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Magnetization reversal in europium sulfide nanocrystals

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The authors report the observation of the reversal in the magnetization hysteresis curve of europium sulfide nanocrystals. This phenomenon was investigated through the temperature-dependent magnetization of two classes of nanomaterials, nanocrystalline (2.0 nm $\leq d_{\rm NCs} \leq 100$ nm) and quantum confined ($d_{\rm NCs} \leq 2.0$ nm), where $d_{\rm NCs}$ is the diameter of the nanomaterial. The effect of the size of the nanomaterial on the magnetization is attributed to the competition between the magnetic properties of strained surface atoms and unstrained core atoms. Superconducting quantum interference device probed the magnetic response. Electron microscopy and X-ray diffraction spectroscopy revealed the crystallinity and monodispersivity of the nanomaterials. © 2006 American Institute of Physics. [DOI: 10.1063/1.2396915]

Europium sulfide (EuS) nanocrystals have been the subject of considerable research interest recently due to their intriguing ferromagnetic and optical properties.^{1–5} Studies have suggested that europium monochalcogenide nanocrystals will exhibit enhancements in their magnetic properties, compared to bulk, when the nanocrystal diameter reaches a critical size. Such traits may lead to a variety of nanomaterial applications, which could supplant those based on bulk EuS or on other magnetic materials.^{4,6–12} Recent research has investigated how the nanocrystal size and surface oxidation affect the magnetic characteristics of EuS nanocrystals.^{4,12} However, the origin of the magnetization in these nanomaterials remains largely unexplored.

To this end, we have investigated the remanent magnetization (M_R) of EuS nanocrystals, the magnitude of magnetization a material maintains once the external magnetic field is removed, and have discovered an unexpected reversal in their magnetization hysteresis curve. We observed this phenomenon in *nanocrystalline* (2.0 nm $\leq d_{NCs} \leq 100$ nm) europium sulfide. However, the reversal vanished as the nanocrystal diameter decreased below 2.0 nm, the critical size that defines the so-called *quantum-confined* ($d_{NCs} \leq 2.0$ nm) regime for EuS. We assert that strain on the surface and core atoms of the nanocrystal creates competing magnetic responses. Thus, the magnetic properties of the strained surface atoms and the unstrained core atoms engender the observed magnetization reversal.

To synthesize the EuS nanomaterials, we employed a thermolysis procedure of a single source EuS precursor.^{4,11,12} This synthesis provided marked control over the EuS nanocrystals' diameter and the size distribution, compared to previously reported techniques. The preparation of the EuS single source precursor was conducted under a nitrogen atmosphere to minimize oxidation. A 1 mM methanolic solu-

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FIG. 1. (a) TEM micrograph of quantum-confined, sub-2.0-nm EuS nanocrystals; (b) SAED pattern of the nanocrystals. Inset: Characteristic x-ray diffraction spectrum for 5.0 nm EuS nanocrystals.

tion of 1,10-phenanthroline was added under vigorous stirring to a 1 mM methanolic solution of europium (II) chloride. Thereafter, 2 mM of diethylammonium diethyldithiocarbamate were added into the reaction mixture, producing an orange precipitate.^{13,14} The resulting solid, dried under vacuum, was transferred to a horizontal tube furnace for a time-sensitive thermolysis. Adjustments to the thermolysis time and temperature yielded narrowly dispersed EuS nanocrystals, devoid of ligand molecules. The nanomaterials were dispersed in 2,2'-bipyridine to inhibit the spontaneous formation of a nonmagnetic surface layer of Eu₂O₂S.¹²

Transmission electron microscopy (TEM) images were obtained using a Hitachi HF-2000 microscope operating at 200 kV. Figure 1(a) shows a group of quantum-confined EuS nanocrystals with an average diameter of 2.0 nm. The interplanar distance, approximately 2.1 Å, matches the (220) lattice plane spacing of face-centered-cubic (fcc) europium sulfide. Selected area electron diffraction (SAED) patterns of the nanocrystals are presented in Fig. 1(b). The measured ring diameters match the values for the (200), (222), and (311) planes of fcc EuS. X-ray diffraction (XRD) measurements of our nanocrystals were obtained using a Scintag $X_1\theta/\theta$ automated powder diffractometer, with a Cu target (Cu K_{α} radiation of $\lambda_a = 1.54$ Å). The XRD spectrum of the EuS nanocrystals is shown in the inset of Fig. 1. The diffraction peak positions and their full width at half maxima were determined from profiles, calculated for each observed peak using a diffraction management system for NT (DMSNT) software package provided by Scintag.¹⁵ The EuS compound was identified by major diffraction peaks at the 2θ angles of 30.0°, 42.8°, 50.7°, and 53.4°, which match the Powder Diffraction File (PDF) for this material¹⁶ and correspond, respectively, to the (200), (220), (311), and (222) planes of fcc EuS.

After identifying the quantum-confined and the nanocrystalline materials, we investigated their magnetization properties via superconducting quantum interference device (SQUID) magnetometry. The magnetic properties of europium monochalcogenides are dominated by the competition between the ferromagnetic indirect exchange among mearest neighbor Eu²⁺ ions and the antiferromagnetic super-



FIG. 2. (a) Magnetization hysteresis curves of 5.0 nm EuS nanocrystals at different temperatures; (b) details of the hysteresis curves about the origin.

exchange among next-nearest neighbor Eu²⁺ ions.¹⁷ For monochalcogenide nanocrystals with small lattice constants (a_0 =0.5968 nm for EuS at 300 K), the ferromagnetic exchange dominates. When the size of a EuS nanocrystal approaches the quantum-confinement regime at 2.0 nm, it contains less than 250 atoms. As the number of lattice sites with a full complement of nearest neighbors and next-nearest neighbors decreases, the antiferromagnetic superexchange is suppressed.^{18–22} The reduced size increases the strain on the surface atoms due to the 1/*R* dependence of the surface-tovolume ratio, which influences the ferromagnetic exchange parameters.^{23–25} To perturb the 4*f*-5*d* dipole transitions of the Eu²⁺ ions, we must change the ions' local environment, using effects such as surface strain.^{26,27}

Figure 2 illustrates the magnetization hysteresis curves of the nanocrystalline samples ($d_{NCs} \sim 5$ nm) as measured via SQUID magnetometry. We surveyed the magnetization response across a temperature range from 2 to 25 K, which includes the Curie temperature ($T_C=17$ K) for the nanomaterials. At 2 K, we observed a typical, counterclockwise hysteresis curve. This meant that the moments aligned parallel with the magnetic field while the magnitude of the field decreased. However, when the temperature increased above 11 K, the hysteresis curve reversed direction, becoming clockwise. This reversal persisted from 11 to 25 K. When



FIG. 3. Remanent magnetization vs temperature for nanocrystalline and quantum-confined EuS materials. Negative values indicate a reversed hysteresis curve.

similar temperature-dependent studies were performed on quantum-confined, sub- 2.0-nm nanocrystals, no reversal was observed. The values for M_R for quantum-confined and nanocrystalline materials are summarized in Fig. 3. Tracking the evolution of the magnitude of M_R , as a function of temperature, confirmed the magnetization reversal phenomena. M_R remained positive at all temperatures up to 90 K for the quantum-confined EuS materials. Although M_R was negative from 11 to 25 K for the nanocrystalline EuS, the trend suggested that the value would have become positive at temperatures higher than 25 K. Further investigation of this temperature dependence is being pursued.

The observed results can be described as a competition between the magnetic response of unstrained, core atoms in the nanocrystal and that due to surface anisotropies.^{26–29} The magnetization of bulk EuS is uniform in zero applied field since surface anisotropies are negligible. Once the material becomes nanocrystalline, for which surface strain effects are pronounced, the magnetic moments of the surface atoms will align along their easy directions.^{26,27} The innermost core atoms will not experience the surface effect. This places the nanocrystal in a bimodal magnetization state, with competing magnetizations from unstrained core atoms and strained surface atoms.

When the material enters the quantum-confined regime, for which the vast majority of the atoms reside at the surface, the net magnetization response of the core atoms will be substantially weaker than that of the surface atoms. This is because most of the atoms will be surface atoms. If the surface anisotropy field is large enough, the magnetic moments of the core atoms of the nanocrystal will be forced to align with those moments at the surface. Thus, if the nanocrystal is so small that the majority of its atoms are at the surface, then the alignment of the moments will be dictated by the surface. The nanocrystal then will respond as if it consisted of just one state, the surface state. When only one dominant state exists (surface atom state, core atom state, etc.), magnetization reversal is not observed. When the magnetization of the core atoms and surface atoms are comparable, as is the case for nanocrystalline materials, the different temperature dependences of the two states will dictate the response. Accordingly, Fig. 3 evinces the evolving positive and negative values of M_R as the magnetization of the surface and core atoms responds to the changing temperature.

In summary, we have observed the reversal in the magnetization hysteresis curves of nanocrystalline europium sulfide. Competition between the magnetic response of strained surface atoms and unstrained core atoms engenders a sizedependent and temperature-dependent magnetization response in quantum-confined and nanocrystalline EuS materials. Further investigation of the magnetic properties of these nanomaterials may lead to applications, such as bioimaging reagents.

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