) temperature. Thus, understanding the relationship between materials properties and magnetic stability of magnetic nanoparticle composite is of crucial importance. Clearly, the ability to design materials at the nanoscale holds significant future scientific and technological opportunities.

Realizing the ultimate potential of nano-structured materials requires an understanding of the quantum mechanical behavior of the materials at the atomic scale which in fact underpins the new structures and phenomena unique to nanostructures. Over the last 2–3 decades there has been significant progress in our ability to calculate the properties of materials at the quantum

level. These advances have largely been based on the local density approximation [4], [5] or the generalized gradient approximation [6], [7] to density functional theory [8], [9]. However, the nano-structured materials place new demands on these *ab initio* methods because of the large numbers of atoms that are present in even the simplest of nanostructures, an example of which is a 5 nm cube of iron that contains the order of 12 000 atoms. Fortunately, recent advances in the locally self-consistent multiple scattering (LSMS) method [10], an *ab initio* order-N scaling technique specifically implemented to exploit massively parallel computing, are making the direct quantum simulation of nano-structured materials possible. We have reported elsewhere [11] the calculation of the electronic and magnetic structure of an iron nanoparticle embedded in iron-aluminide crystal matrix, which involves 16 000 iron and aluminum atoms in total.

In this paper, we present our recent study of the electronic and magnetic properties of a nanostructure made of spherical L1₀-FePt nanoparticles, with diameter between 2–5 nm, embedded in fct-FePt random alloy. We show that there exists a screening region below the surface of each nanoparticle. This screening region essentially screens out the effect of the external random alloy to keep the physical properties of the interior region unchanged from the bulk of L1₀-FePt. We found that the depth of this screening region is around 4 Å and is independent of the size of the nanoparticles we have investigated. We will discuss the formation of this screening region and the effect of the external random alloy on the electronic and magnetic structure of the nanoparticles.

II. THEORETICAL APPROACH

The LSMS method [10] an all-electron (in oppose to pseudopotential methods in which only the valence states are calculated), real space multiple scattering theory [12], [13] based approach to the *ab initio* electronic structure calculation within the framework of density functional theory with local density

approximation. In multiple scattering theory, the Green function for the Kohn-Sham one-electron Schrödinger equation is readily given in such a convenient algebraic expression [14] that its numerical calculation is clearly feasible; particularly when advantage is taken of the analytic properties of the Green's function. Using the Green function allows direct calculation of the charge and magnetic moment densities, which are given by the imaginary part of the Green function, without the need for the Bloch wave functions, and consequently without the need for such time-consuming procedures as the orthogonalization and normalization of the wave functions which are required in other *ab initio* methods.

The multiple scattering matrix describes the multiple scattering processes around each atom, and its computation is an $O(N^3)$ problem, that it takes 8 times longer to calculate if the number of atoms in the unit cell is doubled. The calculation of the multiple scattering matrix is made order- N scaling by neglecting those multiple scattering processes around each atom that involve atoms from a distance greater than some cutoff radius (R_{LIZ}). The space within R_{LIZ} around each atom is called local interaction zone (LIZ) for the atom. The idea behind this approximation is based on the observation that the scattering processes involving far away atoms influence the local electronic states less and less as the distance from the atom under consideration increases. As a result, the computational task becomes implicitly parallel over the atoms in the unit cell which makes the LSMS method an ideal tool for the study of the electronic structure of nano-structured materials.

III. ELECTRONIC STRUCTURE CALCULATION

The magnetic nanoparticle composite in our study is made of FePt nanoparticles embedded in $\text{Fe}_{0.5}\text{Pt}_{0.5}$ random alloy in a face-centered tetragonal (fct) lattice structure. The FePt nanoparticle itself is an ordered compound in $L1_0$ lattice structure, and has the lattice constants, $a_0 = b_0 = 3.8525 \text{ \AA}$ and $c_0 = 3.7133 \text{ \AA}$. Note that, the disordered phase of $\text{Fe}_{0.5}\text{Pt}_{0.5}$ is an fcc structure with $a_0 = 3.82 \text{ \AA}$. Since the atomic volume difference between $L1_0$ -FePt and fcc- $\text{Fe}_{0.5}\text{Pt}_{0.5}$ is very small, we approximate the random alloy with an fct structure of the same lattice constants as $L1_0$ -FePt to avoid lattice mismatch. This approximation can further be justified by our finding that the charge and moment distribution difference between the fcc and fct phases is very small. In this case, the lattice relaxation should be minimal and will be ignored in this study. We considered spherical FePt nanoparticles of three different dimensional sizes, 2.5, 3.86, and 5.0 nm in diameter. Each of these nanoparticles contains 711, 2195, and 4777 Fe and Pt atoms, respectively. The unit cell, a repeating unit along x , y , and z directions, is in tetragonal shape and remains the same dimensional size ($57.7875 \text{ \AA} \times 57.7875 \text{ \AA} \times 59.4128 \text{ \AA}$) for each nanoparticle under consideration. Each unit cell sample contains one nanoparticle together with the surrounding random alloy, and has 14 400 Fe and Pt atoms in total.

We performed spin-polarized LSMS calculation for the unit cell samples described above using 1200 nodes on CRAY XT3, with 12 atoms per node. We simplified the calculation by making the muffin-tin approximation to the potential in which the one-electron potential is assumed to be spherically

symmetric within the muffin-tin sphere around each atom and is assumed to be constant within the interstitial region between the muffin-tin spheres. This is a reasonable approximation for most simple and transition metals and intermetallic alloys due to the nature of metallic bonding. In our calculations, we choose the LIZ for each atom to include 54 neighboring atoms which has proved to be sufficient for close-packed structures [10].

The calculation shows several interesting results. Firstly, despite the fact that the electric charge and magnetic moment vary dramatically from atom to atom in the alloy region, they show a rather uniform distribution pattern in the interior region of the nanoparticles. That is all the atoms of the same type have a constant electric charge and magnetic moment. This essentially suggests that the inhomogeneity effect from the external random alloy has been screened out by the surface layers of the nanoparticle. In the following discussion, we refer to these surface layers as "screening region." Secondly, the calculated electric charge and magnetic moments for Fe and Pt atoms within the interior region are independent of the nanoparticle size, and they essentially retain the same value as in the bulk of $L1_0$ -FePt crystal. Thirdly, while the size of the interior region increases with the nanoparticle size, the radial width of screening region remains the same, at least for the size range of the nanoparticles in this study. That is the width of the screening region is independent of the volume or the surface area of the nanoparticle.

A detailed picture of the electronic and magnetic structure of the nanoparticle composite is shown in Fig. 1, where 14 400 data points, each of which corresponds to the number of excess electrons (Fig. 1(a)) or the magnetic moment [Fig. 1(b)] on each atom, are plotted against the atom distance measured from the center of the nanoparticle. Here, we only show the calculated results for the nanoparticle of 3.86 nm in diameter, since the results for the other two nanoparticle sizes are very much the same except for the size of the interior region. We find that Fe atoms are in general gaining electrons from the Pt atoms and therefore are negatively charged, while Pt atoms are losing electrons and are positively charged. Each Fe atom carries a magnetic moment in the range of $2.7\mu_B$ – $3.1\mu_B$, and in comparison, each Pt atom carries a much smaller magnetic moment, essentially less than $0.4\mu_B$. In the interior region, in particular, the Fe atoms are gaining 0.3 electrons from Pt atoms and carry a magnetic moment of $2.95\mu_B$, while the Pt atoms are losing 0.3 electrons and carry a magnetic moment of $0.37\mu_B$. These values are in agreement with the calculated results for the bulk of $L1_0$ -FePt crystal. For those atoms inside the screening region, the shaded area in the figures in Fig. 1, the net charge and the magnetic moment show rather dramatic fluctuations, induced by the influence from the random alloy. This screening region extends as deep as 4 \AA inward from the nanoparticle surface, and remains the same depth for different nanoparticle sizes. In the random alloy region, as expected, the distribution of the net charge and the magnetic moment is very much random. Interestingly, except for some Fe atoms, most atoms in this region carry less magnetic moment than their counterpart in the interior region in the nanoparticle.

Knowing the charge and moment distribution within a nanoparticle helps to improve our understanding of the size effect as well as the effect of the surrounding environment.

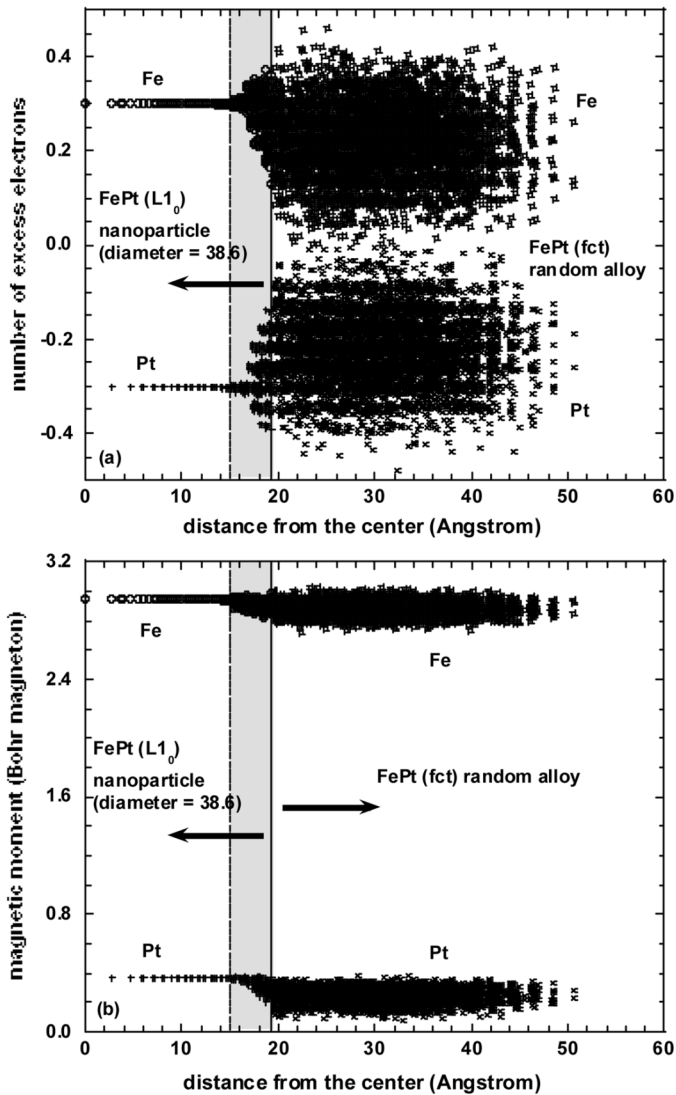


Fig. 1. Distribution of electric charge and magnetic moment in spherical L1₀-FePt nanoparticle and the surrounding fct-FePt random alloy. The shaded area is the screening region of the nanoparticle which screens out the external random alloy effect from influencing the interior region of the nanoparticle. The solid line is the boundary of the nanoparticle sphere. The circles are the data point for Fe atoms in the FePt nanoparticle, the squares are for Fe atoms in the FePt random alloy, the crosses “+” are for Pt atoms in the nanoparticle, and the crosses “x” are for Pt atoms in the random alloy. (a) The number of excess electrons on each of the 14400 atoms versus the atom distance from the center of the nanoparticle. (b) The magnetic moment on each of the 14400 atoms versus the atom distance from the center of the nanoparticle.

It also helps to determine the electrostatic and magnetostatic interactions between nanoparticles. A multi-scale model for complex nano-composites or nano-structured devices in which each nanoparticle is treated as a point particle with proper charge and magnetic moment, determined from the quantum mechanical calculation, can be possibly built.

IV. CONCLUSION

In summary, we have performed direct quantum mechanical simulation of magnetic FePt nanoparticle composites using LSMS method. The results reveal that there exists a screening

region, about 4 Å in radial width, below the surface of the nanoparticle. This region, whose size is found independent of the volume or surface area of the nanoparticle, plays an essential role as an electromagnetic shield that screens the effect of the random alloys from influencing the interior region of the FePt nanoparticle. As a result, the electronic and magnetic structure of the interior region shows no difference from the FePt crystal.

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REFERENCES

- [1] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, “Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices,” *Science*, vol. 287, pp. 1989–1992, 2000.
- [2] J. P. Liu, K. Elkins, D. Li, V. Nandwana, and N. Poudyal, “Phase transformation of FePt nanoparticles,” *IEEE Trans. Magn.*, vol. 42, pp. 3036–3041, 2006.
- [3] H. Zeng, J. Li, J. P. Liu, Z. L. Wang, and S. H. Sun, “Exchange-coupled nanocomposite magnets via nanoparticle self-assembly,” *Nature*, vol. 420, pp. 395–398, 2002.
- [4] L. Hedin and B. I. Lundqvist, “Explicit local exchange correlation potentials,” *J. Phys. C: Solid State Phys.*, vol. 4, pp. 2064–2083, 1971.
- [5] U. von Barth and L. Hedin, “A local exchange-correlation potential for the spin polarized case: I,” *J. Phys. C: Solid State Phys.*, vol. 5, pp. 1629–1642, 1972.
- [6] J. P. Perdew and Y. Wang, “Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation,” *Phys. Rev. B*, vol. 33, pp. 8800–8802, 1986.
- [7] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.*, vol. 77, pp. 3865–3868, 1996.
- [8] P. Hohenberg and W. Kohn, “Inhomogeneous electron gas,” *Phys. Rev.*, vol. 136, pp. B864–B871, 1964.
- [9] W. Kohn and L. J. Sham, “Self-consistent equations including exchange and correlation effects,” *Phys. Rev.*, vol. 140, pp. A1113–A1138, 1965.
- [10] Y. Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson, Z. Szotek, and W. M. Temmerman, “Order-N multiple scattering approach to electronic structure calculations,” *Phys. Rev. Lett.*, vol. 75, pp. 2867–2870, 1995.
- [11] Y. Wang, G. M. Stocks, A. Rusanu, D. M. C. Nicholson, M. Eisenbach, and J. S. Faulkner, “Teraflop computing for nanoscience,” in *Proceedings of The 2006 International Conference on Computer Design & Conference on Computing in Nanotechnology*, H. R. Arabnia and M. M. Eshaghian-Wilner, Eds., Las Vegas, NV, Jun. 2006, pp. 265–171, CSREA Press.
- [12] J. Korrington, “On the calculation of the energy of a Bloch wave in a metal,” *Physica*, vol. 13, pp. 392–400, 1947.
- [13] W. Kohn and N. Rostoker, “Solution of the Schrödinger equation in periodic lattices with an application to metallic lithium,” *Phys. Rev.*, vol. 94, pp. 1111–1120, 1954.
- [14] J. S. Faulkner and G. M. Stocks, “Calculating properties with the coherent potential approximation,” *Phys. Rev. B*, vol. 21, pp. 3222–3244, 1980.