Element-specific magnetometry of EuS nanocrystals

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A soft x-ray absorption and x-ray magnetic circular dichroism (XMCD) study of the ferromagnetism in solution-grown EuS nanocrystals (NCs) is reported. The absorption edges of Eu M_5 and M_4 , S K , O K , and P K were probed to determine elementally specific contributions to the magnetism of EuS NCs. Differential spin absorption was observed by XMCD at the Eu $M_{5,4}$ edges confirming the presence of a magnetic moment on the $\text{Eu}^{2+} 4f$ shell. No dichroic signal was observed for S, O, or P. Vibrating sample magnetometry of ensembles of NCs shows ferromagnetic properties consistent with the XMCD studies. © 2009 American Institute of Physics. [doi:10.1063/1.3251777]

Magnetic semiconductors, materials whose magnetic and electronic properties are coupled, are technologically and fundamentally important. One potential application of these materials is in the field of spintronics where correlation between spin and charge could enable electronic and photonic devices with nonvolatile circuits, faster data processing, and decreased power consumption.^{1,2} Recent focus has been on semiconductors doped with magnetic ions, known as dilute magnetic semiconductors, due to predictions of room temperature ferromagnetism.^{3,4} These hopes have been largely unrealized, however, due to synthetic irreproducibility and concerns over the elemental origin of the observed magnetism.^{5,6} In contrast, the behavior of concentrated magnetic semiconductors, where the both the spin and charge properties are intrinsic to the lattice, are well understood.^{2,7} One such material, europium sulfide (EuS), offers both theoretical clarity as a wide bandgap ferromagnetic semiconductor (1.6 eV) and excellent magnetic properties including a large localized magnetic moment (7.9 μ_B) and spin polarization (86 %).^{8,9} EuS is an ideal Heisenberg ferromagnet with a half-filled $4f$ shell containing seven unpaired electrons localized on every Eu^{2+} ion in its rock-salt lattice. Below its Curie temperature of 16.6 K these electrons ferromagnetically align while maintaining the semiconducting properties of the material.^{8,9} The elemental origins of the magnetism of EuS have been theorized for bulk and thin film samples but not for nanoscale materials, where the surface states can mediate magnetic coupling. For nanoparticles, quantum size effects and a proportionally large surface to volume ratio have been utilized in a variety of materials to modulate both electronic and magnetic properties.¹⁰ For example, room temperature ferromagnetism was induced in ZnO by modulating the electronic behavior of surface states with organic ligands.¹¹ As these size effects can dominate physical properties, it is important to characterize the magnetic properties of nanocrystalline EuS.

X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) are powerful tools for determining the elemental origin of magnetism in magnetic semiconductors. XMCD provides the ability to distinguish between intrinsic magnetism and contributions from local-

ized ions, phase segregated clusters, or contaminants. In this letter, we report XAS and XMCD studies of solution-grown EuS NCs, which have not been previously carried out. The Eu $4f$, S $2p$, O $2p$, and P $2p$ states were probed by using the Eu M , S K , O K , and P K absorption edges, respectively, to determine magnetic contributions from the host lattice and surface species. In addition, magnetic measurements of ensembles of EuS NCs were performed using vibrating sample magnetometry (VSM).

EuS NCs were synthesized through the decomposition of europium diethyldithiocarbamate phenanthroline single source precursor at 300 °C in oleylamine and trioctylphosphine resulting in spherical crystals with a diameter of approximately 10 nm following a previously published procedure.^{12,13} These NCs were capped with oleylamine and trioctylphosphine. Size and morphology were determined using HRTEM (Fig. 1 inset) and the rock salt structure of EuS was confirmed with powder x-ray diffraction (PXRD).¹⁴ Magnetic measurements (VSM) of ensembles of EuS NCs (Fig. 1) showed the Curie temperature (T_C) to be 16.8 K through the use of Arrott plots a method which uses magnetic saturations extrapolated from magnetic isotherms to determine the transition temperature (see supporting information, figure S4 for details).^{14,15} This is in good agreement with the reported bulk value of 16.7 K but contradicts previ-

FIG. 1. (Color online) Magnetization of EuS NCs as function of applied field at 5, 100, and 300 K. Insets show HRTEM image of the EuS NCs (upper left) and field cooled/zero field cooled magnetization scans (bottom right).

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FIG. 2. (Color online) (a) Experimental XAS measured at 6 K and weighted sum of theoretical Eu²⁺ and Eu³⁺ XAS multiplet spectra. (b) Theoretical XAS multiplet spectra for Eu²⁺ and Eu³⁺ ions. The drop-lines guide the eyes to the peaks in the experimental spectrum.

ous reports that EuS NCs in the range of 10 nm will have depressed T_C values due to surface and quantum effects.^{14,16} Using the Curie–Weiss law the Weiss temperature θ was determined to be 15.7 K which is positive indicating ferromagnetic ordering and similar in magnitude to the reported value of 19 K.^{17,18} The effective magnetic moment (μ_{eff}) is 2.0 μ_B , which is much lower than the 7.9 μ_B expected for pure bulk EuS. As will be discussed in greater detail below, XAS showed there to be 30% of ferromagnetically ordered Eu²⁺ and 70% of paramagnetically ordered Eu³⁺ present. Scaling the total moment by the percentage of ferromagnetic Eu ions present yields a μ_{eff} of 2.4 μ_B which is close to the observed value of 2.0 μ_B .^{8,9,14}

XAS and XMCD measurements were performed at the Advanced Photon Source at Argonne National Laboratory using beamline 4-ID-C. The NCs were dropcast onto silicon substrates and placed in a split-coil superconducting solenoid in a liquid He cryostat. Circularly polarized x-rays from a helical undulator were used for XAS and XMCD scans at 6 and 100 K with external fields of up to 2 T where both x-ray polarizations were used for every energy point. The beam was incident at 32° degrees above the plane of the sample. Absorption was measured in both total fluorescence and electron yield modes but only the latter was usable.

Representative XAS and XMCD spectra for the EuS NCs at 6 K are shown in Fig. 2 and Fig. 3, respectively. Atomistic multiplet calculations were done to calculate the theoretical spectra for Eu²⁺ and Eu³⁺ valence using code by van Veenendaal, in which the Hamiltonian includes the Coulomb interactions in the 4f shell and those between the 4f shell and the core hole and the spin-orbit coupling. Parameters were obtained in the Hartree–Fock limit using Cowan’s code^{19,20} and the values for the Coulomb interaction were scaled down to 80% to account for screening effects. This scaling down factor produces good agreement between theory and experiment.^{19,20} The generated XAS spectra for Eu²⁺ and Eu³⁺ were interpolated and fit to the experimental

FIG. 3. (Color online) (a) Experimental XMCD measured at 6 K and weighted sum of theoretical Eu²⁺ and Eu³⁺ XMCD multiplet spectra. (b) Theoretical XMCD multiplet spectra for Eu²⁺ and Eu³⁺ ions. The drop-lines guide the eyes to the peaks in the experimental spectrum.

data as shown in Fig. 2 to yield 30% Eu²⁺ and 70% Eu³⁺. This percentage of Eu³⁺ is significantly higher than expected given that the synthetic procedure followed was reported to produce EuS. From electron diffraction, the ring pattern observed was indexed to EuS, and from PXRD, only peaks from the rock-salt EuS were observed (although an amorphous background was present, see figure S1 in the supplementary information).²⁷ It is likely that some amorphous Eu³⁺ phases were formed due to the surface oxidation of crystalline EuS. This is consistent with previous results which showed by PXRD a significant decrease in crystallinity of EuS NCs after they had been exposed to air for one month.²¹ This high percentage of Eu³⁺ could be somewhat overestimated due to the small probing depth of the soft x-rays used which could result in preferentially higher sensitivity to shell composition.

Theoretical XMCD spectra for both Eu²⁺ and Eu³⁺ were generated and a linear combination of them fit to the experimental XMCD (Fig. 3). Since the $M_{5,4}$ edges result from absorption from the 3d to the 4f state, this edge can be used to measure the polarization of the magnetic Eu 4f shell. The magnetic moments of Eu²⁺ and Eu³⁺ can be estimated using the ratio of the factors used to scale the theoretically generated XAS and XMCD spectra to those measured experimentally. To estimate these moments, ratios were taken of each optimized XMCD fit to its respective optimized XAS fit. These ratios suggest polarizations of 83% for Eu²⁺ and 51% for Eu³⁺. Published theory predict magnetic moments of 7.9 μ_B for Eu²⁺ and 0.36 μ_B for Eu³⁺ at 6 K (as interpolated from low temperature predictions).²² With the polarization ratios and the theoretical moments, the effective magnetic moments of Eu²⁺ and Eu³⁺ for this XMCD sample can be estimated as 6.5 μ_B and 0.18 μ_B , respectively (the apparent contradiction between Hund’s rule predictions and experimental measurement for Eu³⁺ is attributed to the closeness of the lowest multiplet levels).^{22–24} To compare this valence specific estimate to the magnetic moment calculated from the ensemble VSM measurement, the magnetic moments from XMCD are scaled using the percentages of Eu²⁺ to Eu³⁺ suggested by the XAS fit (30% Eu²⁺ and 70% Eu³⁺) and then

FIG. 4. XAS and XMCD for the S K, O K, and P K edges.

summed to give a effective magnetic moment of $2.1 \mu_B$ per Eu which is consistent with the effective magnetic moment of $2.0 \mu_B$ per Eu measured by VSM. The XMCD measurement confirmed the spin imbalance of the Eu^{2+} component of Eu 3d as the elemental origin of ferromagnetism in EuS NCs.

In addition to observing a localized magnetic moment on the Eu^{2+} ions attempts were made to observe magnetic contributions from the other elements present in EuS NCs. The sulfur contained in the lattice as well as the oxygen and phosphorus contained in the organic ligands capping the NCs. A previous XMCD study of the S K edge in bulk EuS has showed a small spin polarization of the 3p band resulting from S 3p–Eu 5d and S 3p–Eu 4f hybridizations.²⁵ The S K absorption edge of EuS NCs was probed and no XMCD signal was observed herein (Fig. 4). This lack of an observable spin imbalance can result from the low overall absorption signal from S. A feature of the nanoscale is a very high surface to volume ratio where ligand molecules coordinated to the surface of NCs have been shown to impact the electronic structure and by extension, they impact the magnetic properties of the materials including ferromagnetism induced in materials that are nonmagnetic in bulk.^{11,26} The EuS NCs studied have oleylamine and trioctylphosphine (which can be potentially oxidized to trioctylphosphine oxide) as capping ligands. Therefore, the absorption edges P K (the element in trioctylphosphine likely to be coordinated to the surface of the crystals) and O K (the element in trioctylphosphine oxide potentially coordinated to the surface) were probed. Nitrogen from oleylamine ligands was likely to be coordinated to the crystal surface, however, its absorption edges are outside the limits of the beamline used and thus could not be investigated. No evidence of ferromagnetic behavior was observed for these elements within the sensitivity of the instrumentation, as clearly shown in Fig. 4.

In conclusion, we have examined solution-grown EuS NCs using soft XMCD and determined that the ferromagnetism arises primarily by the Eu^{2+} ions but with a paramagnetic contribution from the Eu^{3+} ions. We suggest that the Eu^{3+} component came from an amorphous surface phase resulting from partial oxidation of the NCs. Analysis of the XMCD shows magnetic moments of $6.5 \mu_B$ per Eu^{2+} which

is lower than the theoretical expectation or published bulk measurements; however, the total magnetic moment of $2.1 \mu_B$ per Eu (weighted considering the ratio of Eu^{2+} and Eu^{3+}) is consistent with the $2.0 \mu_B$ per Eu moment measured by VSM. No ferromagnetic spin polarization was observed for 4f, S 2p, O 2p, or P 2p states confirming that the sole contributor to the ensemble magnetic properties of EuS NCs is Eu.

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