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Unusual spin correlations in a nanomagnet

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We show how atomic-scale exchange phenomena can be controlled and exploited in nanoscale itinerant magnets to substantially improve magnetic properties. Cluster-deposition experiments, first-principle simulations, and analytical calculations are used to demonstrate the effect in Co₂Si nanoclusters, which have average sizes varying from about 0.6 to 29.5 nm. The cluster-deposited nanoparticles exhibit average magnetic moments of up to 0.70 μ_B /Co at 10 K and 0.49 μ_B /Co at 300 K with appreciable magnetocrystalline anisotropies, in sharp contrast to the nearly vanishing bulk magnetization. The underlying spin correlations and associated cluster-size dependence of the magnetization are explained by a surface induced ferromagnetic spin polarization with a decay length of the order of 1 nm, much larger than the nearest-neighbor interatomic distance in the alloy. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922725>]

Spin-polarized nanoclusters or particles are important research objects due to unique scientific features which are absent in the bulk^{1–4} and due to their potential impact in advanced applications including nanoscale spintronics, magneto-optical devices, ultra-high density magnetic recording, and biomedical imaging.^{5–9} A particularly striking but previously overlooked change in the properties of magnetic nanoclusters occurs when the material is close to the onset of ferromagnetism, that is, in very weak itinerant ferromagnets (VWIFs) and strongly exchange-enhanced Pauli paramagnets. Nanostructuring of this class of weak magnetic materials can open a pathway to improve their magnetic properties and subsequently to exploit them for significant applications.

Co₂Si is an intriguing but poorly explored weak magnetic material in spite the fact that it has a great potential as a material for interconnects, gates, and source electrodes in integrated devices, and for nanoelectronics and spintronics applications.^{10–13} Bulk Co₂Si, which crystallizes in the orthorhombic Co₂Si structure (space group Pnma)¹⁴ and whose unit cell is shown in Fig. 1(a), exhibits a magnetic moment of only about 0.04 μ_B /Co at 4 K.¹⁵ The small moment suggests that bulk Co₂Si is very close to the border between exchange-enhanced Pauli-paramagnetism, as in Pt, and VWIF, as in ZrZn₂, and is located on the VWIF side of the Stoner transition.^{16–19} VWIFs differ from ordinary weak itinerant ferromagnets, as in bcc Fe, by rather a small magnetic moment. On the other hand, Co₂Si nanowires with diameters of about 30 to 80 nm and lengths over 10 μm have shown low-temperature ferromagnetic behavior with nearly zero coercivity and exhibited negative magnetoresistance at temperatures below 50 K.^{11–13} However, the low magnetic ordering temperatures of Co₂Si nanowires and bulk alloys are a major impediment for room-temperature applications.

While the previous studies on nanowires indicate that Co₂Si is a fascinating material for magnetic nanostructuring,

both fundamentally and technologically, there are surprisingly no reports on Co₂Si nanoclusters or particles. Furthermore, we are not aware of any analysis of spin-polarization effects in nanoclusters of VWIFs. In this letter,

FIG. 1. (a) Orthorhombic Co₂Si structure. (b) XRD patterns for bulk alloy and nanoclusters. The vertical lines represent the standard peak positions and corresponding intensities of the diffraction peaks for Co₂Si.¹⁴ (c) HRTEM image of a Co₂Si nanocluster. (d) Fast Fourier transform of the HRTEM image indexed to the [010] zone axis (ZA) for the orthorhombic structure. (e) HAADF image and (f) EDS color map showing Co (red) and Si (blue) distributions for a Co₂Si nanocluster.

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we report the synthesis of Co_2Si nanoclusters, which exhibit large room-temperature magnetic moments. Our measurements are explained theoretically by density-functional theory (DFT) and analytical calculations, which demonstrate how the cluster surface spin-polarizes the interior of the nanoclusters.

Our Co_2Si nanocluster films were produced using a cluster-deposition method described elsewhere.²⁰ A Co-Si composite target was sputtered using a DC magnetron sputtering gun in a water-cooled gas-aggregation chamber to form Co_2Si nanoclusters, which were extracted as a beam collimated towards a deposition chamber and deposited on single-crystalline Si (001) substrate. Nanocluster samples having average sizes varying from 5.9 to 29.5 nm were produced by controlling the growth conditions such as sputtering power (60–250 W) and/or argon flow rates [200–750 SCCM (standard cubic centimeter per minute)]. The composition of the sputtering target was, however, controlled to maintain the desired Co_2Si stoichiometry. The magnetic and structural properties were characterized by a *superconducting quantum interference device (SQUID) magnetometer*, a physical property measurement system (PPMS), and a Rigaku D/Max-B x-ray diffractometer (XRD) using a Co K_α wavelength of about 1.7889 Å. Co_2Si nanoclusters were also deposited on carbon-coated copper grids with low coverage densities and their average size and size distribution were measured with an FEI Tecnai Osiris scanning transmission electron microscope (STEM). A thin SiO_2 or carbon cap layer is deposited on the Co_2Si nanocluster films to prevent the samples from oxidation by exposure to air. The bulk Co_2Si powder samples were prepared by mechanically grinding melt-spun ribbons produced from the arc-melted Co_2Si .

The DFT first-principle calculations were carried out using the projector augmented wave method (PAW), as implemented in the Vienna *ab-initio* simulation package (VASP),²¹ and the exchange-correlation effects were treated by a generalized-gradient approximation (GGA)-Perdew-Burke-Ernzerhof.²² For the bulk calculations, we used a $24 \times 22 \times 16$ Monkhorst-Pack grid for the k -point sampling.²³ For the nanoclusters, the Γ -point was used for k -point sampling, and cubic supercells having an edge length of 30 Å were constructed to ensure that there was no interaction between neighboring Co_2Si nanoclusters. The atomic positions for the nanoclusters were relaxed until the force acting on each atom was less than 0.1 eV/Å, and a convergence criterion of 10^{-4} eV was used for the electronic structure. The magnetic anisotropy was calculated by comparing the selfconsistently determined energies for magnetization along the three principal crystal axes. The calculations were performed using experimental lattice parameters.

Figure 1(b) shows the XRD patterns of Co_2Si bulk and nanoclusters; the vertical lines in Fig. 1(b) represent the standard XRD peak positions and relative intensities for the orthorhombic Co_2Si structure of Fig. 1(a). The XRD pattern of the Co_2Si nanoclusters is very similar to that of bulk, except having small differences between the lattice parameters of bulk alloy ($a = 4.915$, $b = 3.733$, and $c = 7.088$ Å) and nanoclusters ($a = 4.888$, $b = 3.726$, and $c = 7.084$ Å). Furthermore, the high-resolution TEM (HRTEM) image of Fig. 1(c) shows that the Co_2Si nanoclusters are single-crystalline and faceted with

orthorhombic shapes. In good agreement with the XRD result, the fast Fourier transform of the HRTEM image of a nanocluster is indexed to the [010] zone axis of the orthorhombic Co_2Si structure as shown in Fig. 1(d). The composition of the nanoclusters was also investigated using STEM and energy-dispersive x-ray spectroscopy (EDS) measurements. For example, Fig. 1(e) shows a high-angle annular dark-field (HAADF) image of a cluster with Z (atomic number) contrast recorded from a Co_2Si nanocluster sample having an average cluster size of 11.3 nm. The corresponding EDS color map shows uniform Co and Si distributions as shown in Fig. 1(f) and EDS analysis also reveals that nanoclusters have the Co_2Si stoichiometry. The nanocluster samples having average size varying from 5.9 to 29.5 nm were fabricated and their magnetic properties were investigated as a function of cluster size.

Figure 2(a) compares the magnetic hysteresis loops of the Co_2Si nanocluster ensemble having an average cluster size of 11.3 nm with those of bulk Co_2Si , both measured at 300 and 10 K. In a field of 70 kOe, the Co_2Si nanoclusters show relatively large magnetic moments, for example, $0.70 \mu_B/\text{Co}$ at 10 K and $0.49 \mu_B/\text{Co}$ at 300 K, as compared to $0.072 \mu_B/\text{Co}$ at 10 K and $0.001 \mu_B/\text{Co}$ at 300 K for bulk Co_2Si . In addition, the nanoclusters also exhibit an appreciable coercivity, $H_c = 2.1$ kOe at 10 K, Fig. 2(a). The underlying anisotropy is expected for orthorhombic structures and is further seen in Fig. 2(b), which compares the hysteresis loops in different directions for an aligned Co_2Si nanocluster film. For this, the easy-axis of the Co_2Si nanoclusters was aligned *in-plane* with respect to Si substrate using a magnetic field of about 5 kOe prior to deposition as described in earlier studies.²⁰ The loops show a comparatively high coercivity $H_c = 2.2$ kOe and a high remanence ratio $M_r/M_s = 0.76$ along the easy axis, compared to the values measured in the plane formed by the other two axes ($H_c = 1.3$ kOe and $M_r/M_s = 0.44$). The corresponding theoretical lowest-order anisotropy constants,^{18,24} as determined from the DFT calculations for orthorhombic nanoclusters, are $K_1 = -3.9$ Mergs/ cm^3 (-0.39 MJ/ m^3) and $K'_1 = -0.66$ Mergs/ cm^3 .

We have performed DFT calculations for nanoclusters having orthorhombic and spherical shapes. Examples of two typical clusters having orthorhombic (96 atoms) and spherical (132 atoms) shapes used for DFT calculations are shown in Figs. 3(a) and 3(b), respectively.

An intriguing aspect of the Co_2Si system is its very weak itinerant character. This phenomenon, first encountered in alloys such as ZrZn_2 ,^{16–19} is most transparently rationalized in terms of the exchange-enhanced Pauli susceptibility

FIG. 2. In-plane hysteresis loops of Co_2Si : (a) Bulk alloy and nanocluster (NC) measured at 300 (square) and 10 K (circle). (b) Aligned nanoclusters measured at 10 K along the easy and hard axes.

FIG. 3. Schematic of (a) orthorhombic nanocluster having 96 atoms (64 Co and 32 Si) and (b) spherical cluster having 132 atoms (88 Co and 44 Si). Green and yellow spheres represent Co and Si atoms, respectively. Density of states for (c) surface Co atoms and (d) core Co atoms in an orthorhombic Co_2Si nanocluster having 96 atoms.

$$\chi = \frac{\chi_0}{1 - ID(E_F)}, \quad (1)$$

where χ_0 and I are the usual noninteracting Pauli susceptibility and Stoner parameter, respectively.²⁵ When the density of states (DOS) at the Fermi level, $D(E_F)$, reaches the Stoner criterion ($D \geq 1/I$, where $I \sim 1 \text{ eV}$), then the metal becomes ferromagnetic, as epitomized by elemental Fe, Co, and Ni.²⁶ Basically, this means that 3d bands of small width $W \sim 1/D(E_F)$ give rise to ferromagnetism. Metals such as Pt are strongly exchange-enhanced, that is, they do not obey the Stoner criterion but are close to obeying it. In other words, $1/(1 - ID)$ is large but finite, so that a small external magnetic or exchange field creates a substantial magnetization but not the spontaneous or zero-field magnetization required for a ferromagnet.

By comparison, VWIFs barely obey the Stoner criterion, meaning that they exhibit a nonzero but small spontaneous magnetization. As shown in Table I, our DFT calculations on Co_2Si yield a bulk magnetic moment of $0.36 \mu_B/\text{Co}$, which is substantially smaller than the Co moment in the range of 1 to $2 \mu_B$ encountered in most Co-based ferromagnets. This is a clear sign for VWIF in the system.

TABLE I. First-principle magnetic properties of bulk Co_2Si and an orthorhombic Co_2Si nanocluster with 96 atoms ($D = 1.3 \text{ nm}$).

System	Bulk	Nanocluster
E_{PM} (eV)	-83.882	-584.158
E_{FM} (eV)	-83.934	-587.352
$E_{\text{FM}} - E_{\text{PM}}$ (eV)	-0.052	-3.194
Total moment (μ_B)	2.71	52.804
Co moment (average) (μ_B)	0.36	0.84
Si moment (average) (μ_B)	-0.02	-0.037

Furthermore, VWIF is indicated by a small energy difference between the ferromagnetic and paramagnetic states, 0.052 eV per Co_2Si unit cell, or 0.006 eV per Co atom, as opposed to more than 1 eV for elemental Co.²⁷

Similar to the case of exchange-enhanced Pauli paramagnets, small exchange fields strongly amplify the magnetic moment of VWIFs. In clusters, this exchange originates from the surface, because I is basically an invariable atomic quantity, whereas D scales a $1/z^{1/2}$, where z is the number of nearest transition-metal neighbors.²⁸ This number is naturally reduced at surfaces, which therefore tend to exhibit enhanced magnetic moments. Our DFT calculations indicate that the surface Co atoms have a magnetic moment of the order of $1.3 \mu_B$, whereas the moment of the center atoms is about $0.3 \mu_B$, very similar to the calculated bulk moment. Figures 3(c) and 3(d) reinforce this picture by comparing the calculated surface (c) and interior (d) DOS for a orthorhombic nanocluster containing 96 atoms, the latter being very similar to the bulk DOS.

A specific feature of VWIFs is the spatial distribution of the moment created by nearly fully spin-polarized atoms, which are located at the surface in the present nanocluster system. In addition to oscillatory RKKY (Ruderman-Kittel-Kasuya-Yosida) exchange contributions, VWIFs exhibit a strong preasymptotic exponential behavior, which overlays and largely dominates the RKKY contributions.^{29,30}

In nanoclusters, the corresponding VWIF moment decays approximately exponentially from the surface, with some oscillatory RKKY corrections. Inside the cluster, the decay of the moment m per Co atom is described by the differential equation

$$-\nabla^2 m + \kappa^2 m = 0, \quad (2)$$

where κ is the inverse decay length and decreases with $D - 1/I$, meaning that interactions become infinite-range as the Stoner criterion $D = 1/I$ is satisfied. Expressions similar to Eq. (2) are well-known in the context of particle physics, where they describe Yukawa interactions,³¹ and in micro-magnetism, where they refer to angular spin correlations.²⁴ In the present case, the correlations describe the spatial distribution of the magnetic moment away from a perturbation. For a point-like perturbation, Eq. (2) has the well-known solution $m(r) \sim \exp(-\kappa r)/r$, but in nanoclusters the perturbation is at the surface, and the mode $m(r)$ is affected by its confinement inside the nanocluster. The corresponding differential equation involves the operator

$$\nabla^2 m = \frac{d^2}{dr^2} m(\kappa r) + \frac{2}{r} \frac{d}{dr} m(\kappa r) \quad (3)$$

and has the solution

$$m(r) = m(R) \frac{R \sinh(\kappa r)}{r \sinh(\kappa R)}, \quad (4)$$

where $m(r)$ and R are the normalized magnetic moment at a distance r from the cluster center and the radius of the cluster, respectively. Volume integration over Eq. (4) yields the average magnetization $\langle m \rangle = 3 m(R) [\coth(\kappa R) - 1/\kappa R]/\kappa R$, which can be measured directly.

Figure 4(a) compares the prediction of Eq. (4) with the DFT moments for an orthorhombic Co₂Si nanocluster having 324 atoms (216 Co and 108 Si atoms), radially averaged with bins of about 0.2 nm. It is worth mentioning that the radial distribution of magnetic moments in the spherical nanocluster having 132 atoms also shows similar behavior. Note the band narrowing in Fig. 3(c), as compared to Fig. 3(d), which is the reason for the surface moment.

Figure 4(b) shows the size dependence of the averaged moment from 0.6 nm to about 29.5 nm, which also includes the magnetic moments for the experimental cluster sizes and bulk alloy. Note that the cluster size in the bulk alloy is estimated from the width of an XRD peak using Scherrer's equation.

To discuss the magnitude of κ , it is instructive to approximate the magnetic energy per Co atom by the expansion^{16,17,32}

$$E = c(\nabla m)^2 - f(ID - 1)m^2 + gm^4, \quad (5)$$

where c , f , and g are parameters and the fourth-order cutoff term with $g > 0$ ensures a finite spin-polarization once the Stoner criterion is satisfied. In the strongly exchange-enhanced Pauli or "Yukawa" limit ($ID < 1$), Eq. (5) can be linearized directly and reproduces Eq. (2). In the limit of very weak itinerant ferromagnets ($ID > 1$), the linearization requires a renormalization, $f \rightarrow -2f$, which is very similar to the Higgs, Nambu-Goldstone, and Landau mechanisms of spontaneous symmetry breaking.³³⁻³⁵

By analyzing Eq. (5), it is straightforward to show that $f = 2E_o/m_o^2$, $g = E_o/m_o^4$, and $c = f/\kappa_o^2$. Here, the energy $E_o = E_{PM} - E_{FM}$ refers to fully spin-polarized Co ($E_o \sim 1.5$ eV), m_o is the maximum Co moment (about $1.5 \mu_B$), and $1/\kappa_o$ is roughly equal to the minimum interatomic Co-Co distance (about 0.25 nm). Substitution into Eq. (5) and minimization of Eq. (5) yields the following VWIF relations: $m^2 = m_o^2 (ID - 1)$, $E_{PM} - E_{FM} = E_o(ID - 1)$, and $\kappa^2 = \kappa_o^2 (ID - 1)$. These equations summarize how VWIFs exhibit reduced moments, reduced energy difference between ferromagnetic and paramagnetic states, and enhanced spin-polarization decay lengths, all of which can be compared with DFT and/or experiment. In the present system, $\kappa \approx 1.3/\text{nm}$ (experiment) and $\kappa \approx 2.3/\text{nm}$ (DFT), both are much smaller than the decay constant $\kappa \approx 4/\text{nm}$ in the strongly ferromagnetic limit. The agreement between DFT and experiments is reasonably good for

FIG. 4. Radial distribution of magnetic moments from the center of an orthorhombic nanocluster having 324 atoms estimated from DFT (hollow spheres). The solid line corresponds to the fitting of magnetic moments using Eq. (4). (b) Average magnetic moment as a function of cluster size, where the experimental values are magnetic moments measured at 10 K. The solid line is derived from the equation for an average magnetic moment $\langle m \rangle = 3m(R) [\coth(\kappa R) - 1/\kappa R]/\kappa R$ using $m(R) = 1.5 \mu_B$ and $\kappa = 1.3/\text{nm}$.

cluster sizes larger than 1 nm, with deviation for smaller cluster sizes. Possible reasons are experimental real-structure features (defects), the approximate character of Eq. (5), and electron-electron correlation effects. However, the order of magnitude of κ and size-dependent decay of magnetic moment shown in Fig. 4(b) provide a clear proof for the mechanism outlined in this paper.

In conclusion, we have discovered a unique nanoscale moment-enhancement effect in Co₂Si nanoclusters. Our experiments yield room-temperature magnetic moments of up to $0.49 \mu_B$ per Co atom in nanoclusters, two orders of magnitude higher than that of bulk Co₂Si. There is a strong dependence of the magnetic moment on the size of the Co₂Si nanoclusters, which we explain as a polarization of the very weak itinerant core by strongly spin-polarized surface Co atoms. The nanoclusters also exhibit appreciable magneto-crystalline anisotropy and coercivity, which are unusual for very weak itinerant ferromagnetic materials. These results provide a clear insight at nanoparticle magnetism and are technologically important, because they demonstrate how low-dimensional and quantum-confinement effects can be combined in a unique way to achieve useful size-dependent magnetic properties in nanoscale itinerant magnets for significant applications.

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