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# Size-Induced Chemical and Magnetic Ordering in Individual Fe–Au Nanoparticles

Pinaki Mukherjee

*University of Nebraska-Lincoln, pinaki.mukherjee@rutgers.edu*

Priyanka Manchanda

*University of Nebraska-Lincoln, Indian Institute of Technology Mandi, priyanka.manchanda@vanderbilt.edu*

Pankaj Kumar

*Indian Institute of Technology Mandi*

Lin Zhou

*Iowa State University*

Matthew J. Kramer

*Iowa State University, mjkrmer@ameslab.gov*

*See next page for additional authors*

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**Authors**

Pinaki Mukherjee, Priyanka Manchanda, Pankaj Kumar, Lin Zhou, Matthew J. Kramer, Arti Kashyap, Ralph Skomski, David J. Sellmyer, and Jeffrey E. Shield

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# Size-Induced Chemical and Magnetic Ordering in Individual Fe–Au Nanoparticles

Pinaki Mukherjee<sup>1,2</sup>, Priyanka Manchanda<sup>2,3,4</sup>, Pankaj Kumar<sup>4</sup>, Lin Zhou<sup>5</sup>,  
Matthew J. Kramer<sup>5</sup>, Arti Kashyap<sup>4</sup>, Ralph Skomski<sup>2,3</sup>, David Sellmyer<sup>2,3</sup>,  
and Jeffrey E. Shield<sup>1,2</sup>

1. Department of Mechanical and Materials Engineering, University of Nebraska, Lincoln, Nebraska 68588, United States
2. Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, United States
3. Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, United States
4. School of Basic Sciences, Indian Institute of Technology Mandi, HP 175001, India
5. Materials Sciences and Engineering Division, Ames Laboratory, Iowa State University, Ames, Iowa 50011, United States

Corresponding authors – Pinaki Mukherjee, email [pmukherjee@unl.edu](mailto:pmukherjee@unl.edu), and Jeffrey E. Shield, email [jshield@unl.edu](mailto:jshield@unl.edu)

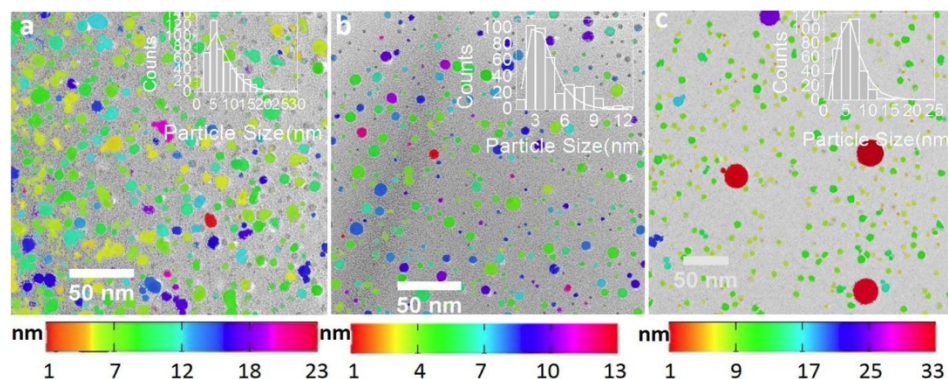
## Abstract

Formation of chemically ordered compounds of Fe and Au is inhibited in bulk materials due to their limited mutual solubility. However, here we report the formation of chemically ordered L1<sub>2</sub>-type Fe<sub>3</sub>Au and FeAu<sub>3</sub> compounds in Fe–Au sub-10 nm nanoparticles, suggesting that they are equilibrium structures in size-constrained systems. The stability of these L1<sub>2</sub>-ordered Fe<sub>3</sub>Au and FeAu<sub>3</sub> compounds along with a previously discovered L1<sub>0</sub>-ordered FeAu has been explained by a size-dependent equilibrium thermodynamic model. Furthermore, the spin ordering of these three compounds has been computed using *ab initio* first-principle calculations. All ordered compounds exhibit a substantial magnetization at room temperature. The Fe<sub>3</sub>Au had a high saturation magnetization of

about 143.6 emu/g with a ferromagnetic spin structure. The FeAu<sub>3</sub> nanoparticles displayed a low saturation magnetization of about 11 emu/g. This suggests an antiferromagnetic spin structure, with the net magnetization arising from uncompensated surface spins. First-principle calculations using the Vienna *ab initio* simulation package (VASP) indicate that ferromagnetic ordering is energetically most stable in Fe<sub>3</sub>Au, while antiferromagnetic order is predicted in FeAu and FeAu<sub>3</sub>, consistent with the experimental results.

**Keywords:** chemical ordering, nanoparticles, Fe–Au, nanomagnetism, thermodynamics

Nanoscale structures, and in particular nanoparticles and other size-constrained systems, continue to be an avenue for accessing structures and phases not observed in commensurate equilibrium or near-equilibrium systems.<sup>1,2</sup> The differing thermodynamics and kinetics in nanoparticles provide an opportunity to explore new phases and phase equilibria and to discover new materials with unique catalytic, magnetic, or optical properties<sup>3–5</sup> for use in a variety of applications. Among the nonequilibrium phenomena observed in metallic particles are the formation of nonequilibrium atomic structures,<sup>6</sup> extension of solid solubility<sup>7</sup> and mixing of immiscible elements,<sup>8,9</sup> and suppression of phase transitions.<sup>2,10,11</sup> The key aspect missing in these works is finding the most stable thermodynamic state of the system, which is usually achieved, experimentally, by heat treatment followed by slow (furnace) cooling. The equilibrium stabilization of a phase or structure is confirmed if the structure is favored energetically, and subsequently, the laws of thermodynamics can be invoked to calculate the energetics of the phase stabilization driven by size. The Fe–Au bimetallic system, as a case study, provides an excellent opportunity to study the size-driven stabilization of the thermodynamic phases because of its contrasting phase behavior in bulk and nanostructures. In the equilibrium Fe–Au system,<sup>12</sup> due to limited solubility and positive heat of mixing,<sup>13</sup> slow cooling results in phase separation for a wide range of composition. Recently, in the Fe–Au nanoparticles, a critical radius-of-transition, which describes the onset of phase-separation (into bulk phases), has been discovered,<sup>14</sup> and similar behavior has been observed in other systems as well.<sup>15</sup> Single-phase solid solutions are stabilized below the critical radius, and phase separation occurs above it. Subsequently, we have discovered chemical ordering within these nanoscale solid solutions, at specific atomic ratios (1:2, 1:1,<sup>16</sup> and 2:1). In this work, we focus on the formation and stabilization (through annealing) of chemically ordered structures in the Fe–Au nanoparticles at 1:2 and 2:1 stoichiometries with an average size below 10 nm. The stability of these nanocompounds has been explained using a size-dependent thermodynamic model and the magnetic behavior measured and predicted using first-principle calculations.



**Figure 1.** Size distribution of Fe–Au nanoparticles: TEM bright-field micrograph of Fe–Au particles deposited on a carbon substrate. The color map superimposed on the actual image shows size distribution of annealed nanoparticles. a, b, c represent 79, 53, and 33 atom % Fe, respectively. (Insets) Histogram with a log-normal fit of the particle size distribution.

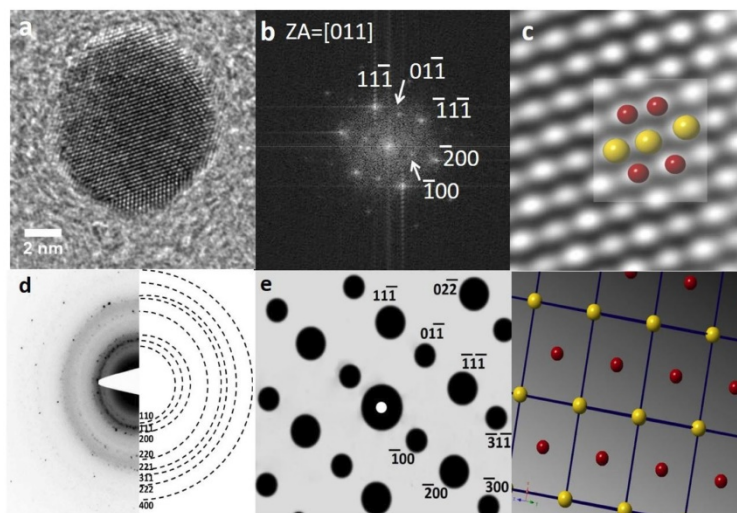
Modifying the atomic (or chemical) ordering in a unit cell provides a means to further control or alter a material's properties.<sup>17,18</sup> This can be observed in many chemically ordered structures in transition-metal compounds, which are especially prevalent between 3d and noble metals, with the most common structure types being L1<sub>2</sub> and L1<sub>0</sub>. For example, alloying ferromagnetic Fe or Co with the exchange-enhanced Pauli paramagnets Pt and Pd yields the highly anisotropic ferromagnetic and chemically ordered compounds FePt, FePd, and CoPt,<sup>19–21</sup> whereas FePt<sub>3</sub> and FeRh are antiferromagnetic.<sup>22,23</sup> Recently, Au-rich chemically synthesized nanoparticles have reportedly formed the L1<sub>2</sub> Au<sub>3</sub>Fe structure,<sup>24,25</sup> and gas-condensed FeAu nanoparticles formed in the L1<sub>0</sub> structure.<sup>16</sup> The Au<sub>3</sub>Fe was reported to be superparamagnetic with a low magnetization at room temperature,<sup>24</sup> while FeAu was ferromagnetic with low magnetization.<sup>16</sup> No further information about magnetic behavior of these ordered structures is provided in these works. In the current research, the stabilization of the nonequilibrium Fe–Au L1<sub>2</sub> and L1<sub>0</sub> phases indicates toward a new set of size-driven spin structures in confined nanosized systems, with no such structural/magnetic phases being present in their bulk counterparts. For the first time, magnetic ordering and spin structures of the newly formed structures are reported from both theoretical (first-principle calculations) and experimental perspectives.

## Results and Discussion

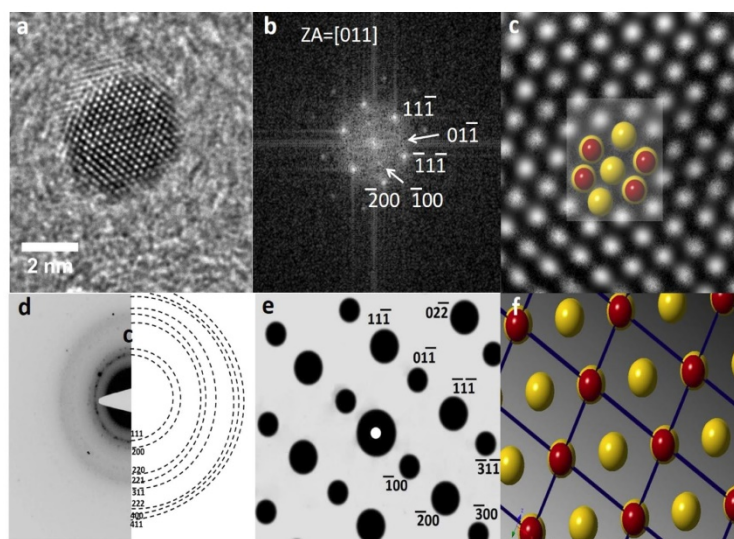
We have investigated three nanoparticle samples with different atomic percentages of Fe, labeled 2P (79 atomic percent Fe), 6P (53 atomic percent Fe), and 8P (33 atomic percent Fe), where “P” refers to number of Au plugs in the Fe target. These compositions are relatively close to those predicted from the sputtering rates and relative area fractions of Au and Fe on the target. The compositions of the annealed particles remain unchanged within experimental error. The as-deposited particles are either bcc (2P) or fcc (6P and 8P). Complete

characterization of the as-deposited particles is reported elsewhere.<sup>7</sup> Here, we focus on structures formed during heat treatment. The heat-treated particles were of uniform size, as indicated by TEM images, although some agglomeration (sintering) of particles in contact with one another did occur during heat treatment. Figure 1 shows the particle-size distribution for each composition. The distribution follows a log-normal function which takes into account asymmetry introduced by the agglomerates.<sup>26</sup> The average particle size was determined to be  $7.9 \pm 4.4$ ,  $4.7 \pm 2.4$ , and  $5.8 \pm 3.5$  nm for the samples 2P, 6P, and 8P, respectively.

The structures formed in the particles after heat treatment were determined using fast Fourier transforms (FFTs) of the high-resolution TEM images as well as selected area electron diffraction (SAED). The high-resolution images revealed that the particles are single crystalline and highly ordered (figs. 2a and 3a). This is confirmed by the sharp diffraction maxima in (figs. 2d and 3a), with minimal defects present. For sample 2P (fig. 2), which contains 79 atom %Fe, the FFT reveals a pattern of intense reflections characteristic of the [011] zone axis for an fcc structure. However, closer inspection reveals a set of weak reflections midway between the {200} and {220} reflections which correspond to the {100} and {110} superlattice reflections of a  $L_{12}$ -type ordered structure with a lattice parameter of 0.365 nm. The composition of these particles is 20 atomic percent Au, close to the required  $\text{Fe}_3\text{Au}$  stoichiometry necessary for  $L_{12}$  ordering. The SAED pattern reveal {110} and {211} superlattice reflections, suggesting  $L_{12}$ -type ordering, while the lattice parameter determined from the FFT was corroborated.



**Figure 2.** Structural analysis of Fe<sub>3</sub>Au (L1<sub>2</sub>) phase: (a) HRTEM image of a particle. (b, e) Experimental and simulated fast Fourier transform of the HRTEM image, which indexes to the [011] zone axis of a ordered L1<sub>2</sub> structure. (d) The SAED pattern was indexed to L1<sub>2</sub> structure with a lattice parameter  $a = 0.365$  nm. (c) A magnified and background refined view of (a) with an overlay of the unit cell projection along [011] zone axis. (f) Simulated projection of L1<sub>2</sub> structure along the [011] zone axis. Red and yellow spheres show Fe and Au atoms, respectively.

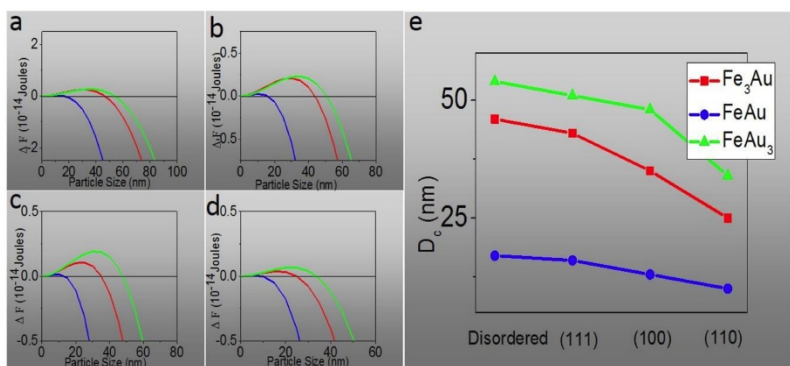


**Figure 3.** Structural analysis of FeAu<sub>3</sub> (L<sub>12</sub>) phase: (a) HRTEM image of a particle. (b, e) Experimental and simulated fast Fourier transform of the HRTEM image, which indexes to the [011] zone axis of a ordered L<sub>12</sub> structure d. The SAED pattern was indexed to the L<sub>12</sub> structure with a lattice parameter  $a = 0.371$  nm. (c) A magnified and background refined view of (a) with an overlay of the unit cell projection along [011] zone axis. (f) Simulated projection of L<sub>12</sub> structure along the [011] zone axis. Red and yellow spheres show Fe and Au atoms, respectively.

For sample 6P, which contains 53 atom % Fe (a composition close to the 1:1 stoichiometry) the structure is determined to be tetragonal with  $c = 0.360 \pm 0.010$  nm and  $a = 0.374 \pm 0.003$  nm. The details about this structure and a more complete analysis can be found elsewhere.<sup>16</sup>

For sample 8P, which contains 33 atom % Fe, the FFT in figure 3b again shows weak {110} and {100} superlattice reflections indicative of structural ordering. This FFT was indexed to the [011] zone axis. The structure was determined to be the L<sub>12</sub> structure with a lattice parameter of 0.371 nm. The SAED pattern here was consistent with the L<sub>12</sub> structure rather than other possible ordered structures such as the tetragonal L<sub>60</sub>, indicated by the presence of the {221} and {411} rings.





**Figure 4.** Energetics of nanocompound formation: Stability factor ( $\Delta F$ ) for three nanocompounds  $L1_2$   $Fe_3Au$ ,  $Au_3Fe$ , and  $L1_0$   $FeAu$ . A positive value of  $\Delta F$  indicates that the heat of formation of these nanocompounds is less than their surface energy for certain size range.  $\Delta F$  is calculated using four different kinds of surfaces: (a) disordered, (b) {111}, (c) {100}, and (d) {110}. (e) The critical diameter of transition  $D_T$ , below which nanocompounds are stable are shown for these four kinds of surfaces. From disordered to {110} surfaces the total surface energy of nanoparticles decreases steadily, and as a consequence the  $D_T$  decreases also.

The formation of ordered structures in the Fe–Au system is surprising given the positive heat of mixing (HOM) in this system, which indicates that Fe–Fe and Au–Au bonds are preferable over Fe–Au bonds and results in the phase separation reflected in the equilibrium phase diagram. However, previous work reported that nanoscale system sizes effectively suppressed equilibrium phase behavior.<sup>27</sup> The stabilization of compounds or phases in nanoparticles arises from a competition between the HOM and the total surface energy ( $SE_{tot}$ ) of the nanoparticle and the interphase interfaces created.<sup>14,27</sup> The HOM is a size-dependent physical property, and with a reduction in system size the HOM decreases, resulting in increasing miscibility between the two constituents (in this case, Fe and Au). The size-dependent HOM can be expressed as<sup>28</sup>

$$\frac{H_m(D)}{H_{mb}} = \exp\left(-\frac{2S_{mb}}{3R} \frac{1}{\frac{D}{D_c} - 1}\right) \left(1 - \frac{1}{\frac{D}{D_c} - 1}\right) \quad (1)$$

where  $H_m(D)$  and  $H_{mb}$  represent the size-dependent and bulk HOM, respectively.  $D$  is the particle diameter and  $D_c$  is the critical diameter, which is usually determined to be half of the bond length of A–B type bonds.  $S_{mb}$  is the bulk entropy of mixing and is given by

$$S_{mb} = -R(x_A \ln x_A + x_B \ln x_B) \quad (2)$$

where  $x_A$  and  $x_B$  are the mole fractions of component A and B, respectively.

The total SE of the nanoparticle ( $SE_{tot}$ ) is the surface energy per unit area ( $SE_A$ ) multiplied by the surface area of the nanoparticle. The ( $SE_A$ ) is determined by the composition of the



nanocompounds and atomic arrangement of the relevant crystallographic surface. The  $(SE)_{\text{tot}}$  decreases with size because the surface area decreases with particle diameter. However, the decrease in HOM is an exponential function of particle size  $D$ , and decreases more rapidly than the  $(SE)_{\text{tot}}$ , which is proportional to the square of the particle size  $D$ . The model excludes edge effects and the size dependence of the  $(SE)_A$  is not considered. Thus, at small particle sizes a system that normally prefers atomic clustering or segregation due to a positive HOM can instead form an ordered compound because the surface energy is minimized in an ordered structure while the HOM is decreased.

The transition point (critical size) where ordered compounds are energetically favored compared to the HOM can be quantified by comparing the changes in HOM due to size with the effects of different surface configurations on the total surface energy (see the Supporting Information for details of the calculations). To accomplish this, a stability factor  $\Delta F$  can now be introduced; this is simply the difference between the total surface energy of a nanoparticle  $(SE)_{\text{tot}}$  and the size-dependent HOM  $H_m(D)$ . When  $\Delta F$  is negative,  $H_m(D)$  is larger and atomic clustering/segregation is preferred. When  $\Delta F$  is positive, nanocompound formation (i.e., chemical ordering) can occur. Here, four different kinds of surfaces were considered for each of the three nanocompounds: chemically disordered and ordered  $\{111\}$ ,  $\{110\}$ , and  $\{100\}$  surfaces (fig. 4a–d). The values of the bulk HOM and elemental surface energies were obtained from refs 29 and 30, respectively. Figure 4a–d shows the critical nanoparticle diameters  $D_T$  (the size at which  $\Delta F$  changes sign) below which an ordered structure can form. The lowest values of  $D_T$  are obtained for  $\{110\}$  surfaces. For this surface configuration, the L1<sub>2</sub>-ordered FeAu<sub>3</sub> and Fe<sub>3</sub>Au are stable below 34 and 25 nm, respectively. The L1<sub>0</sub>-ordered FeAu is stable below 10 nm. The nanoparticles investigated in this study were all below these critical sizes. There is a steady decrease in  $D_T$  when the nanoparticle surface changes from disordered  $\rightarrow \{111\} \rightarrow \{100\} \rightarrow \{110\}$  as the surface energy of the nanoparticles  $(SE)_{\text{tot}}$  decreases through this sequence. There are some reports<sup>31,32</sup> of an increase in  $(SE)_A$  with decreasing particle size, which would increase the critical size. The surface energies calculated here represent approximate values, as the necessary parameters such as heat of atomization and melting temperature for calculating the surface energies of these newly discovered compounds are not known. However, we used our method of approximating surface energies for systems with known surface energies (NiAl, Ni<sub>3</sub>Al, FePt, and CoPt).<sup>33,34</sup> Our approximate values are within 15%, and usually much closer, of the reported values for these compounds. Thus, the approximate surface energies used in our models for these new Fe–Au compounds are reasonable. The stabilization of nanocompounds as a consequence between surface energy and heat of formation is similar to the stabilization of solid-solution phases in finite-sized systems arising from an inability of the system to accommodate an interphase interface.<sup>14</sup>

Figure 5 shows the magnetization behavior for the three ordered structures. The saturation magnetization for FeAu and FeAu<sub>3</sub> are very low, corresponding to 0.23 and 0.51  $\mu_B$  per Fe atom, respectively. Fe<sub>3</sub>Au, on the other hand, was observed to have a significant magnetization with a magnetic moment per Fe atom close to bulk Fe values (table 1). The low magnetization of the FeAu and FeAu<sub>3</sub> can be explained by the presence of antiferromagnetic order, with the low magnetization values arising from uncompensated surface spins.<sup>35</sup> Approximating the number of surface Fe atoms and assuming that they all have a

magnetic moment close to the surface value of  $2.84\mu_B^{36}$  results in a saturation magnetization close to the experimentally observed value (table 1). Thus, it is reasonable to assume AFM ordering in FeAu and FeAu<sub>3</sub>. The presence of a ferromagnetically ordered structure with a high magnetization in Fe<sub>3</sub>Au may make this structure useful in a number of applications, particularly in biomedical applications.

**Table 1.** Magnetic Properties of Ordered Nanoparticles<sup>a</sup>

ordering type	particle size (nm)	$M_s$ (emu/g)		coercivity (Oe)		moment/Fe atom ( $\mu_B$ )	
		10 K	300 K	10 K	300 K	expt 10 K	theory 0 K
Fe <sub>3</sub> Au	$7.9 \pm 4.4$	143.62	142.5	790	580	2.98	2.49
FeAu	$4.7 \pm 2.4$	9	6	52	39	0.23	0
FeAu <sub>3</sub>	$5.8 \pm 3.5$	11	9	90	50	0.85	0.51

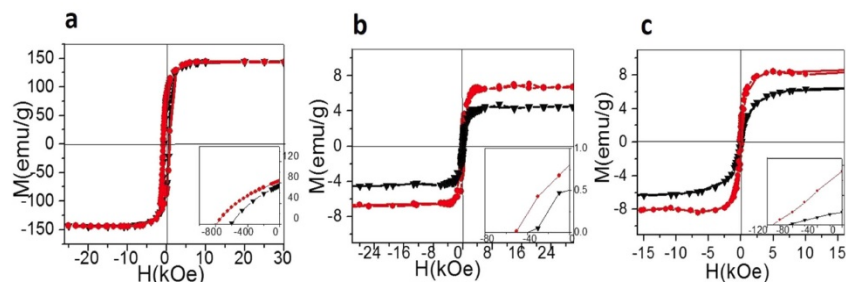
a. Net moments per Fe atom were deduced from the saturation magnetization  $M_s$  (mass polarization) of the nanoparticles.

All three ordered structures displayed low coercivity, including the tetragonal L1<sub>0</sub> structure (FeAu). However, in the case of FeAu, the anisotropy may be sufficiently high to prevent magnetization switching in a field of 70 kOe [7 T], particularly if the magnetization is rather low.

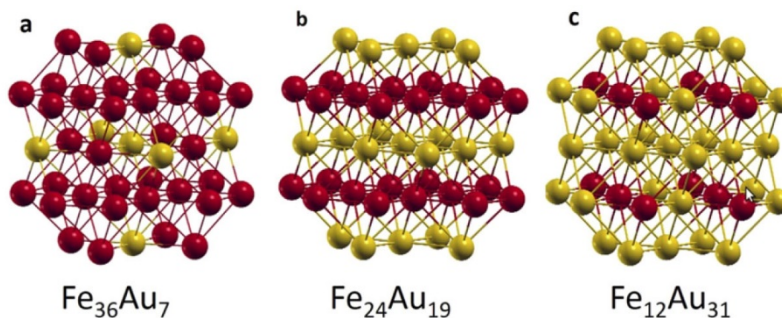
The magnetic ordering of Fe–Au compounds was studied theoretically in bulk and nanoparticle configurations. The stable magnetic configurations of L1<sub>2</sub> Fe<sub>3</sub>Au and FeAu<sub>3</sub>, and L1<sub>0</sub> FeAu in bulk were determined using first-principles calculations. The magnetic ordering has been calculated by comparing the energy difference of ferromagnetic and antiferromagnetic configurations. For the L1<sub>2</sub>-ordered Fe<sub>3</sub>Au, the ferromagnetic configuration was determined to be more stable, consistent with experimental observations. For L1<sub>2</sub>-ordered Au<sub>3</sub>Fe, the antiferromagnetic configuration was calculated to have lower energy, again consistent with the experimental explanation of the low magnetization value. For L1<sub>0</sub>-ordered FeAu, the ferromagnetic configuration is slightly more favorable than the antiferromagnetic (AFM) configuration, but the calculated energy difference is very small, about 3.5 meV/unitcell, and small perturbations may be sufficient to stabilize an AFM structure.

Modeling of small, 43 atom clusters was utilized to determine the magnetic moments carried by each kind of atom. The compositions of the model particles are Fe<sub>36</sub>Au<sub>7</sub>, Au<sub>31</sub>Fe<sub>12</sub>, and Fe<sub>24</sub>Au<sub>19</sub>, which correspond to L1<sub>2</sub>–Fe<sub>3</sub>Au, L1<sub>2</sub>–Au<sub>3</sub>Fe, and L1<sub>0</sub>–FeAu, respectively. Figure 6 shows the atomic arrangements of these clusters. The calculated magnetic moments for Au atoms were of the order of  $0.05\mu_B$ ; as a result, the contribution of Au to the total magnetization was neglected. Thus, we assumed that the total magnetization arose from only the Fe atoms. The relaxation of atomic coordinates did not change the values of atomic moments beyond the error. Experimentally, the magnetic moment per Fe atom was determined by converting emu per gram to  $\mu_B$  per Fe atom by normalizing to the approximate number of Fe atoms in a typically sized nanoparticle (the approximate no. of atoms is  $\sim 10^4$  for a 5 nm particle). Similarly, the total moment for the entire 43 atom cluster is calculated and then normalized to the number of Fe atoms. In this way, we can more easily compare

the calculated magnetic moments with the experimental results on a per Fe atom basis (table 1).



**Figure 5.** Magnetization ( $M$ ) Vs. Applied field ( $H$ ) loops of Au-Fe nanoparticles at 10 and 300 K: (a, b, c) compositions 79, 53, and 33 atom % Fe, respectively. The properties at 10 and 300 K are represented by red dots and black triangles, respectively. The insets show second quadrant behavior.



**Figure 6.** Fe-Au nanoparticle structures used in the density-functional calculations of the magnetic properties: (a) in  $L_{12}$ -ordered  $\text{Fe}_3\text{Au}$ , (b)  $L_{10}$   $\text{FeAu}$ , and (c)  $\text{Au}_3\text{Fe}$ . Each nanoparticle contains 43 atoms, and the structural and compositional data are taken from experiment. Red and yellow spheres indicate Fe and Au atoms, respectively.

For  $\text{Fe}_{36}\text{Au}_7$ , the calculated average Fe moment is  $2.49\mu_B$ , which is reasonably close to the experimental value of  $2.98\mu_B$ . The calculated average Fe moment of  $\text{Au}_{31}\text{Fe}_{12}$  is  $0.51\mu_B$  per Fe atom which agrees approximately with experiments (about  $0.85\mu_B$ ). The nonzero magnetic moment is due to uncompensated surface spins for both 43 atom model cluster and nanoparticle. For  $\text{Fe}_{24}\text{Au}_{19}$ , which in this case is antiferromagnetic, the calculated average Fe moment is zero because of the lack of uncompensated surface spins in the 43 atom cluster; in the nanoparticle, uncompensated surface spins exist, giving rise to the small net magnetization and nominal magnetic moment of  $\sim 0.23\mu_B$  per Fe atom. In all three cases, the calculated and observed magnetic moments are in good agreement, suggesting that the spin structure and atomic structure observed experimentally in each case are correct.

## Conclusions

In summary, we have demonstrated that the nonequilibrium chemically ordered  $L_{12}$  and  $L_{10}$  phases are stable phases in Fe–Au nanoparticles. These structures, obtained after heat treatment followed by slow cooling, are effectively products of solid–solid phase transformations and a disorder–order transformation upon cooling. The occurrence of these phases is in contrast to the equilibrium phase diagram. The finite size of the nanoparticles plays a crucial role in the formation of these ordered structures, as the equilibrium phase formation is suppressed by the scale of the system. The enthalpy of formation of the compounds decreases as the particle size decreases, and below a critical size this becomes smaller than the surface energy of the particles. The nanoparticle in this size range can sustain a metastable compound structure. Magnetic ordering of these compounds changes with structure. Ferromagnetic behavior with a high saturation magnetization has been observed in  $\text{Fe}_3\text{Au}$ . The other two compounds ( $\text{FeAu}$  and  $\text{FeAu}_3$ ) show very low saturation magnetization, which cannot be explained by the dilution of Fe with Au. The low magnetization values can be explained by an antiferromagnetically ordered core along with the presence of uncompensated surface spins. The magnetic spin ordering associated with these chemically ordered structures is calculated from first-principle. The calculations predict that ferromagnetic ordering is the energetically most favorable configuration for  $\text{Fe}_3\text{Au}$ . For the  $L_{12}$   $\text{FeAu}_3$  structure, antiferromagnetic ordering is the most stable configuration. The energy difference between ferromagnetic and antiferromagnetic configurations is negligible for  $\text{FeAu}$ , and stabilization of either spin structure is possible, although experimentally it appears to be AFM. The experimentally observed Fe magnetic moments in these three configurations agree approximately with the theoretical calculations as well.

## Methods

FeAu alloy particles were prepared by inert gas condensation<sup>37</sup> within a sputtering chamber whose base pressure was kept below  $10^{-7}$  Torr. A mixture of Ar/He gas was used to sputter the target and maintain temperature balance inside the chamber. The deposition rates were measured *in situ* using a quartz crystal thickness monitor. The atomic mixture of Au and Fe was condensed to form particles at  $-130^\circ\text{C}$  inside a liquid nitrogen cooled chamber. The as-formed particles were deposited onto a C coated Cu grid for TEM characterization and on a Si substrate for magnetic measurements. Alternate layers of C/SiO<sub>2</sub> and Fe–Au particle layers were deposited to isolate the particles during heat treatment.

The composition of the particles was controlled by using a composite target with different numbers of Au “plugs” inserted into a Fe target. Here, 2, 6, and 8 Au plugs, each  $\frac{1}{4}$ ” in diameter, were inserted around the characteristic “racetrack” typical of magnetron sputtering. From estimates using sputtering rates for both Fe and Au, each plug increases the Au content by approximately 8 atomic percent. Samples are denoted as 2P, 6P, and 8P. For the characterization using transmission electron microscopy (TEM), the particles were deposited directly onto carbon support films and subsequently covered with about 5 nm C or SiO<sub>2</sub> films using a second RF sputtering system available in the system to avoid oxidation. The heat treatment of the nanoparticle samples was performed at  $600^\circ\text{C}$  for 15 min in

a quartz capsule filled with ultrahigh purity Ar after repeated evacuations. The samples were furnace-cooled to room temperature.

The structural and compositional characterizations of the nanoparticles were performed using TEM with an FEI Osiris and Tecnai G<sup>2</sup> F20. The image analysis was carried out using ImageJ. The compositions of the particles were determined by energy dispersive X-ray spectroscopy (EDS) in the transmission electron microscope using a nonconverged electron probe for simultaneous sampling of a large number of particles and standardless analysis.

For the magnetic measurements, the particles were embedded in a C or SiO<sub>2</sub> matrix by alternate deposition from the particle source and the RF source. The total thickness of these composite films was between 30 to 60 nm. The magnetic measurements were conducted at 10 and 300 K using a Quantum Design Magnetic Property Measurement System (MPMS) superconducting quantum interference device (SQUID) magnetometer with a maximum field of 7 T. The magnetic signal from the diamagnetic Si substrate was subtracted from the sample signal by fitting a straight line to the high-field region and subtracting the linear portion from the measured signal. The saturation magnetizations were calculated by plotting  $M$  vs.  $1/H^2$  in the high-field regions and extrapolating to  $1/H^2 = 0$ .

The magnetization was normalized to the number of Fe atoms ( $n_{\text{Fe}}$ ) in the nanoparticles. First of all, nanoparticles were deposited on the TEM grid and the Si substrate (for magnetic measurement) under the same deposition conditions (deposition rate, chamber pressure, gas flow rate, and average film thickness). An individual layer of the multilayer sample for magnetic measurement was identical to the sample on the TEM grid. The size distribution was calculated from the TEM images and from this the average volume of the nanoparticles in a single layer was determined. The saturation magnetization of the sample was then normalized to the overall volume of the nanoparticles in the multilayer film. As the structure of the nanoparticles were known, the theoretical density and subsequently the mass of the nanoparticles were determined. The number of Fe atoms ( $n_{\text{Fe}}$ ) in a nanoparticle is calculated from the lattice parameter and the nanoparticle volume. The same ( $n_{\text{Fe}}$ ) for a single layer was calculated from the volume distribution. The saturation magnetization was then finally normalized to the number of Fe atoms in a multilayer film.

The first-principle calculations have been performed in the framework of density functional theory (DFT) using projected augmented method (PAW) as implemented in Vienna ab initio simulation package (VASP).<sup>38</sup> The exchange-correlation effects were treated using generalized gradient approximation (GGAPBE). The calculations have been performed using lattice parameters obtained in our experiments. For the bulk calculations,  $20 \times 20 \times 10$  Monkhorst-Pack grid for  $k$ -point sampling is used.<sup>39</sup> For the particles calculations,  $\Gamma$ -point is used for  $k$ -point sampling. All the particles are placed in a cubic supercell with 1.5 nm of vacuum to ensure that there is no interaction between neighboring particles. The convergence criterion of  $10^{-4}$  eV has been used for electronic structure. Our experimental results are supported by the DFT simulations.

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