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Observation of exchange bias and spin-glass-like ordering in ε-$Fe_{2.8}Cr_{0.2}N$ nanoparticles

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Abstract. Nanoparticles of ε-$Fe_{2.8}Cr_{0.2}N$ system exhibit the exchange bias phenomenon due to the exchange coupling of the spins of the antiferromagnetic (AF) oxide/oxynitride surface layer and the ferromagnetic (FM) nitride core. Exchange bias is observed at 10 K both in the absence and presence of cooling field. Due to the interface disorder, a mixture of parallel and anti-parallel/perpendicular coupling of the AF and FM spins is observed. The roughness of AF–FM interface induces disorder due to the random exchange anisotropy. The saturation magnetization is also found to be drastically lowered as compared to parent ε-Fe_3N. Below 58 K, the broad peak ($T_E \cong T_f$) in zero-field cooled (ZFC) magnetization curves indicates the presence of unidirectional anisotropy and spin-glass-like ordering, that arises from the freezing of localized frustrated spins.

Keywords. Nanoparticles; nitride; exchange bias; spin glass.

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1. Introduction

The 3*d* transition metal nitrides are not extensively studied since they are relatively less stable as compared to oxides due to their low decomposition temperature owing to the high bond energy of nitrogen (941 kJ $mole^{-1}$). These nitride materials have a wide range of technological functions [1]. Iron and chromium forms a ternary phase Fe–Cr–N, consisting of a mixture of non-magnetic γ'-$(Fe,Cr)_4N_x$ phase and ferromagnetic α-Fe(Cr) phase located at the grain boundaries [2]. According to the literature reports, the diffusion of Cr into Fe is sluggish and hence kinetically they form an immiscible system [3,4]. In this context, it is a challenge to synthesize a single phase Fe–Cr–N compound and this has been the motivation of the present work. In this study ε-$Fe_{2.8}Cr_{0.2}N$ is a single phase compound with the highest Cr content ($x = 0.2$) that can be incorporated into the ε-Fe_3N lattice. ε-$Fe_{2.8}Cr_{0.2}N$ phase shows a much better exchange bias effect than the ε-Fe_3N-CrN nanocomposites studied previously [5]. In this regard, Cr substitution into ε-Fe_3N represents an exchange bias system and acts better than other substitutions like Co, Ni, Ga to combat the superparamagnetic limit in magnetic recording media [6]. The Fe-containing nitride nanoparticles show interesting magnetic ordering

phenomena [7]. The Fe–N nanoparticles are ferromagnetic (FM) and the FM core is covered by an anti-ferromagnetic (AF) surface oxide/oxynitride layer. The interactions at this AF–FM interface (exchange bias) have been extensively studied over the years [8,9]. Exchange bias depends on the orientation of the spins at the AF–FM interface. The randomness in the orientation of spins gives rise to spin freezing at lower temperature along with exchange bias coupling [10]. However, the exchange bias and spin-glass-ordering phenomena are rarely studied in nitrides.

2. Experimental details

The aqueous solution of 0.22 (N) $Fe(NO_3)_3{\cdot}9H_2O$ (Merck 99.9%) was mixed with 0.2 (N) $Cr(NO_3)_3{\cdot}9H_2O$ (Merck 99.9%) solution according to the stoichiometric Fe : Cr atomic percentage ratio of 93 : 07. A little excess citric acid (Merck 99.9%) solution was added, followed by refluxing at 353 K for 12 h. The homogeneous solution was dried and Fe–Cr–citrate powder was obtained. The mixed metal citrate was decomposed in air at 773 K for 4 h, to get the Fe–Cr–oxide nanoparticles. The oxide precursors were nitrided at an ambient pressure under flowing NH_3 (g) at a flow rate of 240 cm^3/min and a heating rate of 0.03 K s^{-1} at 983 K for 24 h followed by normal cooling to room temperature, to obtain the ε-$Fe_{2.8}Cr_{0.2}N$ nitride nanoparticles. The stoichiometry of iron, chromium and nitrogen were confirmed by quantitative estimation with chemical methods and EDAX.

X-ray diffraction (XRD) patterns have been recorded using a Rich-Seifert X-ray diffractometer (model Isodebyeflex 2002). Scanning electron microscope (SEM) micrographs are recorded by inserting a brass stub with nitride sample on the mounting table of SEM instrument (Model no. JEOL-JSM-840A). Transmission electron microscope (TEM) micrographs are recorded with the TEM instrument (Phillips Model E-301). Magnetic measurements are carried out using SQUID (superconducting quantum interference device) magnetometer model Quantum Design (MPMS-XL).

3. Results and discussion

3.1 *Structural characterization*

The XRD-Rietveld and chemical analyses indicate that a solid solution with composition, ε-$Fe_{2.8}Cr_{0.2}N$ was formed crystallizing in the space group $P6_3/mmc$. The X-ray diffraction (XRD) pattern is shown in figure 1. The lattice parameters are calculated to be $a = 2.725$ and $c = 4.442$ Å. These values are little higher than the reported values of $a = 2.695$ and $c = 4.362$ Å [11], which may be due to lattice strain involved due to the nanostructured nature. The XRD pattern was plotted on a logarithmic scale and checked for additional impurity peaks. However, no impurity peak was observed corresponding to Cr, CrN, β-Cr_2N, Fe and other Fe–N phases. The XRD crystallite size is measured to be 20 nm. In the SEM and TEM micrographs (figure 2), the particle sizes measured are 45 and 24 nm respectively.

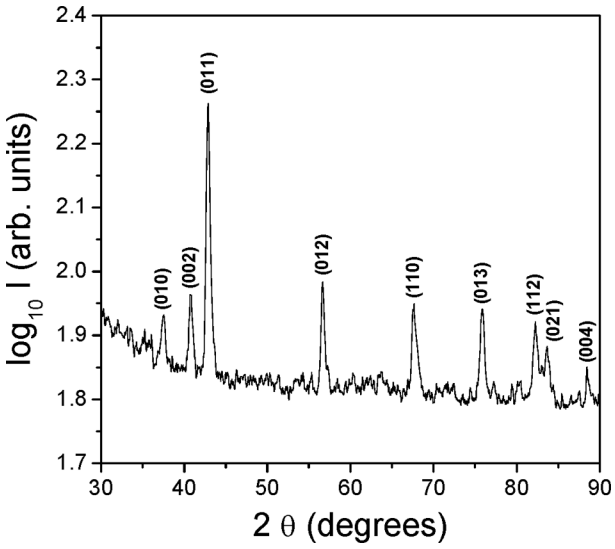

Figure 1. X-ray diffraction pattern of ε-$Fe_{2.8}Cr_{0.2}N$ nanoparticles.

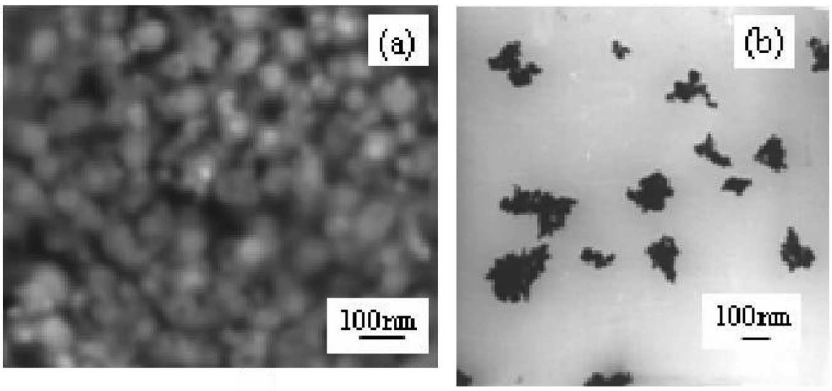

Figure 2. (**a**) SEM and (**b**) TEM images of ε-$Fe_{2.8}Cr_{0.2}N$ nanoparticles.

3.2 *Magnetic interactions*

The field-dependent magnetization curve at 10 K is not saturated, with a maximum applied field of 3 T (figure 3). The saturation magnetization (σ_s) value at 10 K is 14.6 emu/g. At 10 K, the presence of both ferromagnetic and superparamagnetic fractions is evident. The presence of AF oxide/oxynitride surface layer, spin-disorder at the interface between AF oxide/oxynitride and FM nitride, spin-pairing effects, finite-size effects and the superparamagnetic fractions drastically lower the σ_s values from the reported value of 133 emu/g for bulk ε-Fe_3N [12]. The unidirectional pinning of the FM spins by the AF spins and the interparticle interactions influence the coercivity (H_c) value which is 215 Oe at 10 K (figure 3 inset).

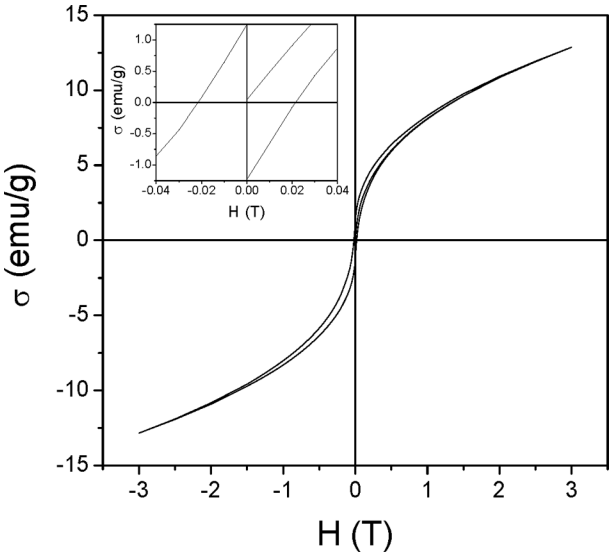

Figure 3. Plot of magnetization (σ) as a function of field (H) measured at 10 K. (Inset) Enlarged view of σ–H curve.

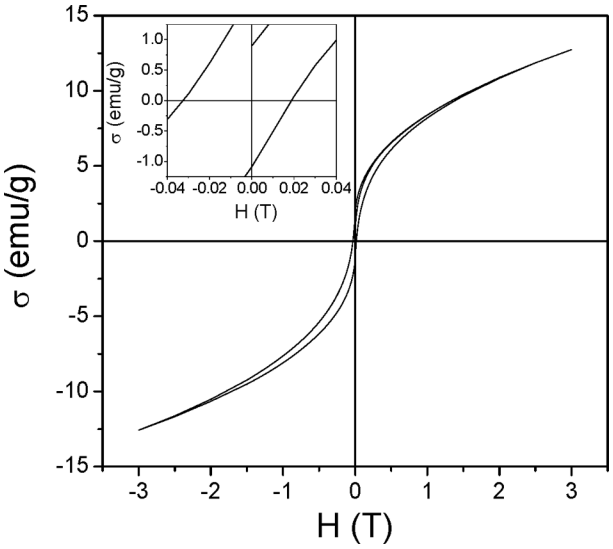

Figure 4. Plot of magnetization (σ) as a function of field (H) measured at 10 K and 3 T cooling field. (Inset) Enlarged view of σ–H curve, showing hysteresis loop shift.

3.3 *Exchange bias studies*

The interfacial coupling between the AF and FM phases at lower temperatures results in the shift of the σ–H hysteresis loops, when the system is cooled through

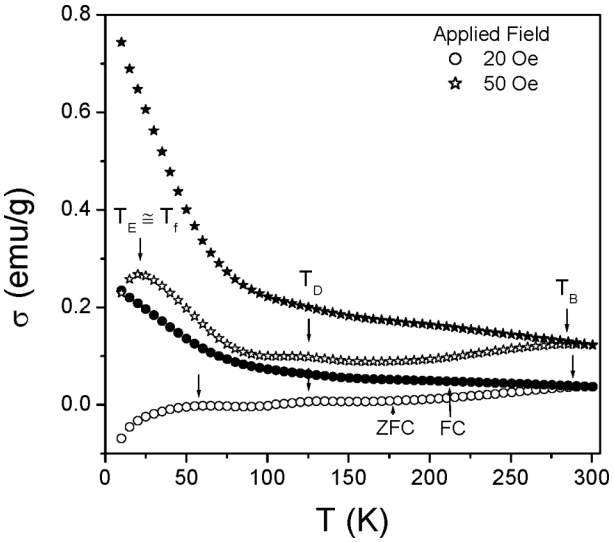

Figure 5. ZFC/FC magnetization curves at external applied fields of 20 and 50 Oe.

the Néel temperature (T_N) of the AF, in the presence of an applied positive field. In this system, the hysteresis loop (at 10 K) is shifted from the origin, even in the absence of cooling field (figure 3 inset). The presence of residual field ($\sim 10^{-3}$ Oe) in the SQUID magnetometer has been corrected in all the measurements. The hysteresis loop is shifted by -17 Oe in the positive direction of the field axis. The negative sign of H_E indicates that the spins at the AF–FM interface are coupled anti-parallel and/or perpendicular to each other due to the non-uniform AF–FM interface [13]. This is obvious, since in nanoparticles, the AF–FM interface is rough unlike smooth interfaces in thin films and multilayers. When ε-$Fe_{2.8}Cr_{0.2}N$ nanoparticles are cooled from 300 K to 10 K with 3 T applied field, relatively higher H_E is observed in the negative direction of the cooling field (figure 4). The H_E value observed is 78 Oe and the H_c value is 326 Oe (figure 4 inset). The AF surface oxide/oxynitride layer produces an appreciable exchange bias effect. Such coupling of the AF oxide/oxynitride surface layers with the FM phases has been reported in [14]. In the case of ε-Fe_3N–CrN nanocomposites, the direct contact of AF surface layer and FM ε-Fe_3N is decreased with the presence of additional AF CrN phase, which does not assist significantly to increase the magnitude of H_E [5]. Hence H_E decreases from 78 Oe for ε-$Fe_{2.8}Cr_{0.2}N$ to 37 Oe in the presence of 32 mass% of CrN in the nanocomposites [5].

3.4 *Thermomagnetic studies*

Figure 5 shows the zero-field cooled (ZFC) and field cooled (FC) magnetization curves as a function of temperature (10–300 K) at external applied fields of 20 and 50 Oe. There are two peaks observed in the ZFC magnetization curves, a weak

peak around 126 K (T_{D}) and a strong broad peak around 22–58 K ($T_{\mathrm{E}} \cong T_{\mathrm{f}}$). In the FC measurements, the applied external field dominates the interaction field and hence the transition temperatures observed in ZFC are not observed in the FC curves. The blocking of these nanoparticles occurs near 300 K at the blocking temperature, T_{B}. The irreversible temperature (T_{irr}) occurs at 290 K in the case of 20 Oe applied field. The strong broad peak, below 58 K in the ZFC curve, arises due to the enhanced unidirectional anisotropy because of the exchange bias coupling (T_{E}) and also the spin-glass-like ordering (T_{f}). Interestingly, both T_{E} and T_{f} peaks overlap at the low temperature.

The blocking temperature (T_{B}) decreases from 290 to 284 K when the field is increased from 20 to 50 Oe. When the external applied field is further increased, it dominates over the anisotropy field, the particles are saturated and the irreversibility is supposed to vanish. In ZFC magnetization curve, the dipolar interaction temperature $T_{\mathrm{D}} = 126$ K does not change with increase in applied field. The origin of T_{D} may be ascribed to the blocking temperature of the Fe–O/Fe–O–N/Cr–O–N surface layer on the nitride nanosystem [15]. T_{D} may also be due to the dipolar interactions present in these dense nanoparticles. The randomness of the relative orientation of the dipoles may lead to the spin-glass phase from the dipolar interactions at lower temperatures [16].

In ZFC curves, the strong broad $T_{\mathrm{E}} \cong T_{\mathrm{f}}$ peak, with maximum in magnetization at 57.7 and 21.5 K is measured at 20 and 50 Oe respectively. The spin-glass-like ordering arises from the localized disordered interactions of the randomly oriented spins. The disordered spins are clustered and these clusters/domains are distributed at random at the AF–FM interface. The flipped spins freeze at lower temperatures. However, the coexistence of the spin-glass-like phase and exchange bias phenomena giving rise to random exchange anisotropy is obvious from the broad nature of the peak at $T_{\mathrm{E}} \cong T_{\mathrm{f}}$. The random exchange anisotropy becomes maximum at the temperature of maximum magnetization (enhanced unidirectional anisotropy, T_{E}). T_{E} shifts because of the presence of uncompensated spins in AF phase.

4. Conclusions

In summary, the ε-$Fe_{2.8}Cr_{0.2}N$ nanoparticles, successfully prepared by the precursor technique, demonstrates exchange bias phenomena and spin-glass-like ordering below 58 K. The low magnitude of the exchange bias results from the coupling of the spins at the rough AF–FM interfaces. Due to the interface disorder, a mixture of parallel and anti-parallel/perpendicular coupling of the AF and FM spins is observed. The spin-glass-like ordering arises from the freezing of these localized frustrated spins in the interface between AF surface oxide/oxynitride layer and the FM ε-$Fe_{2.8}Cr_{0.2}N$ nitride core.

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