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Effects of Cu dilution in NiO on the magnetic properties of $NiFe_2O_4/Ni_{1-x}Cu_xO$ nanocomposites

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ABSTRACT

A granular system composed of ferromagnetic $NiFe_2O_4$ nanoparticles embedded in the Cu diluted NiO matrix has been synthesized by the chemical concentration precipitation method. Phase composition analysis shows that Cu ions have been successfully incorporated into NiO matrix substituting for Ni ions. The magnetic properties of all the bulk samples were investigated by measuring their magnetization as a function of temperature and magnetic field. The field-cooling hysteresis loop shift was observed after cooling the nanocomposites. With the increase of the Cu dilution ratio, the saturation magnetization first increases, and then decreases after reaching a maximum. The exchange bias field gradually decreases with the Cu dilution ratio, reaching a plateau when $x \geq 0.05$. These results are tentatively interpreted by the misalignment of magnetic moments between the ferromagnetic and the antiferromagnetic spins. The decrease of the coupling area between the ferromagnetic phase and the antiferromagnetic phase at the interface is another possible reason.

1. Introduction

In recent years, the potential applications of ultrahigh-density data storage devices using magnetic nanoparticles as memory elements demand magnetic particles as small as possible for effective utilization [1]. However, with decreasing the particle size, the anisotropy energy, which keeps the particle magnetization in the easy anisotropy axis direction, becomes comparable to the thermal energy, and thus makes the particle magnetization flip in all easy directions. As a result, the magnetic nanoparticles lose their stable magnetic order states and become superparamagnetic [2]. This is the so-called "superparamagnetic limit" [3] which limits the use of ultrafine particles for various applications.

Exchange bias (EB), discovered more than 50 years [4], has received considerable attention again in these days because of its function for overcoming the superparamagnetic limit of ultrafine particles. The exchange bias effect is referred to a shift in the hysteresis loop along the magnetic field axis [5,6], due to the interaction at the interface between ferromagnetic (FM) and antiferromagnetic (AFM) materials. When such materials are cooled down below the Néel temperature (T_N) of the AFM in an external magnetic field (with the Curie temperature, T_C, of the FM larger than T_N) an anisotropy (exchange bia) is induced in the FM. The EB magnitude depends on intrinsic parameters such as the exchange interaction at the FM/AFM interface, interface roughness, individual FM and AFM magnetic structure, and their thicknesses [7,8]. It has been reported that EB can be tuned by various extrinsic parameters [9]. However, all these attempts to tune EB externally involve tedious experimental treatments or impractically strong magnetic fields, which make them unsuitable for practical applications.

Recently, based on the domain state model, some reports have reported that the magnitude of the EB field (H_E) could be controlled by intentionally diluting the FM phase [10], AFM phase [11,12] or introducing non-magnetic defects [13,14] in the AFM phase. A distinct enhancement of H_E (more than 60%) with a Cu dilution of only 5% is observed in the IrMn layer [15]. Dai et al. [16] reported that by introduction of FeMn or Mn at the interface or throughout the volume part of the AFM PtCr layer, the pinning field was largely increased and thus the exchange bias field was increased. More recently, the effect of the Mg dilution on the exchange-coupled $Ni_{1-x}Mg_xO/Ni$ ($0 \leq x \leq 0.3$) granular systems has been investigated. But the EB field H_E and coercivity H_c decrease with the Mg content [17]. The results, different from the aforementioned reports indicate that some divarications exist in diluted AFM/FM EB systems.

To understand the dilution effects on the exchange bias in the AFM body, we prepared a series of $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($x = 0$, 0.01, 0.03, 0.05, and 0.1) bulk samples using the chemical concentration precipitation method. In our previous report [18], we have

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investigated the microstructure and origin of the exchange bias in a granular system of $NiFe_2O_4$ nanoparticles embedded in an antiferromagnetic NiO matrix. Based on that work, the effects of Cu dilution on the microstructure, magnetic and exchange bias properties are systematically investigated in this report. It indicates that the proportion of ferromagnetic $NiFe_2O_4$ increases but the EB field H_E decreases with the increase of the Cu content. The magnetic measurement demonstrates that the exchange bias effect in all samples might originate from the pinned spins of the ferromagnetic particles along the cooling field direction due to the interfacial exchange interaction.

2. Experimental

The synthesis of the bulk samples was performed by the chemical concentration precipitation method. According to the formula of $Ni_{0.95-x}Fe_{0.05}Cu_xO$ ($0 \le x \le 0.1$), high-purity (99.99%) ferri chloride ($FeCl_3 \cdot 6H_2O$), nickel chloride ($NiCl_2 \cdot 6H_2O$), cupric chloride ($CuCl_2 \cdot 2H_2O$) and ammonium bicarbonate NH_4HCO_3 were employed as the starting materials. Firstly, nominal amounts of $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were weighed and dissolved in the distilled water. Subsequently, the ammonium bicarbonate (NH_4HCO_3) solution with the appropriate amount was slowly poured into the mixed solution under the constant stir to reach the pH of 7. After that, the precipitation was washed and dried in air at 473 K to obtain precursor powders. Finally, the obtained powders were sintered at 973 K for 3 h in air, forming the resultant nanopowders.

The phase compositions of all the bulk samples were analyzed by the X-ray diffraction (XRD) technique using the Cu Kα radiation. The magnetic measurement was performed using the physical property measurement systems (PPMS). And the field-cooling (FC) hysteresis loops were measured after cooling the sample to the measurement temperature (10, 50, 100, and 200 K) from 300 K in the presence of 20 kOe. The zero-field-cooling (ZFC) hysteresis loops (10 and 300 K) were also measured. For the measurements of FC and zero-field-cooling (ZFC) magnetization as a function of temperature, the cooling process (in the case of FC) and the magnetization measurement were performed in the presence of 1000 Oe.

3. Results and discussion

Fig. 1 shows the diffraction patterns of all the bulk samples $Ni_{0.95-x}Fe_{0.05}Cu_xO$ ($0 \le x \le 0.1$). It can be found that all the samples consist of the NiO phase and $NiFe_2O_4$ phase as shown in Fig. 1(a) and no traces of iron and cuprum, oxides and any binary compound oxides are detected. Accordingly, all the samples are $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($0 \le x \le 0.1$) nanocomposites. It is noted that with increasing the Cu content, the peak intensity of $NiFe_2O_4$ increases gradually, implying the increase in the proportion of the $NiFe_2O_4$ phase. A shift of the XRD peaks to large angles related to the lattice spacing change is clearly observed when increasing Cu content. And the monotonous decrease of the a axis lattice spacing with increasing x suggests that the doped Cu ions have been incorporated into the matrix lattice via substituting for Ni ions for the samples with $x \ge 0.01$, as shown in Fig. 1(b). The grain size of ~40 nm calculated by Debye–Scherrer formula indicates that the samples are nanomaterials.

The temperature dependent magnetization curves in the zero-field-cooling (ZFC) and field-cooling (FC) processes with an applied field of 1 kOe are shown in Fig. 2 for the sample with $x = 0.03$. It can be seen that in the whole measurement temperature range, the ZFC and FC magnetization curves show a distinct irreversible behavior, indicating that a strong FM/AFM exchange coupling exists in this granular system. The FC curve shows a FM-type magnetization which increases continuously with the decrease of temperature and reaches a saturated state below 50 K. It is interesting that the ZFC magnetization exhibits a typical blocking process, i.e., it firstly increases, and reaches its maximum around the temperature of ~200 K, and then decreases gradually. All these results indicate that there exists a collective freezing process for the moments of FM clusters. And thus T_b can be regarded as the blocking temperature for the FM clusters [19]. Furthermore, the ZFC curve has a broad peak around 200 K which may be ascribed to the broad distribution of the blocking temperature in magnetic moments [20].

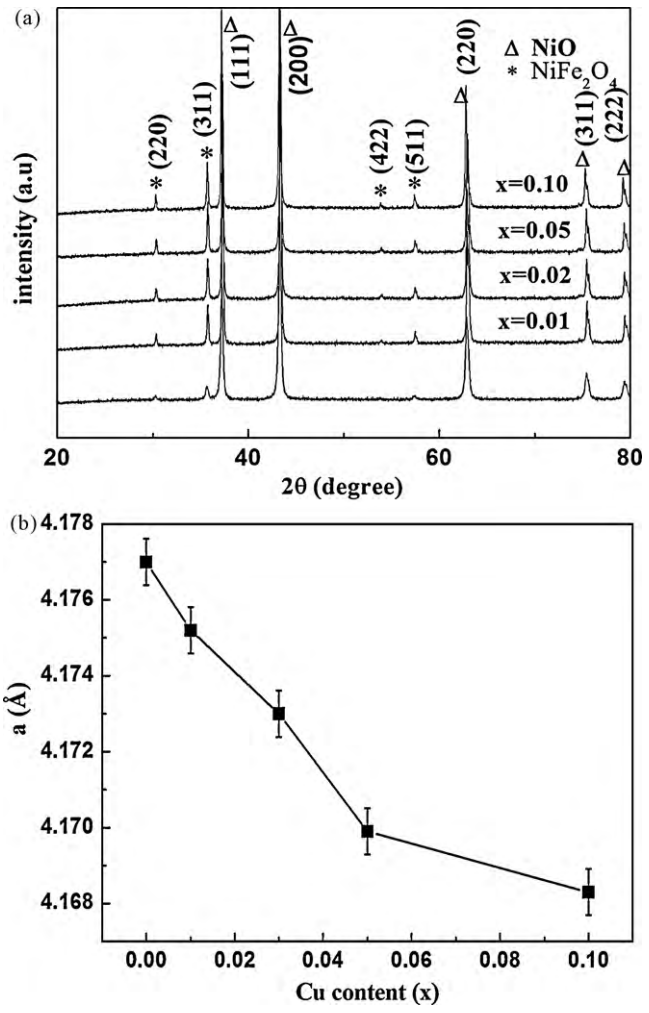

Fig. 1. (a) X-ray diffraction patterns of $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($0 \le x \le 0.1$) samples, the peaks labeled by a star mark are from $NiFe_2O_4$. (b) Evolution of the lattice parameters a with increasing x in $NiFe_2O_4/Ni_{1-x}Cu_xO$ nanoparticles.

In this study, due to the effect of the Cu dilution, which gives rise to the mismatch of the AFM matrix lattice or chemical bond breaking of the FM phase, the interface between FM and AFM becomes disordered for spins. Therefore, at low temperatures, the nanocom-

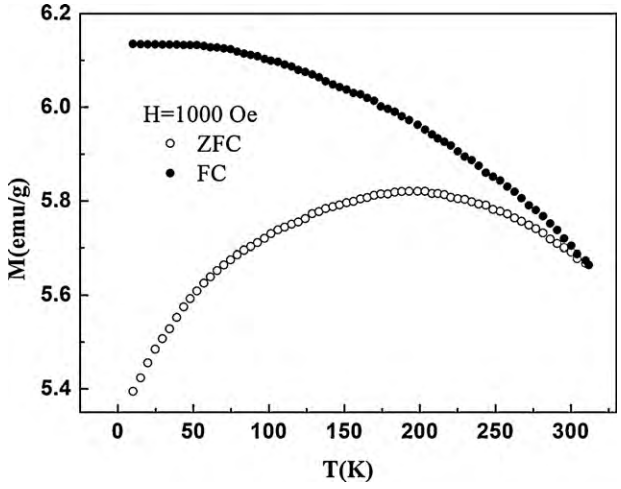

Fig. 2. Temperature dependence of magnetization with ZFC and FC processes for the sample $x = 0.03$.

posites could reach a blocking process state with the decrease of temperature due to the disorder state at the interface between FM and AFM.

It is well known that a spin-disordered interface or surface layer is usually formed when a FM particle is embedded in a non-FM matrix or the magnetic particle size is small enough (the finite size effect) [21,22]. The exchange bias could also be expected from the coupling between the FM and the AFM in these nanocomposites. To test this hypothesis, the magnetic hysteresis loops of the $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($x = 0.03$) nanocomposites at different temperatures (10, 100, 200, and 300 K) after both FC and ZFC processes are shown in Fig. 3(a), which are recorded after cooling from room temperature in a field of 20 kOe ($H_{cool} = 20$ kOe). The inset of Fig. 3(a) is the enlarged M–H curves. It is evident that the hysteresis loops at 10, 100, and 200 K show a negative horizontal shift, but the ZFC hysteresis loop keeps good central symmetry (the ZFC hysteresis loop at 10 K is shown in the inset of Fig. 3(b)). The results indicate the presence of the unidirectional anisotropy below the blocking temperature in the sample with $x = 0.03$ cooled in an applied field. However, above T_b, the FM spins are free to reverse along the external applied field and exhibit no shift. In order to further understand the exchange bias behavior, the temperature dependences of the exchange bias field (H_E) and coercivity (H_C) are shown in Fig. 3(b). The values of the H_E and H_c are estimated from the shift of the centroid and the half-width of the loop in the field axis, respectively. It is clear that H_E decreases rapidly at low temperature ($T < 50$ K) and slowly at elevated temperature. At the same time, the coercivity monotonously decreases from 1350 Oe at 10 K to 500 Oe at 300 K, indicating the blocking of the matrix, which exerts a strong pinning

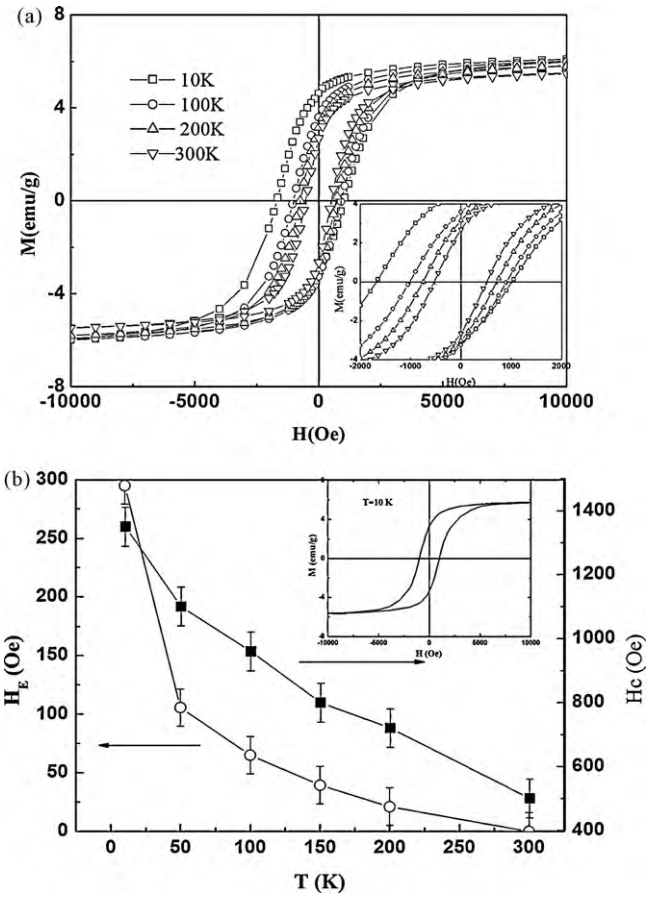

Fig. 3. (a) Representative FC hysteresis loops measured at different temperature for the sample $x = 0.03$. The inset is enlarged curves. (b) Temperature dependence of H_E and H_C of the sample $x = 0.03$. The inset is ZFC hysteresis loop at 10 K.

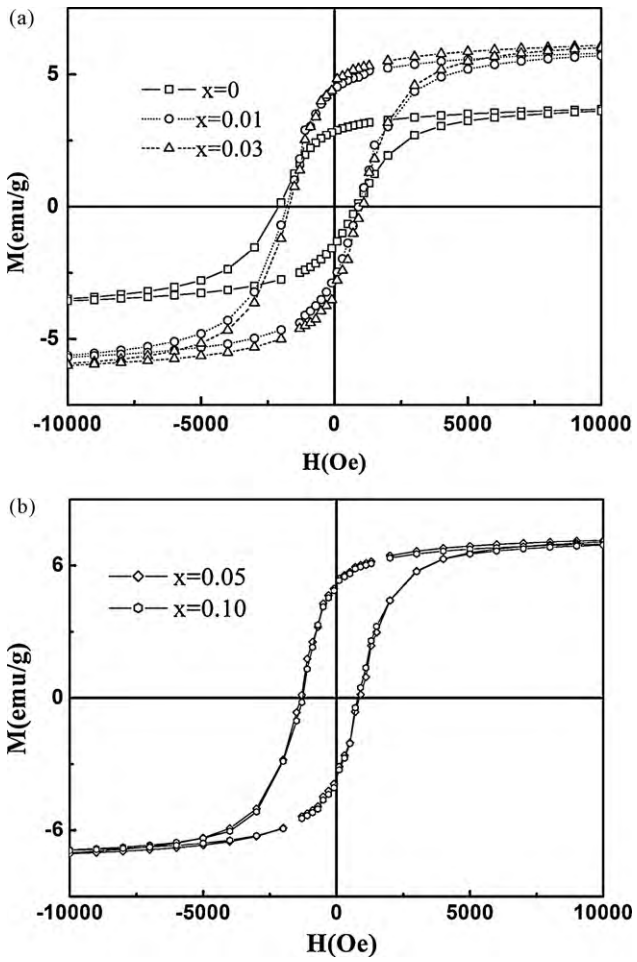

Fig. 4. (a) Hysteresis loops of $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($x = 0$, 0.01 and 0.03) bulk samples measured at 10 K. (b) Hysteresis loops for the samples $x = 0.05$ and 0.1.

action against the reversal of the FM particle moments, because of the exchange interaction. For the present FM/AFM system, as the sample is cooled in an external magnetic field, the moments of FM particles line up along the field, while the AFM spins remain random due to the spin-disordered zone on the surface of AFM. When cooling through T_b, exchange interaction at the interface of magnetized FM and AFM leads to a preferred FM spin orientation. Thus, below T_b, the AFM spins at the interface exert a microscopic torque on the FM spins to keep them in their original direction. As a result, the exchange bias appears and manifests itself in the form of a shift of the hysteresis loop along the field axis.

To study the effect of Cu doping on the magnetic properties of the ferric $NiFe_2O_4$ embeded in NiO system, magnetic hysteresis loops of the $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($0 \le x \le 0.1$) nanocomposetes at 10 K after field-cooling (FC) from 300 K under a magnetic field of 20 kOe are shown in Fig. 4(a) and (b). Notable shifts in the hysteresis loops for all samples are observed, indicating that the resulting materials show the exchange bias effect and can be considered as a granular system of FM $NiFe_2O_4$ nanocomposites embedded in an AFM NiO matrix. The saturation magnetization for the sample with $x = 0$ is 3.62 emu/g at 10 K, then it increases and reaches the maximum 7.02 emu/g for the sample $x = 0.05$ with the increase of the Cu content. However, when $x = 0.1$, the magnetization value is 6.97 emu/g. In other words, the saturation magnetization of the samples initially increases, and decreases with the further increase of the Cu content after reaching its maximum. It suggests that with doping the Cu ions into the NiO matrix, more Ni ions segregate at the interface of the NiO grains and form $NiFe_2O_4$ particles which

are well dispersed in the AFM NiO matrix, resulting in the increase of the saturation magnetization. As the Cu content continuously increases, the system may be close to the percolation threshold [23], and more $NiFe_2O_4$ grains form magnetic clusters which are responsible to the decrease of the saturation magnetization. As shown in Fig. 4(b) the shape of the hysteresis loop for the sample with $x = 0.05$ is nearly identical to the sample with $x = 0.1$, suggesting that the sample with $x = 0.05$ is close to the percolation threshold of the present exchange bias system.

Fig. 5(a) and (b) shows the dependence of the exchange bias field, H_E, on the Cu dilution at 10 and 50 K, respectively. For the samples with $0.01 \le x \le 0.05$, H_E decreases with the increase of the Cu content for both temperatures. With the further increase of Cu content, one noticeable feature is that a plateau for $x > 0.05$ appears. The results are different from that in the Cu diluted IrMn layer [15]. It has already been reported that the enhancement of H_E with Cu dilution is ascribed to the creation of AFM domains by the FM/AFM interaction and the increase of the AFM's uncompensated moments next to the adjacent FM [15]. Our results are similar to the report by Cui et al. [17], who explained that, the net magnetization was coupled with the moments of the FM phase, exhibiting unidirectional anisotropy and EB within a finite region, which was supposed to cause the formation of domain states when Ni atoms in the NiO lattice were replaced by Mg atoms. However, the exchange coupling at the interface of the two phases will also be weakened by the substitution of non-magnetic Mg for Ni. Unfortunately, the authors did not provide the origin of the weakening effect of the substitution of non-magnetic Mg for Ni.

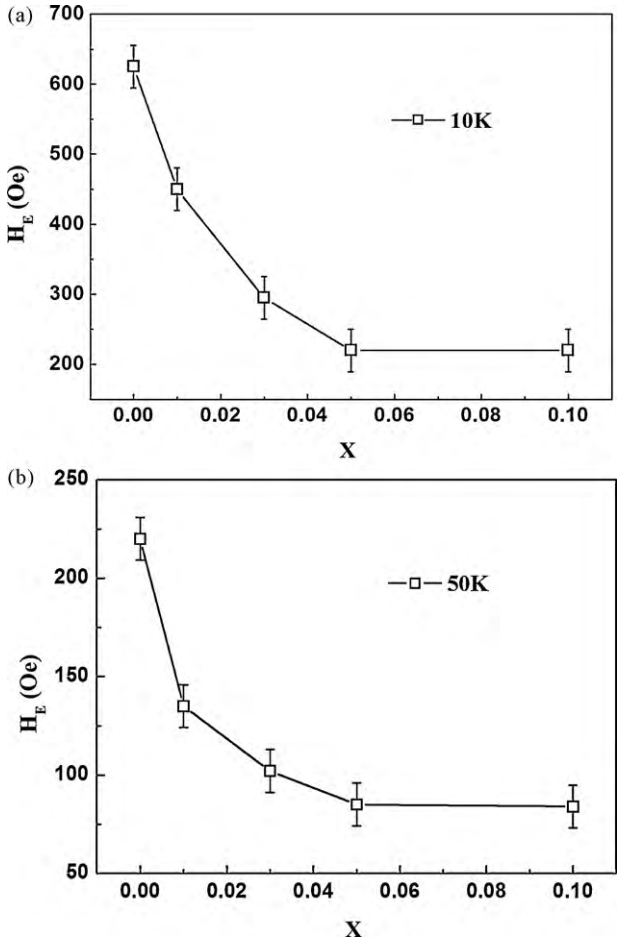

Fig. 5. (a) Cu dilution (x) dependence of exchange bias field (H_E) at 10 K. (b) Cu dilution (x) dependence of exchange bias field (H_E) at 50 K.

For the present study, when Ni ions in the NiO lattice are replaced by Cu ions, the lattice distortion in AFM lattice is induced and the chemical bond of FM is changed due to the different ionic radius (Cu^{2+} is 0.072 nm and Ni^{2+} is 0.078 nm). This results in the emergence of the spin disorder and residual stress existing at the interface between FM and AFM. The applied field may not turn all spins along the field direction due to the presence of disorder and stress. Some of the FM and AFM spins in the corresponding particles may remain at an angle rather than in parallel or antiparallel alignment. This misalignment between the FM and the AFM spins reduces the exchange coupling [24] and a certain fraction of spins in the AFM rotate reversibly with the FM spins, thus the H_E is decreased. Furthermore, it is expected that part of the Ni ions will be separated from the lattices to form more $NiFe_2O_4$ particles at the interface between FM and AFM with the Cu dilution. When the content of the $NiFe_2O_4$ particles increases the interface direct coupling between FM particles is also increased. As a result, the coupling area between FM and AFM at the interface is decreased so that the exchange interaction is weakened. As the Cu content is further increased ($x > 0.05$), FM $NiFe_2O_4$ grains exceed the percolation threshold to form into magnetic clusters, and do not contribute to the exchange bias anymore. Accordingly, H_E reaches a plateau with the further increase in the Cu content ($x > 0.05$) as illustrated in Fig. 5(a) and (b).

4. Conclusions

In conclusion, in the $NiFe_2O_4/Ni_{1-x}Cu_xO$ ($0 \le x \le 0.1$) nanocomposites, exchange bias effect is caused by the exchange interaction between the FM phase and the AFM phase at the interface. It has been found that the saturation magnetization and EB field of the granular systems depend strongly on Cu concentration. Dilution with Cu causes that saturation magnetization increases, and the formation of more $NiFe_2O_4$ grains embeded in AFM NiO matrix with the Cu dilution is responsible to this result. The decrease of exchange bias field is ascribed to the misalignment between the AFM and FM spins. In addition, owing to the Cu dilution, the decrease of coupling area between FM particles and AFM phase at the interface is also the reason for the decrease of exchange bias.

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