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Magnetic properties of chalcogenide spinel $CuCr_2Se_4$ nanocrystals

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ABSTRACT

The magnetic properties of chalcogenide spinel $CuCr_2Se_4$ nanocrystals have been studied as a function of crystallite size (15–30 nm). A solution-based method is used for the facile synthesis of the nanocrystals with good size control. They have close to cubic morphology with a narrow size distribution and exhibit superparamagnetic behavior at room temperature. The Curie temperature and saturation magnetization of the nanocrystals are lower as compared with the bulk and decrease with decreasing nanocrystal size. A similar trend is observed in the paramagnetic state for the Curie–Weiss temperature and effective magnetic moment. The low temperature magnetization behavior can be qualitatively explained by spin glass dynamics.

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1. Introduction

The family of chalcogenide spinels has the general formula AB_2X_4, where X represents a chalcogen, e.g. S, Se, or Te. Among them, the chromium-based spinel family ACr_2X_4 (A (group II)=Cu, Cd, Hg, Zn, etc.) has been quite broadly investigated, in large part motivated by their unique properties [1–5]. While the structurally related spinel oxychromites (X=O) are super-exchange mediated antiferromagnetic insulators, a number of the chalcospinels are distinguishably ferro/ferrimagnetic insulators, semiconductors, or even metals [5]. A basic structural component of the Cr-based chalcospinels is an anion bonded to one A cation and three Cr ions. They are *normal* spinels in that the nominally divalent metal ions A occupy the tetrahedral sites (1/8 filled by A), while the trivalent Cr ions occupy the octahedral sites (1/2 filled by Cr). The positions of the cations are fixed by the symmetry of the structure, but the anion positions are variable and are specified by the parameter u [5]. A local structural deformation is observed in these materials induced by cation–anion interaction and is characterized by a small deviation of the anion parameter u from the ideal value of 0.375.

Room temperature ferromagnetism with a Curie temperature of 430 K makes $CuCr_2Se_4$ an interesting system of study among the chalcospinels [5]. It is metallic and exhibits a pronounced magneto-optical Kerr effect at room temperature [6]. Additionally, band structure calculations indicate that both cation and anion substitution of the parent compound can induce half-metallicity over a range of compositions [7]. Different models of the electronic structure have been proposed to explain the physical properties of $CuCr_2Se_4$. An initial attempt to explain the ferromagnetism and metallic conductivity of the material was made by Lotgering [2] with the assumption that the valence distribution in the compound is given by the formula $Cu^{+}[Cr^{3+}Cr^{4+}][Se^{2-}]_4$. Thereby, the ferromagnetism and conduction are attributed to double exchange mechanism between Cr^{3+} and Cr^{4+}, with ferromagnetic moment of 5 μ_B per formula unit (f.u.), when their moments align in parallel. A subsequent model by Goodenough [4] proposed the Cu ions to be in a divalent state with the *d*-hole giving rise to a metallic band and providing the means of indirect exchange coupling. Neutron diffraction studies show the presence of only the Cr^{3+} state and a nonlocalized moment of 1 μ_B which is antiparallel to the Cr moment giving rise to the measured magnetic moment of 5 μ_B [8]. A detailed X-ray magnetic circular dichroism (XMCD) study [9] also shows that the Cr ions are in the Cr^{3+} state and the Cu ions are in the monovalent state. However, recent soft X-ray absorption spectroscopy and XMCD studies of a series of Ti-substituted compounds suggests

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the Cu d-hole possibly play a crucial role in determining the electrical/magnetic properties of $CuCr_2Se_4$ [10].

As in the case of other magnetic systems, the utility of the chalcospinels can be augmented if they can be synthesized as colloidal nanocrystals with highly controlled dimensions. But while the magnetic properties of metallic and oxide-based nanocrystals have been studied quite extensively in recent years [11], those of chalcogenide-based materials remains largely unexplored. With decrease in the particle size below ~100 nm, a large fraction of atoms are presented on the surface of the crystal. This causes significant changes in the magnetic properties of nanostructured materials as compared with the bulk and leads to new phenomena, such as superparamagnetism [12], effects of surface anisotropy [13,14], and spin canting at the surface, i.e. disorientation of spin directions [11,15].

At low temperatures the magnetization of the individual nanocrystals is fixed by the energy minimum provided by the anisotropy of the system. Upon increasing the temperature, the thermal energy will overcome the anisotropy barrier above the blocking temperature T_B, which to a first approximation is proportional to the volume V of the single-domain particle, and the total magnetization of the particle can thermally fluctuate like a single spin in a classical paramagnetic material. The actual magnetic behavior of the nanocrystals depends on the value of the measuring time t_m of the specific experimental technique with respect to the characteristic relaxation time τ associated with overcoming the energy barrier, $\tau=\tau_0 \exp(E_B/k_BT)$ [11]. The superparamagnetic condition corresponds to $t_m \gg \tau$. If $t_m \ll \tau$, the magnetic moment is blocked in one of the potential wells, and this state corresponds to stable magnetization of a bulk ferromagnet. In general, the magnetic behavior of a nanocrystal assembly will depend on the interplay between magnetocrystalline characteristics, size effects, and interparticle interactions, including magnetic dipolar and exchange interactions. With increasing the interparticle interaction, nanoparticle systems can change their magnetic behavior from superparamagnetic to spin-glass like behavior. Spin-glass behavior is a consequence of disorder and frustration which can be caused by fluctuations of superexchange interactions producing an energy landscape with multiple degenerate ground state configurations separated by barriers of variable height [11].

We recently reported on the facile synthesis of size-controlled $CuCr_2Se_4$ nanocrystals (~15–30 nm) using a solution-based thermolysis process [16]. In this paper, we report on the detailed magnetic measurements of samples of $CuCr_2Se_4$ with controlled crystallite size. The experiments have been performed on four different samples, consisting of nanocrystals with average size of 15, 18, 25, and 30 nm.

2. Experiment

The synthesis of size-controlled $CuCr_2Se_4$ nanocrystals (~15–30 nm), which are nearly monodisperse and readily form a colloidal suspension, has been described in a previous publication [16]. Briefly, the nanocrystals are produced by the thermal decomposition and reaction of metal-acetylacetonate precursors with selenium in a high boiling organic solvent mixture of oleylamine and 1-octadecene. These coordinating solvents play the dual role of forming an organo-Se complex and in selectively adsorbing on the surface of the nucleated product to passivate and control their size. This eliminates the need of using a separate reducing agent and surfactant for the reaction process.

The dc magnetic measurements of the $CuCr_2Se_4$ nanocrystals, with four different average sizes (15, 18, 25, and 30 nm), were performed using a commercial Quantum Design SQUID magnetometer (Model MPMS-5S) equipped with a sample oven, which permits sample heating to perform measurements at temperatures up to 800 K. Measurements were carried out by placing the sample inside a quartz sample holder [17]. To perform the zero-field cooled (ZFC) measurements, the sample was cooled from 400 to 5 K in zero magnetic field, a magnetic field was then applied (50 and 1000 Oe) and the magnetization recorded during reheating. For the field-cooled (FC) magnetization measurements the sample was cooled in the measurement field, and the magnetization recorded again during reheating. For high temperatures, the sample oven was installed and the measurements repeated over the same range of magnetic field. The magnetization measurements as a function of field (M vs. H) were performed at temperatures of 5, 150, and 300 K in the presence of a magnetic field of up to 20 kOe.

3. Results and discussion

The morphology of the synthesized nanocrystals has been investigated using transmission electron microscopy (TEM). As shown in Fig. 1, the nanocrystals with an average size of 18 nm exhibit close to cubic morphology. The nanocrystals are relatively monodisperse with a size distribution of $\pm$15%. The inset of Fig. 1 shows the high resolution TEM (HRTEM) image of a nanocrystal that exhibits lattice fringes. A lattice spacing of d=0.625 nm is measured, corresponding to the (111) lattice planes of the face-centered cubic chalcospinel phase. A similar shape and size distribution is observed for the other nanocrystals [16].

X-ray measurements of all the samples showed the same set of diffraction peaks, with the positions and relative intensities of the peaks matched well with the powder diffraction data for $CuCr_2Se_4$ (JCPDS no. 81-1986). A broadening of the peaks was observed, consistent with the observed particle size [16]. There was no evidence of secondary phases in the diffraction patterns, and the composition was also confirmed using energy dispersive X-ray

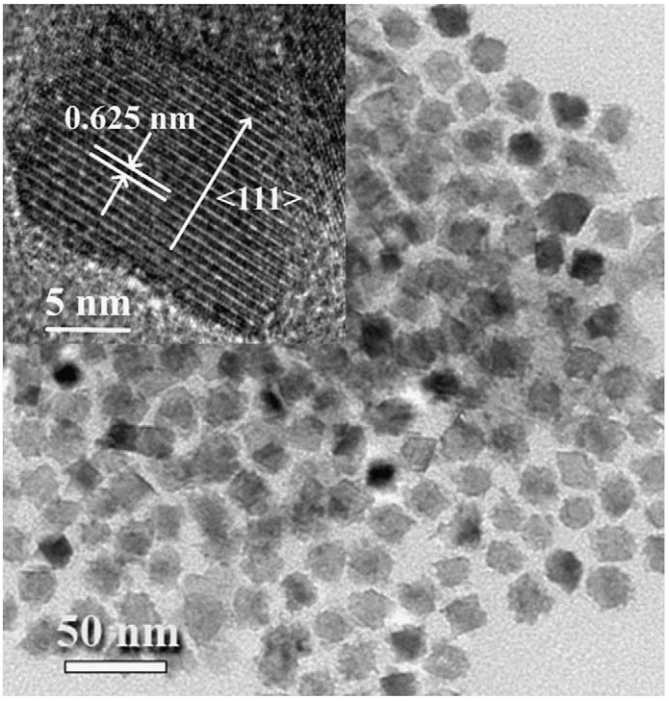

Fig. 1. TEM image of $CuCr_2Se_4$ nanocrystals with an average size of 18 nm. The inset shows the HRTEM image of an individual nanocrystal exhibiting lattice fringes.

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