# Ferromagnetism in Fe-doped CuO nanopowder

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**Abstract:** The Fe-doped CuO nanopowder was synthesized by following the standard solid-state reaction method. The structure and magnetic properties of the Fe-doped CuO nanopowder were investigated. X-ray diffraction spectra confirmed the monoclinic structure of CuO and no secondary phase was detected, indicating that the Fe ions were incorporated into CuO. The ferromagnetism in Fe-doped CuO was studied and is believed to originate from the interaction between Fe ions and Cu ions via a super-exchange interaction or F-center mediated exchange interaction.

**Key words:** diluted magnetic semiconductors; ferromagnetism; Fe-doped CuO

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## 1. Introduction

Oxide diluted magnetic semiconductors (DMS) have attracted great attention due to their unique characteristics and potential applications as spintronic devices[1, 2]. The strong electronegativity of oxygen in oxide semiconductors is expected to bring strong p-d exchange coupling between the carriers and localized spins. For practical applications, the prime requirements are to raise the Curie temperature above room temperature with the absence of dopant clusters and a secondary phase. In 2000, Dietl *et al.*[3] theoretically predicated that room temperature ferromagnetism should exist in p-type Mn-doped ZnO. Since then, numerous theoretical and experimental studies have been focused on high temperature ferromagnetism (FM) in various kinds of transition-metal (TM)-doped semiconductor oxides, such as TM-doped ZnO, $TiO_2$ and $In_2O_3$[4–6].

Pure CuO is a monoclinic structure p-type semiconductor with an indirect band gap of 1.2 eV. According to resent research, it is an antiferromagnetic semiconductor with two magnetic transitions near 215 and 230 K[7]. CuO is a compound associated with high-TC superconductors. It has also been widely used as a catalyst[8] and in solar cells[9]. Research on ferromagnetism in TM-doped semiconducting CuO is important in both theory and experiment.

In the recent years, several studies on Fe-doped CuO nanomaterials have been reported[10–12]. The synthesized methods focused on the co-precipitation, sol–gel and hydrothermal method, and room temperature ferromagnetism was observed in some samples. However, some reports cannot avoid the infection of impurity phases and exchange bias behavior was common. Furthermore, the real ferromagnetism mechanism has not been fully understood.

In this work, we prepared the Fe-doped CuO DMS by following the solid-state reaction method. The structure and magnetic properties of the nanopowders have been studied.

## 2. Experimental methods

The $Cu_{0.95}Fe_{0.05}O$ nanocrystal was prepared by following a solid-state reaction method. In typical Fe-doped CuO synthesis, stoichiometric amounts of copper sulfate ($CuSO_4$) and ferrous sulfate ($FeSO_4$) powders are prepared with the cation ratio of Cu : Fe = 19 : 1. The mixture powder is mixed with an appropriate amount of NaOH and milled for about 30 min to ensure that the reaction progresses adequately. The resulting powder is then cleaned with deionized water, dried and then annealed at 500 ℃ in Ar atmosphere for 1 h.

Structural and morphological studies are done by using X-ray diffraction (XRD) and the high resolution transmission electron microscopy (HRTEM) technique. XRD is done with CuK$\alpha$ irradiation on an 800 W Philips 1830 powder diffractometer. HRTEM results are obtained from a Hitachi S-4800 microscope instrument with an accelerating voltage of 15 kV. The magnetization measurements are performed on a quantum design superconducting quantum interference device (SQUID) system.

## 3. Results and discussions

Figure 1 shows the X-ray diffraction pattern of the $Cu_{0.95}Fe_{0.05}O$ and CuO samples. All diffraction peaks could be indexed as the monoclinic structure CuO (JCPDS No. 80-1916) and no diffraction peaks of impurity phases are observed in $Cu_{0.95}Fe_{0.05}O$. The peak at 12° in CuO shows the existence of a small amount of undecomposed $Cu(OH)_2$. Calculated by Rietveld refinements[13], the lattice constants are $a = 4.699$ Å, $b = 3.444$ Å, $c = 5.091$ Å and vol = 81.32 $Å^3$. The lattice constants are a little smaller than the literature data of monoclinic structure CuO ($a = 4.703$ Å, $b = 3.426$ Å, $c = 5.148$ Å, and vol = 81.84 $Å^3$) at the same condition. The decrease of lattice constants is due to the ionic radius difference between $Cu^{2+}$ (0.72 Å) and $Fe^{2+}$ (0.77 Å) or $Fe^{3+}$ (0.64 Å). It indicates that the Fe ions are indeed incorporated in the CuO lattice and

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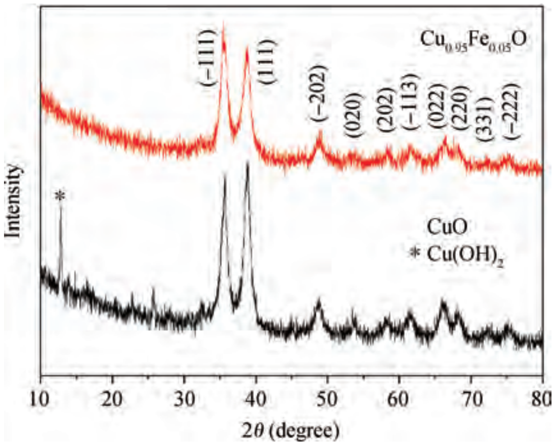

Fig. 1. XRD patterns for the Fe-doped CuO powder.

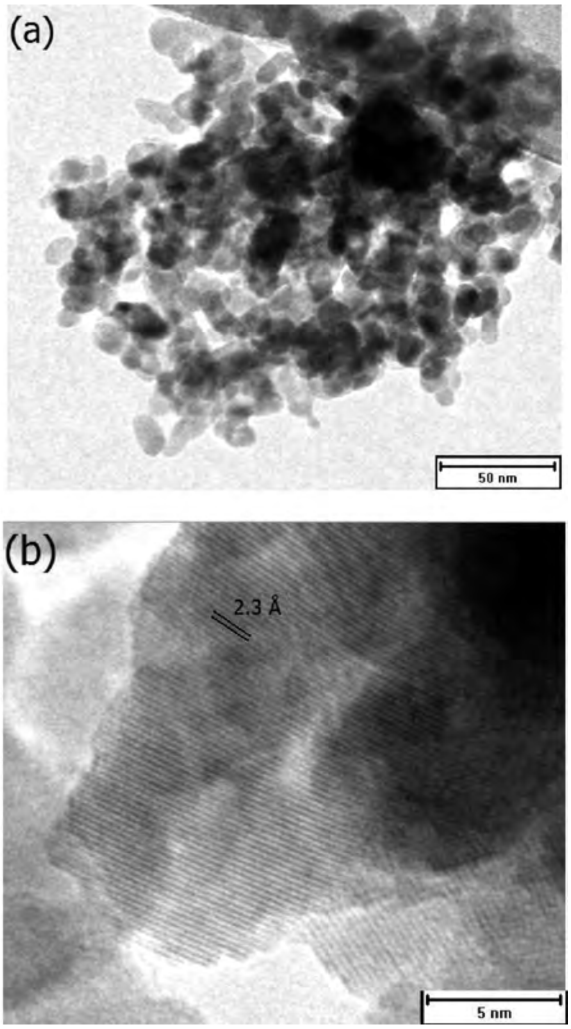

Fig. 2. (a) TEM and (b) HRTEM images of the Fe-doped CuO powder.

replaced Cu ions.

Figure 2(a) shows the TEM image of the $Cu_{0.95}Fe_{0.05}O$ sample, which indicates that the average grain size is about 10 nm. The HRTEM image is shown in Fig. 2(b). From the figures, one can see that no sign of segregation of impurity or clusters could be detected, indicating that the grain is single crystalline and free of secondary crystalline phases. In addition, the sample shows clear lattice fringes, with interplanar spacing of 2.30 Å, which is a little smaller than the inter-planar distance of the (111) plane for the monoclinic structure CuO of 2.325 Å. Both XRD and HRTEM results show that the Fe ions are perfectly substituted for Cu ions.

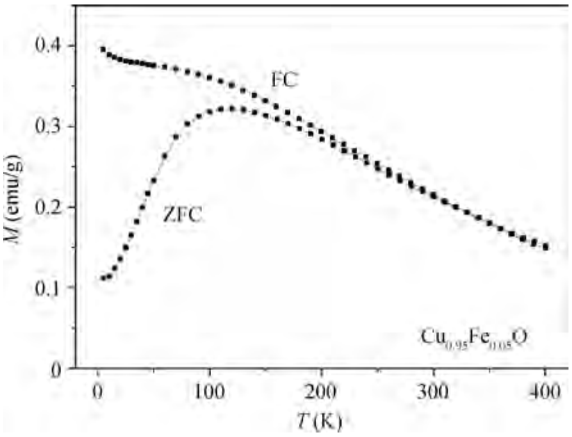

Fig. 3. FC-ZFC $M$–$T$ curve of the Fe-doped CuO powder.

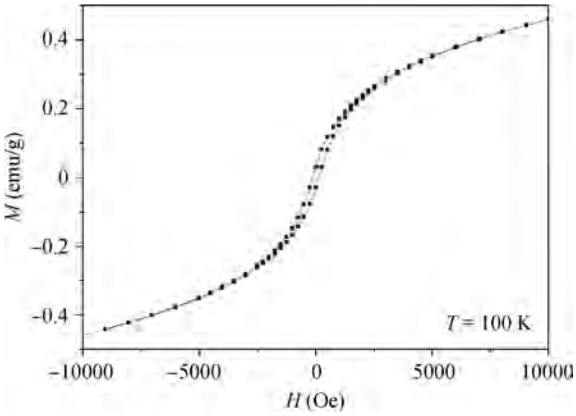

Fig. 4. $M$–$H$ curve of the Fe-doped CuO powder taken at 100 K.

The magnetization versus temperature ($M$–$T$) curve is shown in Fig. 3. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements are performed from 5 to 400 K. The FC is obtained by measuring the magnetic moment of the sample which is first cooled in a magnetic field of 1000 Oe and then heated in the same magnetic field. The ZFC is obtained with the same method, except for the absence of a magnetic field. The $M$–$T$ curve shows that the Curie temperature of the Fe-doped CuO nanocrystal was about 200 K. The nonzero difference between the FC and ZFC magnetization curve shows distinct irreversibility behavior. The FC magnetization curve shows ferromagnetism below the Curie temperature. The ZFC magnetization curve increases with temperature and reaches a peak at the blocking temperature of about 120 K. It suggests spin-glass-like phase transition.

Figure 4 shows the magnetization versus applied magnetic field ($M$–$H$) curve of the $Cu_{0.95}Fe_{0.05}O$ sample measured at 100 K after subtracting the diamagnetic background. The well-defined hysteresis loops show that the nanocrystal i clearly ferromagnetic at 100 K. At the maximum applied field of 10 kOe, the maximum magnetization ($M_s$) is about 0.46 emu/g and the coercivity ($H_c$) is 126 Oe. The absence of any detectable traces of secondary phases or clusters from the XRD and HRTEM results clearly confirm that the ferromagnetic signal is not produced by impurities in the sample. Contamination during sample preparation or annealing also could be ruled out as the experimental conditions are precisely controlled.

The ferromagnetism in Fe-doped CuO could be explained by the following two mechanisms. The first mechanism is super-exchange interaction. In a high spin state, a Fe ion has five d electrons with the total spin of $S = 5/2$ or 2 for the valence of 2 and 3, respectively. A $Cu^{2+}$ ion has a total spin of 1/2. Fe ion substitution into $Cu^{2+}$ ion enhances the magnetic moment. The extra magnetic moment may be coupled to the lattice of $Cu^{2+}$ spins via a super-exchange interaction, through an $O^{2-}$ ion. The second possible origin of ferromagnetism is an F-center mediated exchange interaction[14]. For the oxide materials, there exist oxygen vacancies. So indirect ferromagnetic coupling among the neighboring $Fe^{3+}$ ions via a localized carrier at near oxygen vacancy could occur.

## 4. Conclusions

In summary, ferromagnetism is well obtained in Fe-doped CuO fabricated by following the solid state reaction method. Analyses of the XRD, TEM and magnetization data indicate that the Fe ions are substituted Cu ions in Fe-doped CuO. The ferromagnetic Fe-doped CuO is discussed. Two mechanisms were proposed. One is the super-exchange interaction between Fe ion and Cu via a super-exchange interaction through $O^{2-}$ ion. Another is the F-center mediated exchange interaction.

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