Contents lists available at ScienceDirect



Journal of Magnetism and Magnetic Materials



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Room temperature ferromagnetism in Fe doped CuO nanorods

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ARTICLE INFO

Article history: Received 8 October 2009 Received in revised form 19 January 2010 Available online 13 April 2010

Keywords: Magnetic semiconductor Hydrothermal synthesis Nanorod Magnetic properties Jahn-Teller distortion Mixed valency

1. Introduction

The potential of exploiting the spin of the electron (in addition to its charge) in novel new electronic devices and the associated opportunities for new science have led to extensive search for viable magnetic semiconductors with room temperature ferromagnetism [1,2]. Some success for ferromagnetism has been reported in dilute magnetic semiconductors (DMS) and dilute magnetic oxides (DMO) containing a few percent of transition metal ions such as (Ga,Mn)As [3,4], (Zn,M)O [5,6], and (Ti,M)O₂ [7,8] with M=V, Cr, Mn, Co, Ni, and Cu. Most of the earlier works were concentrated on transition metal doped non-magnetic semiconductors. Nevertheless much more detailed investigations are required to understand the origin of ferromagnetism and possible applications in spintronic devices.

Transition metal monoxides MO, M=Mn, Co. Ni and Cu reveal complicated magnetic as well as electronic structure. Ferromagnetic property was observed in nanosized MO and 3d metals doped MO by modifying the original magnetic order. Among transition metal monoxides,Cupric oxide CuO is a strongly correlated electron system which exhibits Mott insulating behavior and anti ferromagnetic (AFM) with two magnetic transitions near 215 and 230 K [9], possesses complicated monoclinic tenorite structure. The magnetic structure of CuO consists of Cu–O parallel sheet of plane in which oxygen atom is located at the center of a copper distorted tetrahedron in (110) plane. The exchange in the Cu–O–Cu chains along the (101) direction is strongly and completely antiferromagnetic. Recently Zheng and his co workers [10,11], observed dramatic suppression of AFM

ABSTRACT

One dimensional CuO and Fe doped CuO nanorods have been synthesized by template free solution phase hydrothermal methods. The typical diameter and the length of the $Cu_{1-x}Fe_xO$ nanorods (x=0, 0.02, 0.05, 0.10) are 20–25 and 300–400 nm. Pure CuO nanorods show weak ferromagnetism and the introduction of Fe within CuO lattice improves significantly the ferromagnetic property with the Curie temperature far above room temperature. The shape anisotropy is the key point to understand ferromagnetism in Fe doped CuO nanorods.

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coupling in Li doped CuO and CuO nanoparticles. Punnose et al. [12,13] explained the particle size dependence exchange bias and large coercivity in CuO nanoparticles on the basis of uncompensated surface spin of the nanocrystal. Li et al. [14] observed ferromagnetism in Mn doped bulk CuO and ferromagnetism enhanced by the co-doping of Al ion with low Curie temperature (below 100 K). Anomalous ferromagnetic behavior have observed in CuO nanorods [15]. Nanorods also have a number of advantages over thin films or nanoparticles with respect to studying ferromagnetism in DMSs. Specifically, they offer thermodynamically stable features and are typically single-crystalline and defect free. They can thus safely exclude the effect of defects and nonuniform distribution of dopants that are typically observed in DMSs prepared by nonequilibrium processing (e.g., molecular beam epitaxial process). All spin rotations in the nanorods could be limited to a single axis. Possible tetragonal distortion and shape anisotropy in the nanorods could also be helpful for the evolution of ferromagnetism [16,17]. Nanorods themselves are attractive building blocks for electronic devices. So nanorods could further fuel the development of ferromagnetism in DMSs.

In this article, we report the room temperature Ferromagnetic properties of Fe doped CuO nanorods. It was observed that the ferromagnetic coupling interaction increases with Fe concentration. The effect of Fe doping is discussed and relevant mechanism is proposed.

2. Experimental

Pure CuO and Fe doped CuO nanorods were synthesized by hydrothermal method. For the hydrothermal synthesis of the CuO nanorods, a closed cylindrical teflon linked autoclave with 23 ml

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^{0304-8853/\$ -} see front matter \circledcirc 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jmmm.2010.04.020

capacity was used. In a typical preparation, 0.01 M cupric acetate $Cu(CH_3COO)_2 \cdot 6H_2O$, 1.25 mM NaOH and the required amount of ferric nitrate [Fe(NO₃)₃ · 9H₂O] were dissolved in deionised water to form an alkali solution. The mixture was stirred for 45–50 min and then it was transferred to an autoclave. The hydrothermal synthesis was conducted in an electric oven at 140 °C for 12 h. After the reaction was over, black crystalline products were harvested by centrifugation and through washing with deionised water and ethanol for several times. Finally the samples were dried at 60 °C for 24 h.

X-ray diffraction patterns of the samples were recorded by high resolution X'Pert PRO PANalytical X-ray diffractometer in the range $30-90^{\circ}$ using Cu K_a radiation. Microstructure and crystal structures of the nanorods were obtained using transmission electron microscope (TEM) and high-resolution TEM (HRTEM, JEOL 2010) studies. The metal contents in the nanorods were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES), (Perkin Elmer). Doped samples were characterized by X-ray photoelectron spectroscopy (5400 ESCA). DC Conductivity was measured by high resistance electrometer (Keithley 6517A) in two probe configuration. Magnetization measurements were carried out by SQUID magnetometer, quantum design, MPMS XL (evercool).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $Cu_{1-x}Fe_xO$ samples. It can be seen that all the samples contain a single CuO monoclinic phase. Because the radius difference between Cu^{2+} ion 0.73 Å and Fe^{3+} ion 0.64 Å or Fe^{2+} 0.74 Å is not remarkable, Cu^{2+} ions in lattice structure can be replaced by Fe ions. Here we have adopted modified Rietveld refinement procedure to obtain the refined values of structural and microstructural parameters. The whole pattern fitting has been done with the help of the software MAUD [18]. Initial simulation of the diffraction pattern was carried out with the CuO phase having space group C2/*c*. Then the Cu atom is accordingly substituted with the Fe atom for the doped samples. Fig. 1(b) shows the variation of unit cell volume as a function of dopant concentration. Clearly, the unit cell volume contraction by very small amount confirm the incorporation of Fe ion in CuO host lattice.

The atomic compositions of constituent elements in $Cu_{1-x}Fe_xO$ were determined from ICP-AES spectra with instrument resolution of 1 ppm. The concentration of Fe in pure CuO nanorods is about 100 ppm. The atomic ratio of Fe to Cu was quantitatively determined as 0.016 for CuO:2% Fe 0.041 for CuO:5%Fe and 0.098 for CuO:10%Fe nanorods.

Morphology of as synthesized samples was obtained using high-resolution transmission electron microscope studies. TEM and HRTEM images of the 10% Fe doped CuO nanorods are presented in Fig. 2. Inset shows a single nanorod grown along (110) direction. The average diameters of the nanorods vary between 20 and 25 nm. Length of nanorods are in the range 300–800 nm. The aspect ratio of the nanorods lies between 15 and 40. The high resolution TEM image is shown in Fig. 2(b) which exhibits clear lattice fringes. Homogeneous and parallel lattice fringes imply the single crystalline behavior of prepared samples. The interval between two adjacent lattice fringes is distinctly shown by arrows in Fig. 2b is 2.749 Å which corresponds to the (110) plane of the monoclinic structure of CuO. The oriented (110) nanorods are formed from dehydration of Cu(OH)₂ in solution medium by oxolation process [19].



Fig. 1. (a) XRD patterns of the $Cu_{1-x}Fe_xO[x=0, 0.02, 0.05, 0.10]$ at room temperature. The calculated and observed diffraction profiles are shown at the top with the color solid line and open circle, respectively. The lower trace is a plot of the difference between calculated and observed intensities. (b) Fe Concentration dependence of unit-cell volume. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. (a) Typical TEM image of $Cu_{0.90}Fe_{0.10}O$ nanorods. Inset shows a single nanorod. (b) HRTEM image of a nanorods.



Fig. 3. Fe 2p core level X-ray photoelectron spectrum of 10% Fe doped CuO nanorods. Inset shows fitted X-ray photoelectron spectrum of $Fe2P_{1/2}$ peak. Fig shows that the $Fe2P_{1/2}$ peak around 710.23 eV contains the contribution from the Fe⁺² and Fe⁺³ ion.

The chemical valence state of Cu and Fe in doped samples were characterized by X-ray photoelectron spectroscopy (XPS) (5400 ESCA). The characteristic peaks of Cu $2p_{1/2}$ and $2p_{3/2}$ appear at 954.3 and 934.4 eV which are consistent with Cu⁺² valence state [20]. The Fe 2p core level spectrum for the x=0.10 sample is depicted in Fig. 3. This shows that Fe 2p spectrum is split into Fe $2p_{1/2}$ at 721.44 eV and Fe $2p_{3/2}$ at 710.23 eV due to spin orbit interaction. The absence of peak at 706-707 eV rules out the presence of metallic Fe in doped samples. The broad spectrum of Fe $2p_{3/2}$ with binding energy (B.E.) 710.23 eV has been analysed by fitting the experimental data using Gaussian-Lorentzian functions as shown in inset. The main peak is deconvoluted into two peaks centered at 709.01 and 710.84 eV. The best fitted two peaks are in agreement with that for Fe^{+2} (B.E.=709-710 eV) and Fe⁺³ (B.E.=710-711 eV) ion [21,22]. Thus, the present XPS investigation gives an evidence for the coexistence of the Fe⁺² and Fe^{+3} ions in $Cu_{1-x}Fe_xO$. The tetrahedral Fe^{3+} ion is expected to form CuO through the oxidation of the Fe⁺² ion.



Fig. 4. Variation of logarithm resistivity as a function of inverse temperature for pure and iron-substituted CuO samples.

The dc resistivity (ρ_{dc}) for all compositions have been measured. The values of ρ_{dc} at room temperature are 4.69×10^6 , 2.38×10^6 , 1.43×10^6 and $7.95 \times 10^5 \Omega$ cm for x=0, 0.02, 0.05 and 0.10, respectively. Room temperature resistivity decreases by about one order of magnitude with Fe doping. This clearly indicates that the incorporated Fe ions are donating extra electrons to the host CuO lattice. Resistivity measurements suggest that some doped Fe ions exist in Fe⁺³ state for the enhancement of carrier concentration. Fig. 4 represents the resistivity variation with temperature for four different samples. Monotonous increase of resistivity with decrease of temperature indicates semiconducting behavior. Temperature dependence of resistivity is generally described by hopping transport mechanism [23],

$$\rho(T) = \rho_0 \exp\left(\left(\frac{T_0}{T}\right)^{\gamma}\right) \tag{1}$$

where ρ_0 and T_0 are constants. The exponent γ depends on the dimension. The values of γ are 0.25, 0.33 and 0.50 for three, two and one dimensional system. Experimental data are fitted to Eq. (1) as shown in Fig. 4. The best fitted value of γ is 0.48 for undoped CuO nanorods which supports one dimensional conduction process. Straight line behavior of $\ln\rho(T)$ Vs. 1000/*T* plots as depicted in Fig. 4 shows thermally activated conduction for $\gamma = 1$. Low resistive Fe doped samples favors band conduction mechanism.

Fig. 5 illustrates the field (H) dependent magnetization (M) of pure CuO (inset) and Fe doped CuO nanorods at room temperature. The M–H curve for pure CuO reveals hysteresis loop but it does not saturate up to 5 kOe. The almost linear behavior of M at higher H suggests that ferromagnetic and antiferromagnetic components are present in pure CuO nanorods. The coercive field is 421 Oe. Shape anisotropy plays an important role to affect magnetic properties. The shape anisotropy constant is proportional to the aspect ratio. The coercive filed (H_c) increases with the



Fig. 5. Magnetization (M) versus magnetic field (H) of Fe doped CuO nanorods measure at room temperature. Inset shows for pure CuO nanorods.

increase of aspect ratio. Spherical nanoparticles do not posses any shape anisotropy, hence have smaller H_c as reported by Punnoose et al. [12] The aspect ratio of the present nanorods is about five times larger than the previous studied nanorods [15]. This clearly indicates that larger H_c is consistent with higher shape anisotropy.

The M–H curve tends to saturate with increase of Fe concentration as depicted in Fig. 5. The highest Fe doped sample (x=0.10) shows distinct M–H loop which almost saturates at 2.5 T. The saturated magnetic moment is 0.428 μ_B /Fe. The saturation magnetization increases significantly with increase of Fe concentration. This clearly indicates that the incorporated Fe ions enhance ferromagnetic coupling. The M–H hysteresis curve at lower magnetic field for 10% Fe doped CuO at different temperatures are shown in Fig. 6 which exhibits well-defined hysteresis at room temperature with a coercive field of 33 Oe and a remnant magnetization of 0.065 μ_B /Fe. The corresponding values at 5 K are 846 Oe and 0.281 μ_B /Fe. It can be clearly seen that the coercivity increases significantly with decreasing temperature. Inset shows the variation of coercivity with temperature.

The temperature dependence of the susceptibility $\chi(T) = M(T)/H$ for all samples are shown in Fig. 7. The thermal variation of $\chi(T)$ for undoped nanorods is similar to pure CuO [12]. The increase of $\chi(T)$ below 50 K (FC) and 75 K (ZFC) is due to the presence of some paramagnetic centers arising from the defects and surface layers [24]. The substitution of Cu ions by Fe ions shifts the magnetic contribution is totally suppressed due to the prominent ferromagnetic component. The Fe doping modifies the shape as well magnitude of $\chi(T)$.

The possible impurities in all samples are metallic Fe, magnetite Fe₃O₄ and maghemite γ - Fe₂O₃. The most intense peaks in XRD for Fe₃O₄ and γ - Fe₂O₃ phases are not observed. The absence of noticeable peaks indicates that a solid solution of



Fig. 6. Hysteresis loops (M–H) obtained at different temperatures for 10% Fe doped sample. Inset shows temperature dependent coercivity (H_c).

 $Cu_{1-x}Fe_xO$ is formed even for the highest x=0.10. The XPS results exclude the presence of metallic Fe. At room temperature, the electrical resistivity of Fe₃O₄ is about $10^{-3} \Omega$ cm and the γ - Fe₂O₃ is an insulator. The electrical resistivity of Fe₃O₄ increases by two orders of magnitude at around 120K due to Verway transition [25]. The resistivity of CuO nanorods is much higher than that of Fe₃O₄ and also it does not reveal any sharp rise up to 100 K. Hence the temperature dependence of resistivity discards the presence of Fe_3O_4 . The magnetite Fe_3O_4 is a ferromagnet with Curie temperature 860 K and magnetic moment $1.33 \mu_B$ /Fe. The susceptibility decreases sharply around 120K characteristic of Verway transition. The Fe content of pure CuO nanorod is 100 ppm. The saturation moment for γ - Fe₂O₃ is 0.5 μ_R /Fe. The contribution from Fe to saturation magnetization is about two orders magnitude smaller than the present values. The thermal behavior of $\chi(T)$ for all samples can not be accounted for Fe oxides. All the experimental evidences suggest that the samples are not contaminated with Fe oxides. Secondary phases as sources for the observed ferromagnetism can be ruled out.

The electronic configurations of Cu^{+2} , Fe^{+3} and Fe^{+2} are $3d^9$ 3d⁵ and 3d⁶. The magnetic moments of Cu⁺², Fe⁺³ and Fe⁺² are 1.73 μ_B , 5.9 μ_B and 4.89 μ_B , respectively, in high spin state. The magnetic moments of Fe ions are larger than Cu ions. The incorporation of Fe in CuO lattice enhances the magnetic moment. Ferromagnetism has not been obtained in Fe⁺³ doped bulk CuO although its magnetic moment is enhanced greatly [26]. CuO nanocrystals with size larger than 10 nm behave like bulk CuO without ferromagnetic order [12]. Antiferromagnetic nanocrystals reveal ferromagnetic property due to the uncompensated surface spins. Nanorods with large aspect ratio have more uncompensated surface spins which assist the formation of ferromagnetic behavior. In octahedron crystal field, eg levels of Cu⁺² ions are more than half filled which renders Jahn-Teller distortion. First principle self-interactions-free density functional calculation suggest that the hybridizations between Cu d₇₂ and O p orbitals are responsible for antiferromagnetic Cu–O–Cu chain along *z*-axis and ferromagnetic Cu–O chain in (x,y) plane [27]. The antiferromagnetic state is stabilised by the structural distortion. Both Fe⁺³ and Fe⁺² are not Jahn–Teller ions and do not produce local lattice distortion. Antiferromagnetic exchange interaction is weaken in Fe doped CuO samples. The oriented nanorods along



Fig. 7. (Left) Field cool (FC) and zero field cool (ZFC) susceptibility of pure CuO nanorods. (Right) Field cooled susceptibility for all doped samples.

(110) direction may strengthen the ferromagnetic coupling in (x,y) plane. The mixed valency of Fe ions gives rise to double exchange interaction which favors the ferromagnetic spin order.

4. Conclusion

CuO nanorods with high aspect ratio 15–20 have been successfully prepared by template free hydrothermal method. Analysis of XPS and resistivity data suggest that Fe ions in CuO nanorods exist in mixed valence state. Room temperature ferromagnetism in CuO nanorods is significantly enhanced by the substitution of Cu by Fe ion. Shape anisotropy, mixed valency of Fe ions and non-Jahn–Teller property of Fe ions play important roles to produce ferromagnetism with high Curie temperature in Fe doped CuO nanorods.

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