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Novel structures and physics of nanomagnets (invited)

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Nanoscale magnets with characteristic dimensions in the range of 1–100 nm are important in several areas of nanoscience and technology. First, this length scale spans the typical important dimensions of exchange lengths and domain-wall widths, which means that significant control of magnetic properties can be obtained by varying grain or particle dimensions. Second, the nonequilibrium synthetic processes used for clusters, particles, and films, often lead to new real-space crystal structures with completely novel spin structures and magnetic properties. Third, a basic-science challenge in this class of matter involves the spin-polarized quantum mechanics of many-electron systems containing 10–10 000 atoms. Finally, the materials under study may have important future applications in high-density data storage, ultra-small spintronic devices, or high-energy magnetic materials. In this article, we discuss our recent work on novel Fe-Au nanoclusters, MnAu-Mn core-shell structures, and complex high-anisotropy Co-rich intermetallic compound clusters. We also present new results on Fe-based alloys including the magnetic properties of semiconducting FeSi₂ nanoclusters and spin correlations in FeGe nanocluster films. © 2015 AIP Publishing LLC.

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Research on nanoscale magnetic clusters and particles has gained importance recently in order to understand nanoscale magnetism and create complex structures with novel magnetic properties.^{1–7} As the structural length scale approaches the nanoregime, the magnetic properties are a complex function of size-modified electronic structure, defects, and surface effects, and this can lead to unusual magnetic ordering or transitions, modified ordering temperatures, and entirely different spin structures in nanoparticles and clusters as compared to the corresponding bulk alloys.^{8,9} In the case of bulk and thin-film magnets constructed with nanoscale building blocks, the exchange interactions between the nanoclusters or grains also control the coercivity H_c . In addition, it is also important, for both basic science and technological reasons, to understand the ground-state electronic structure including spin polarization in objects at length scales smaller than 20 nm. Competing exchange, phenomena involving spin-orbit coupling such as magnetic anisotropy and Dzyaloshinsky-Moriya (DM) interactions, and magnetostatic interactions yield novel skyrmion-like phenomena (vortex-like spin structures) in nanostructured magnets.^{10–14} Interestingly, in addition to real-space images using Lorentz force microscopy, the skyrmion spin-structures also have shown sharp peaks/features in dc susceptibility spectra derived from the magnetization curves for thin films just below the ferromagnetic or antiferromagnetic ordering temperatures.^{15,16}

Nanomagnetic assemblies produced using wet-chemical, conventional thin-film, and gas-aggregation-type cluster-

deposition methods have shown uniform distribution of particle sizes with well-controlled compositions and interfaces.^{1,17–25} In particular, the non-equilibrium cluster-deposition method has produced directly nanoparticles of metastable and traditional magnetic phases with a high degree of crystalline ordering.^{5,21–25} In addition, during the crystallization process, the modified thermodynamic and kinetic factors lead to new crystal structures in nanoclusters that are not possible in the case of bulk alloys,^{6,26,27} and also favor specialized nanostructures such as core-shell and composite nanoclusters with interesting magnetic properties.^{6,28} It is important to note that the sintering associated with the annealing process is avoidable in the case of the cluster-deposition method, and thus nanoclusters can be assembled with atoms forming a second phase with properties that complement those of the nanocluster phase.^{23–25} An intriguing example is the aligned exchange-coupled hard-soft nanocomposite films made of high-anisotropy nanoclusters with a high H_c and soft phase matrix having a high saturation magnetization M_s .^{24,25} In this paper, we review our recent work along with new results from experimental and theoretical studies on the structural and magnetic properties of Co-, Fe- and Mn-based nanoclusters having average sizes varying from about 1 to 20 nm.

The cluster-deposition method used for producing magnetic nanoparticles is described elsewhere and consists of a water-cooled or liquid-nitrogen-cooled gas-aggregation chamber and a deposition chamber.^{5,6,23–26} In brief, a composite target of desired stoichiometry is sputtered in the gas-aggregation chamber using a mixture of Ar and He by direct current (DC) magnetron sputtering and the sputtered atoms are condensed to form nanoclusters, which are extracted as a

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collimated beam moving towards the substrate kept at room temperature in the deposition chamber. When the nanoclusters are created as single-crystal uniaxial particles, they can be aligned in the gas phase by applying a magnetic field ($H_{al} \approx 5$ kOe) using a set of permanent magnets prior to deposition and also co-deposited with a second magnetic phase or a non-magnetic layer using another DC/RF magnetron sputtering gun employed in the deposition chamber.^{5,6,23–25}

Chemically ordered and/or high-anisotropy crystal structures are obtained in nanoclusters by post-deposition annealing or by directly controlling the sputtering power and gas-aggregation conditions.^{6,23–28} Let us consider Fe-Au and Mn-Au bimetallic nanoclusters, which are formed via condensing Fe or Mn and Au atoms at about -130°C in the gas-aggregation chamber cooled by liquid nitrogen.^{6,26,27} The nanoclusters formed at liquid nitrogen temperature always show disordered crystal structures, and thus a post-deposition annealing is required to achieve chemically ordered and/or high-anisotropy crystal structures. In order to mitigate the agglomeration or growth of nanoparticles during the annealing, the nanoclusters can be essentially separated from each other by dispersing them in a non-magnetic matrix such as SiO_2 or carbon *via* sequential depositions of nanoclusters and non-matrix layers.^{6,26,27}

In the case of Fe-Au, nanoclusters of three different stoichiometries have been synthesized with disordered crystal structures including Fe_3Au (bcc), FeAu (fcc), and FeAu_3 (fcc). The nanoclusters are smaller than 10 nm and transform into the chemically ordered crystal structures $L1_2$ (Fe_3Au), $L1_0$ (FeAu) and $L1_2$ (FeAu_3) upon annealing at 600°C .²⁶ This is significant because the limited mutual solubility of Fe and Au prohibits the formation of chemically ordered compounds in Fe-Au bulk alloys. For example, Fig. 1(a) shows a high-resolution transmission electron microscope (HRTEM) image of an annealed FeAu_3 nanocluster, which forms a $L1_2$ -ordered structure similar to the schematic picture shown in Fig. 1(b).²⁶ A magnified and background refined view of Fig. 1(a) exactly overlays with

FIG. 1. Fe-Au bimetallic nanoclusters. (a) A HRTEM image of an annealed FeAu_3 nanocluster. (b) $L1_2$ -ordered FeAu_3 structure. (c) A magnified and background refined view of (a) with an overlay of the unit cell projection of the $L1_2$ -ordered structure along [011] zone axis. (d) The stability factor (ΔF) as a function of particle size for three different kinds of chemically ordered Fe-Au nanocompounds along {111} direction. Reproduced with permission from P. Mukherjee, P. Manchanda, P. Kumar, L. Zhou, M. J. Kramer, A. Kashyap, R. Skomski, D. J. Sellmyer, and J. E. Shield, ACS Nano **8**, 8113 (2014). Copyright 2014 American Chemical Society.

the unitcell projection of $L1_2$ -ordered structure along [011] zone axis as shown in Fig. 1(c). Similarly, HRTEM analysis shows that the annealed FeAu and FeAu_3 nanoclusters exhibit $L1_0$ - and $L1_2$ -ordered structures, respectively.^{26,27}

The stability of the ordered structures in the case of nanoclusters is discussed in terms of a stability factor ΔF using a size-dependent equilibrium thermodynamic model.²⁶ In brief, ΔF is the difference between the total surface energy of a nanocluster (SE_{tot}) and the size-dependent heat of mixing $H_m(d)$, where d is the diameter or cluster size. When ΔF is positive, an intermetallic compound with chemical ordering forms and for negative ΔF , $H_m(d)$ is larger leading to the segregation of Fe and Au. The estimated values of ΔF along the {111} direction of the lattice is plotted as a function of cluster size as shown in Fig. 1(d) and the results show a positive ΔF below a critical size for all three chemically ordered structures.²⁶ Regarding magnetic properties, $L1_2$ - Fe_3Au nanoclusters show a high moment, $2.98 \mu_B/\text{Fe}$, at 10 K, as compared to $L1_0$ - FeAu ($0.23 \mu_B/\text{Fe}$) and $L1_2$ - FeAu_3 ($0.85 \mu_B/\text{Fe}$).²⁶

MnAu nanoclusters also form a structure not seen in the bulk equilibrium phase diagram. The as-produced MnAu nanoclusters form a disordered fcc structure and an annealing at 500°C is required for transforming fcc to the $L1_0$ -ordered structure, as shown in Fig. 2(a).^{6,29} The experimental results and density functional calculations (DFT) together show that the $L1_0$ -ordered structure is increasingly favorable on increasing the cluster size from 1.0 to 6.5 nm, but the lattice parameters, tetragonal distortion ratio, and Mn concentrations increase monotonically with cluster size as shown in Fig. 2(b).^{6,29} In particular, annealed MnAu nanoclusters larger than a critical value ($d_c \approx 3.6$ nm) have Mn/Au ratios of above equiatomic concentration and form a novel $L1_0$ MnAu-fcc Mn core-shell structure. This result is clearly revealed by Fig. 2(c), an electron energy loss spectroscopy

FIG. 2. MnAu nanoclusters. (a) $L1_0$ -ordered MnAu structure; (b) The critical size d_c , above which the nanoclusters are Mn-rich, is also marked. Size-dependent tetragonal distortion ratio (c/a) and Mn concentration, where squares and stars correspond to the values obtained from experiment and DFT calculations, respectively. The dotted and solid lines are polynomial fits to the corresponding data. (c) EELS element mapping for an annealed 6.5 nm cluster. (d) Hysteresis loops at 10 K for MnAu core and MnAu-Mn core-shell nanoparticles. Reproduced with permission from X. Wei, R. Zhou, W. Lefebvre, K. He, D. Le Roy, R. Skomski, X. Z. Li, J.E. Shield, M. J. Kramer, S. Chen, X. C. Zeng, and D. J. Sellmyer, Nano Lett. **14**, 1362 (2014). Copyright 2014 American Chemical Society.

(EELS) elemental mapping of a high-angle annular dark field (HAADF) image of a 6.5 nm MnAu cluster measured using scanning transmission electron microscope.⁶

Asymmetric atomic migration leads to the formation of core-shell structures in the larger clusters and is explained by Ostwald ripening, describing the migration of atoms from small to larger clusters in a liquid or solid solution.⁶ The formation of a core-shell structure is presumably a consequence of the following changes during the annealing process: the smallest metastable clusters with $d < 1.5$ nm decompose into free Mn and Au atoms; the clusters with $d < d_c$ on average lose Mn to become Mn-poor MnAu clusters; the clusters with $d > d_c$ on average receive Mn to become Mn-rich MnAu clusters. The free Mn atoms are preferentially redeposited on the surface of the largest clusters to form fcc-Mn nanoshells on $L1_0$ -MnAu clusters.⁶ The evolution of nanostructural changes also subsequently leads to the size-dependent magnetic properties in MnAu nanoclusters; $L1_0$ MnAu-fcc Mn core-shell structures exhibit net ferromagnetic ordering with a large average magnetic moment, $1.4 \mu_B/\text{Mn}$, at 10 K, as compared to $L1_0$ MnAu clusters that exhibit anti-ferromagnetic ordering with a moment of only $0.17 \mu_B/\text{Mn}$. This structure-dependent magnetic transformation is shown in Fig. 2(d) and is also consistent with the DFT results.⁶

Uniaxially aligned nanoclusters having appreciable magnetocrystalline anisotropies ($K_1 > 10$ Mergs/cm³) can be used as building blocks for creating high-energy magnetic materials, but the easy-axis alignment process is strongly hindered by the post-deposition annealing often required to obtain the high-anisotropy structure.¹⁹ In this regard, we have used successfully the cluster-deposition method to produce nanoclusters of high-anisotropy Co-rich intermetallic compounds without the requirement of a subsequent post-deposition annealing. The compounds include traditional R-Co alloys ($R = \text{Y}$ or Sm) such as RCo_5 with hexagonal CaCu_5 -type structure and R_2Co_{17} with rhombohedral $\text{Th}_2\text{Zn}_{12}$ -type structures,^{5,30–32} and also complex rare-earth-free HfCo_7 and $\text{Zr}_2\text{Co}_{11}$ alloys having orthorhombic and rhombohedral structures, respectively, as shown in Fig. 3(a).^{23–25,33,34} Note that the synthesis of single-phase HfCo_7 and $\text{Zr}_2\text{Co}_{11}$ has been challenging using bulk preparation methods due to the metastable nature and/or secondary phase formation during the cooling process.^{35,36} In the case of cluster-deposition method, the high-anisotropy nanoclusters with a high degree of crystalline ordering is achieved directly by sputtering the composite target at a high power ($P_{dc} > 120$ W), precisely controlling the gas flow rates and gas-aggregation length, and using water to cool the gas-aggregation chamber.^{5,23–25} As an example, the sputtering power-dependent crystal structures and room-temperature coercivities of isotropic Y-Co nanocluster films are shown in Fig. 3(b) and this result shows a high $H_c = 8.0$ kOe for YCo_5 produced at $P_{dc} = 150$ W.⁵ Similarly, the high-power sputtering method also yields appreciable room-temperature coercivities for isotropic SmCo_5 ($H_c = 4.5$ kOe), $\text{Zr}_2\text{Co}_{11}$ ($H_c = 3.0$ kOe), and HfCo_7 ($H_c = 7.3$ kOe) nanocluster films.^{24,25,30} The co-rich high-anisotropy nanoclusters showing high coercivities have average size in the range of 7–15 nm.

FIG. 3. High-anisotropy Co-rich intermetallic clusters. (a) Rhombohedral $\text{Zr}_2\text{Co}_{11}$ and orthorhombic HfCo_7 structures.^{33,34} (b) The sputtering power dependent coercivity and crystal structures observed for Y-Co nanoclusters. Reproduced with permission from B. Balasubramanian, R. Skomski, X. Z. Li, S. R. Valloppilly, J. E. Shield, G. C. Hadjipanayis, and D. J. Sellmyer, Nano Lett. 11, 1747 (2011). Copyright 2011 American Chemical Society. (c) Room-temperature hysteresis loops for aligned HfCo_7 and $\text{Zr}_2\text{Co}_{11}$ nanoparticle films measured along the easy-axis direction.^{24,25} (d) The measured H_c (open sphere) and remanent magnetic polarization J_r (solid sphere) as a function of temperature for a $\text{Zr}_2\text{Co}_{11}$ nanoparticle film, where the temperature range 27–180 °C is marked by a dotted rectangle.

The direct ordering obtained during the gas-aggregation process also provides an opportunity to align the easy axes of nanoparticles in the gas phase using a magnetic field $H_{\text{al}} \approx 5$ kOe, prior to deposition on a substrate,^{23–25} and this is important to achieve a high remanent magnetization M_r , close to M_s . For example, the room-temperature in-plane easy-axis hysteresis loops of the aligned $\text{Zr}_2\text{Co}_{11}$ and HfCo_7 nanoparticle films are shown in Fig. 3(c). The results show promising room-temperature permanent-magnet properties with $H_c = 4.2$ kOe, $J_s = 10.2$ kG, and $M_r/M_s = 0.88$ for $\text{Zr}_2\text{Co}_{11}$ and $H_c = 8.7$ kOe, $J_s = 10.9$ kG, and $M_r/M_s = 0.82$ for HfCo_7 ,^{24,25} where $J_s = 4\pi M_s$ is the saturation magnetic polarization. However, it is also of paramount importance to maintain a high coercivity H_c and a remanent magnetic polarization J_r at elevated temperatures of typically up to 180 °C for exploiting the nanoparticles for high-temperature permanent-magnet applications. $\text{Zr}_2\text{Co}_{11}$ nanoparticles show high J_r (9.6–7.9 kG) and appreciable H_c (4.2–1.7 kOe) for temperatures 27–180 °C as shown in Fig. 3(d). Similarly, HfCo_7 nanoparticles exhibit $J_r = 9.2$ –9.0 kG and $H_c = 8.7$ –4.5 kOe in this temperature range.²⁵ The results yield appreciable average temperature coefficients for $\text{Zr}_2\text{Co}_{11}$ ($\Delta J_r \approx -0.10\%/^\circ\text{C}$ and $\Delta H_c \approx -0.43\%/^\circ\text{C}$) and HfCo_7 ($\Delta J_r \approx -0.02\%/^\circ\text{C}$ and $\Delta H_c \approx -0.26\%/^\circ\text{C}$), which are comparable to the values obtained for the leading high-performance permanent-magnet material $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($\Delta J_r \approx -0.10\%/^\circ\text{C}$ and $\Delta H_c \approx -0.40\%/^\circ\text{C}$).^{25,37,38} Earlier work has reported that thermal fluctuations of nanoparticles reduce H_c substantially on increasing temperature.^{39,40} However, in the present study, the magnetic nanoclusters are exchange-coupled in films and this substantially reduces the thermally activated reversal of individual nanoparticles and leads to appreciable coercivities at elevated temperature.²⁵

The coercivities of Co-rich intermetallic nanocluster films are smaller than the corresponding ideal Stoner-Wohlfarth value, $H_c = 2K_1/M_s$, expected for non-interacting nanoclusters, because the exchange interactions created by nanoclusters in

the films lower H_c . In order to understand the effect of inter-cluster interactions, let us consider two sample structures, shown in Figs. 4(a) and 4(b), constructed using about 3.5 nm SmCo_5 clusters as building blocks.³² Figure 4(a) shows a dense nanocluster film of 168 nm thickness coated with a 78 nm thick carbon film as top and bottom layers and this sample exhibits almost zero coercivity at room temperature due to strong exchange interactions. Figure 4(b) shows a sample structure in which nanoclusters are dispersed in a carbon matrix and this is obtained by sequential depositions of 50 layers of nanoclusters and carbon layers. Note that each layer of clusters is deposited only for shorter times (about 10 s) in order to have essential isolation between the clusters, and different samples with carbon layer thickness varying from 6.5 to 52 nm is also fabricated in order to change the vertical separation of nanoclusters. As shown in Fig. 4(c), the room-temperature coercivity increases with an increase of the carbon layer thickness (or vertical separation of nanoclusters) and reaches a maximum value of about 12 kOe for 52 nm carbon layer thickness, and this result shows that the separation of nanoparticles decreases the inter-cluster interactions and subsequently improves the coercivity.³² However, for creating high-energy hard-soft magnetic materials, we require dense-packed nanostructured magnetic materials with a strong exchange coupling to obtain a high M_s , while maintaining somewhat reasonable H_c .

Aligned high-anisotropy nanoclusters, such as the rare-earth-free HfCo_7 or $\text{Zr}_2\text{Co}_{11}$, are co-deposited with a soft $\text{Fe}_{65}\text{Co}_{35}$ phase to form exchange-coupled nanocomposite films.^{23–25} The deposition rate of nanoclusters and soft phase layer can be controlled to vary the soft phase fraction (f). For example, Fig. 5(a) shows energy dispersive x-ray spectroscopy (EDS) elemental color mapping obtained from a HAADF image for a HfCo_7 :Fe-Co nanocomposite film having 22 vol. % of the soft Fe-Co phase (or $f=0.22$).²⁵ The result shows that the nanoclusters are coated by and embedded in the soft phase and suggests a nanostructure similar to the schematic shown in Fig. 5(b) for HfCo_7 :Fe-Co and $\text{Zr}_2\text{Co}_{11}$:Fe-Co nanocomposite films. In this nanostructure, the magnetization of the soft phase is also aligned with hard magnetic nanoparticles due to the strong exchange coupling.

FIG. 4. Schematic diagrams: (a) Dense SmCo_5 nanocluster film only covered with a carbon film at top and bottom and (b) SmCo_5 nanoclusters dispersed in a carbon matrix via sequential depositions of 50 layers of nanoparticles and carbon film. (c) Room-temperature coercivity of SmCo_5 nanoclusters as a function of carbon layer thickness (or vertical separation). Reproduced with permission from O. Akdoğan, W. Li, B. Balasubramanian, D. J. Sellmyer, and G. C. Hadjipanayis, Adv. Funct. Mater. 23, 3262 (2013). Copyright 2013 WILEY-VCH Verlag GmbH & Co.

FIG. 5. Exchange-coupled hard-soft nanocomposite films. (a) EDS elemental color mapping for HfCo_7 :Fe-Co having a soft Fe-co fraction of 22 vol. % ($f=0.22$) (Adapted from Ref. 25). (b) A schematic sample structure, where ϕ and a are the local magnetization angle with respect to the easy axis of hard magnetic nanoclusters and distance between two nanoclusters, respectively. The easy axis of nanoclusters and measurement field are along the x-axis direction. (c) Room-temperature hysteresis loops for $\text{Zr}_2\text{Co}_{11}$:Fe-Co having different Fe-Co content f . (d) A thin film model structure with a total area of $10\text{ nm} \times 10\text{ nm}$ and having a soft phase content $f=0.25$ and a three-dimensional visualization of the onset of magnetization reversal or nucleation mode ϕ (Adapted from Ref. 25).

This behavior is revealed by the single-phase easy-axis hysteresis loops with improved magnetizations for $\text{Zr}_2\text{Co}_{11}$:Fe-Co nanocomposite films as shown in Fig. 5(c), and similar results also are observed in the case of HfCo_7 :Fe-Co nanocomposite films.²⁵ It is worth noting that the addition of soft phase does not deteriorate the coercivity excessively, and appreciable room-temperature coercivities are achieved for HfCo_7 :Fe-Co with $f=0.22$ ($H_c=6.0$ kOe) and $\text{Zr}_2\text{Co}_{11}$:Fe-Co with $f=0.15$ (3.5 kOe).

In a reasonable approximation, the nucleation mode (or onset of magnetization reversal) for aligned hard-soft nanocomposites obeys $-A\nabla^2\phi + (K_1(\mathbf{r}) - \frac{M(\mathbf{r})H}{2})\phi = 0$, where the nucleation mode $\phi(\mathbf{r})$ defines the local magnetization angle relative to the easy axis of the hard phase and $K_1(\mathbf{r})$ and $M(\mathbf{r})$ are the local anisotropy and local magnetization, respectively.²⁵ We also estimated the nucleation mode numerically using the above equation for an ideal thin-film model structure having a total area of $10\text{ nm} \times 10\text{ nm}$ with $f=0.25$, which is similar to our nanocomposite films. The model structure (bottom image) is shown along with the estimated nucleation mode (top image) in Fig. 5(d) and the result indicates that the magnetization reversal is not entirely localized around the soft phase, but it is centered around the soft phase and penetrates deep into the hard region.²⁵ Thus, the nanocomposite films are expected to retain a reasonable amount of coercivity from the hard magnetic nanoparticles. For example, nanocomposite films such as $\text{Zr}_2\text{Co}_{11}$ with $f=0.15$ and HfCo_7 with $f=0.22$ retain almost 83% (3.5 kOe) and 69% (6.0 kOe) of coercivities, respectively, from the corresponding hard-phase nanoparticles.

The improved magnetic properties of the aligned exchange-coupled nanocomposite films translate into high energy products. For example, the nominal or intrinsic energy product for thin films is calculated in the standard way from the maximum product of B and H in the second

quadrant of the BH curve $[(BH)_{\max}]$. Nanocomposite films such as $\text{Zr}_2\text{Co}_{11}:\text{Fe}_{65}\text{Co}_{35}$ with $f=0.15$ and $\text{HfCo}_7:\text{Fe}_{65}\text{Co}_{35}$ with $f=0.07$ yield room-temperature energy products of 19.5 and 20.3 MGOe, respectively.^{24,25} These values are the highest among permanent-magnet alloys not containing critical rare-earth elements or expensive Pt;^{24,25,41–45} they also are comparable with the energy product (20.1 MGOe) obtained for chemically prepared exchange-coupled FePt- Fe_3Pt nanoparticle assemblies.¹ In addition, the low temperature coefficients of the high-anisotropy nanoclusters also result in appreciable energy products at elevated temperatures. For example, $\text{HfCo}_7:\text{Fe}_{65}\text{Co}_{35}$ nanocomposites with $f=0.07$ have shown an energy product of about 17.1 MGOe at 180 °C.²⁵ An intriguing feature of the system is that the Kronmüller factor α increases with temperature, where $H_c = 2\alpha K_1/M_s - N_{\text{eff}}M_s$ is the phenomenological expression for coercivity. α increases with temperature, because the micromagnetic exchange-coupling length scales as $K_1^{-1/2}$ and K_1 decreases with increasing temperature.²⁵

Nanoclusters of Fe-based alloys with Si and Ge are of interest due to their unique magnetic properties and spin structures associated with their electronic and crystal structures. In this study, our focus is on two systems including semiconducting $\beta\text{-FeSi}_2$ nanoclusters crystallizing into an orthorhombic structure^{46–48} and FeGe nanoclusters with the B20 type structure.^{49,50} Figure 6 summarizes the structural and magnetic properties of FeSi_2 nanoclusters. FeSi_2 nanoclusters exhibit a single-crystalline structure with a high degree of atomic ordering as shown in the HRTEM image (Fig. 6(a)), and a fast Fourier transform (FFT) of the HRTEM image is indexed to the $(\bar{1}10)$ zone axis of the orthorhombic structure (Fig. 6(b)). Figure 6(c) shows a HAADF image with Z (atomic number) contrast and the corresponding EDS elemental color maps for FeSi_2 nanoclusters. The results show a uniform distribution of Fe and

FIG. 6. FeSi_2 nanoclusters. (a) A HRTEM image. (b) Fast Fourier transform of the HRTEM image, which is indexed to the $(\bar{1}10)$ zone axis of the orthorhombic structure. (c) A HAADF image with Z-contrast and the corresponding EDS elemental color mappings showing Fe and Si and combined Fe and Si. (d) Hysteresis loops measured at 300 and 10 K.

Si across the nanoclusters and a stoichiometry close to the $\beta\text{-FeSi}_2$ phase. Interestingly, FeSi_2 nanoclusters are ferromagnetic and exhibit coercivities of 50 and 200 Oe at 300 and 10 K, respectively, as shown in Fig. 6(d), as compared to bulk alloy and previous reports on chemically disordered nanoparticles.^{46,48} Bulk FeSi_2 has been reported to be a non-magnetic material, whereas the chemically disordered $\beta\text{-FeSi}_2$ nanoparticles with average sizes varying from 15 to 55 nm have shown superparamagnetic behavior.^{46,48}

FeGe nanoclusters are expected to exhibit a particularly intriguing behavior due to the rich physics and complicated spin structure of bulk and thin-film FeGe.^{49,50} For example, FeGe films have shown stable formation of skyrmions for a wide range of field and temperature ranges and also up to a comparatively high temperature of about 280 K.^{49,50} In this study, we have fabricated FeGe nanocluster films and investigated their structural and magnetic properties. A HAADF image with Z contrast and the corresponding elemental color maps for FeGe nanoclusters show a uniform distribution of Fe and Ge across the nanoclusters as shown in Fig. 7(a). In addition, FeGe nanoclusters are single crystalline as shown in Fig. 7(b), and the corresponding FFT image is indexed to the $[001]$ zone axis of the cubic B20 type structure as shown in Fig. 7(c). The temperature-dependent magnetization curves measured at 10 kOe for a FeGe nanocluster film under zero-field-cooled (ZFC) and field-cooled (FC) conditions are shown in Fig. 7(d) and suggests a T_c , a temperature range similar to the bulk value of about 271 K.⁴⁹ Figure 8 shows the temperature-dependent magnetization curves and dc susceptibility spectra (derived from the magnetization curves). Interestingly, the dc susceptibility curve shows a peak/feature around 0.4 kOe at 200 K (indicated by a red arrow in Fig. 8(b)), which is similar to the signature of the skyrmion-like spin structure observed in thin films.^{15,16} In particular, this peak appears weakly at 220 K (Fig. 8(a)), becomes relatively intense at 200 K (Fig. 8(b)), tends to disappear at

FIG. 7. FeGe nanoclusters. (a) A HAADF image with Z-contrast and the corresponding EDS elemental color mappings showing Fe, Ge and combined Fe and Ge. (b) A HRTEM image, which indexes to the $[001]$ axis of B20-type cubic structure. (c) Fast Fourier transform of the HRTEM image, which indexes to the $[001]$ axis of B20-type cubic structure. (d) Field-cooled and zero-field-cooled magnetization curves measured at 10 kOe for nanocluster film as a function of temperature T .

FIG. 8. Magnetization and dc susceptibility curves for FeGe nanocluster film measured at different temperatures.

190 K (Fig. 8(c)), and completely vanishes at low temperatures as shown in the case of dc susceptibility curve at 80 K (Fig. 8(d)). These results in 10 nm clusters suggest that a further investigation is worthwhile, and is in progress to understand the effects of size confinement on ground-state electronic structure and associated spin correlations in nanocluster films, in which complex interactions including Dzyaloshinsky-Moriya effects may exist.

We have discussed recent results on the synthesis, structure and magnetic properties of Co-, Fe-, and Mn-based nanoclusters having average particle sizes varying from 1 to 20 nm. Fe-Au and Mn-Au bimetallic nanoclusters show size-dependent evolution of new crystalline nanostructures and associated novel magnetic properties. Interestingly, FeSi₂ nanoclusters exhibit room-temperature ferromagnetic ordering and the preliminary results on FeGe nanocluster films have shown a possible Skyrmion-like behavior around 200 K in the dc susceptibility curves. The rare-earth free high-anisotropy Co-rich intermetallic clusters such as HfCo₇ and Zr₂Co₁₁ show appreciable permanent-magnetic properties and also are used as building blocks to fabricate rare-earth-free exchange-coupled nanocomposite films with energy products as high as 20.3 MGOe (at 27 °C) and 17.1 MGOe (at 180 °C). The various types of magnetic nanoclusters and nanostructures discussed in this work provide useful insights for developing future magnetic materials with improved performance for many important applications.

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