



Local structure and magnetization of ferromagnetic Cu-doped ZnO films: No magnetism at the dopant?



P.S. Vachhani^{a, b, *}, O. Šipr^c, A.K. Bhatnagar^{a, d}, R.K. Ramamoorthy^{b, d, 1}, R.J. Choudhary^e, D.M. Phase^e, G. Dalba^b, A. Kuzmin^f, F. Rocca^g

^a School of Physics, University of Hyderabad, Hyderabad 500 046, India

^b Department of Physics, University of Trento, 38123 Povo, Trento, Italy

^c Institute of Physics AS CR v. v. i., Cukrovarnická 10, Prague, Czech Republic

^d School of Engineering Sciences & Technology, University of Hyderabad, Hyderabad 500 046, India

^e UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore 452 017, India

^f Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia

^g IFN-CNR, Institute for Photonics and Nanotechnologies, Unit "FBK-Photonics" of Trento, 38123 Povo, Trento, Italy

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ABSTRACT

Relationship between magnetism and structure of Cu-doped ZnO was investigated at macroscopic and microscopic levels. Thin $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films ($x = 0.02, 0.04, 0.07$ and 0.10) were prepared by a pulsed laser deposition and characterized via superconducting quantum interference device (SQUID) magnetometry, high-resolution x-ray diffraction, and Cu *K*-edge and Zn *K*-edge x-ray absorption, x-ray linear dichroism and x-ray circular magnetic dichroism spectroscopy. Even though the samples exhibit room-temperature ferromagnetism with magnetization that increases with Cu concentration, we did not detect signatures of local magnetic moments associated with Cu atoms, as evidenced by the lack of any XMCD signal. The host ZnO wurtzite lattice is not significantly altered by the addition of Cu. At the same time, most of the Cu atoms are not incorporated into the wurtzite lattice but rather have a CuO-like coordination. These results indicate that ferromagnetism of the investigated $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films is not directly linked to the doping atoms but rather is due to some other changes which have been introduced to the host ZnO by the dopants.

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1. Introduction

The focus of current materials science is on versatile materials which exhibit more interesting properties at the same time. Among these materials, there are the magnetic semiconductors, where the main current issue is to design materials which would be ferromagnetic not only at low temperature but at room temperature as well. In this respect, doped ZnO attracted a lot of attention, with ample experimental evidences of room-temperature ferromagnetism (RTFM) in ZnO doped with transition metal (TM) ions such as Ti, V, Mn, Fe, Co, Ni, or Cu [1–3]. Despite the enormous effort that has been devoted to research on doped ZnO, the issue remains

controversial both as concerns the mechanism of the RTFM phenomenon and as concerns the phenomenon itself or, more precisely, the conditions under which it arises. This is at least partially due to the fact that the magnetic behavior of doped ZnO is strongly linked to how the material was prepared. More reliable data on well-defined systems characterizing as many aspects as possible are therefore needed.

One of the major questions is whether the observed RTFM is an intrinsic property of the TM-doped ZnO or whether it is due to extrinsic causes such as nanoclustering of the dopant [4–7]. Therefore, when studying the intrinsic RTFM, it is convenient to turn to dopants which are non-magnetic in elemental form, to minimize the possibility that the magnetism is due to dopant precipitates. In this respect Cu-doped ZnO (Cu:ZnO) is an especially attractive material and indeed a lot of studies were devoted to it. However, the results are quite diverse, e.g. controversial conclusions were reached on whether the RTFM can be observed only in p-type Cu:ZnO or whether ferromagnetic Cu:ZnO can be also of n-type [8–12].

* Corresponding author. Current address: D.K.V. Arts and Science College, P.N. Marg, Jamnagar 361008, India.

E-mail address: prashjdg@gmail.com (P.S. Vachhani).

¹ Current address: LIONS, CEA Saclay, IRAMIS/UMR CEA CNRS 3299 NIMBE, 91191 Gif-sur-Yvette, France.

The large spread of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ properties reported in the literature suggests that there may be in fact several different kinds of this material. To distinguish between them, more information on the structure is needed, both at the long-range order (to understand how the ZnO host is affected by dopants) and at the short-range order (to learn about the local geometry around the doping ions), which can be probed by x-ray diffraction and x-ray absorption spectroscopy, respectively. The latter technique has an additional asset that it can also probe element-specific magnetic properties via x-ray magnetic circular dichroism (XMCD). This is especially attractive because then one can investigate the structure and magnetism simultaneously as a pair.

X-ray absorption spectra probe transitions of core electrons to unoccupied states. By a proper choice of the absorption edge, one can further specify that these transitions occur only to states with a particular symmetry with respect to atoms of given chemical type. The choice of the absorption edge depends, among others, on whether one is interested in studying the geometrical structure or the electronic structure. In particular, the *K* edge spectra of transition metals (TM's) involve delocalized *p* states which make them sensitive to the geometry around photoabsorbing atom. They cover a wide energy range, so one can measure the extended x-ray absorption fine structure (EXAFS), the analysis of which has become a powerful technique for structure determination. The $L_{2,3}$ edge spectra involve more localized *d* states and cover only a short energy range (for 3d TM's), so they are not very suitable for structural studies. On the other hand, the $L_{2,3}$ edge-XMCD has been conveniently used to study magnetism because the magnetization of TM atoms is carried mostly by the *d* electrons. Nevertheless, magnetism can be studied also via the *K*-edge XMCD because it is linked to a small but still detectable *p* component of the orbital magnetic moment [13]. So the *K*-edge x-ray absorption spectroscopy can be used as a tool for studying both the structure and magnetism simultaneously. Let us recall that the local view on magnetization via XMCD may indeed bring different information than global magnetization measurement based on superconducting quantum interference device (SQUID) magnetometry, as it was demonstrated for Co:ZnO as well as for Cu:ZnO [14,15].

Earlier studies of Cu:ZnO via the *K*-edge x-ray absorption near edge structure (XANES) or EXAFS focused on the structure, without carrying out XMCD measurements [16–18]. On the other hand, when local magnetic properties were studied via $L_{2,3}$ edge XMCD, it was not possible to do a full structural analysis simultaneously because the $L_{2,3}$ edge x-ray absorption spectra allow only limited structural analysis via “XANES fingerprinting” [15,19–21].

In a previous work, we have presented a combined study of local structure and local magnetism via the Cu *K*-edge XANES, EXAFS and XMCD spectroscopy for the Cu:ZnO pellets that were used as a target for the pulsed laser deposition (PLD) of the films investigated in the present paper [22]. Since the pellets were characterized as paramagnetic, it would be very interesting to perform such a study also for the ferromagnetic $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films, so that links between magnetization and structure can be drawn.

Therefore, we undertook a study of a series of ferromagnetic Cu:ZnO films with varying Cu concentrations, characterizing the magnetic properties via SQUID and the Cu *K*-edge XMCD, and the structural properties via x-ray diffraction and the Zn and Cu *K*-edge XANES, x-ray linear dichroism (XLD), and EXAFS. We will demonstrate in the following that most of the Cu atoms are not incorporated in the wurtzite ZnO lattice but rather reside in a CuO-like environment while the host ZnO lattice is left mostly unperturbed. Even though the samples exhibit RTFM with magnetization that increases with Cu concentration, no detectable Cu *K*-edge XMCD signal can be identified. This implies that the measured

ferromagnetism of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films is not directly associated with the magnetic properties of the doping atoms.

2. Methods

2.1. Sample preparation

Oriented Cu:ZnO films were prepared by employing the PLD technique to transfer the target material onto the substrate. First, powdered $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.02, 0.04, 0.07, 0.10$) was synthesized by mixing ZnO and CuO powders (purity 99.99%, Sigma Aldrich) in stoichiometric proportions and calcinating the mixture at 400 °C for 12 h. Polycrystalline pellets were then obtained by grinding, pelletizing and sintering the powders at 1000 °C for 12 h. The properties of these pellets were investigated in an earlier study [22]. We only recall here that these pellets are paramagnetic, and that there was a clear Cu *K*-edge XMCD signal proving that the Cu atoms are magnetic in the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ pellets.

By analyzing the XAS data, we found that at low Cu content most of the Cu atoms substitute for Zn inside the ZnO wurtzite lattice, while for higher Cu concentrations some unreacted CuO remains segregated from the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ solid solution.

To get oriented $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films, the above mentioned pellets were used as targets for PLD to deposit the material onto the *c*-plane of a sapphire substrate. Prior to deposition, the substrate was cleaned ultrasonically using trichloroethylene, acetone, methanol and distilled water. A pulsed KrF excimer laser with a wavelength of 248 nm was used for the PLD, with a repetition rate of 10 Hz. The laser beam had an energy density at the target of $\sim 2 \text{ J/cm}^2$. The deposition on substrates maintained at the temperature of $\sim 500 \text{ °C}$ for 30 min was done under oxygen partial pressure of 2 mTorr, with a nominal deposition rate of 10 nm/min ($\pm 10\%$). Similar preparation technique was used in earlier study [23].

2.2. Experimental procedures

The magnetization of cleaned substrate as well as films was measured using a SQUID magnetometer (Quantum Design) in the temperature range of 10–300 K. Figs. 1 and 2 contain only the signal from the films, after correction. In addition, it should be noted here that similar ZnO films doped with 2% Co or Ti were also prepared with the same experimental parameters, but they were found to be non-magnetic.

A high resolution x-ray diffraction (HR-XRD) characterization of the samples was performed at room temperature using a Bruker D8 advanced diffractometer, equipped with copper anode x-ray tube (Cu K_α radiation).

The x-ray absorption experiments were performed at the ESRF

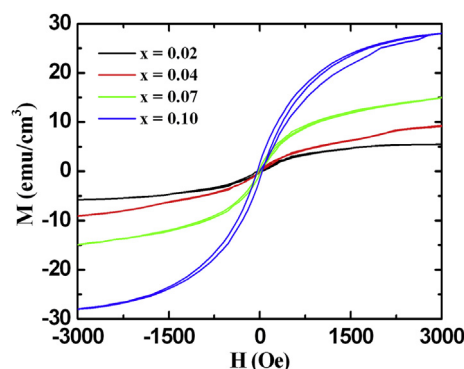


Fig. 1. Magnetization curves for the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ films measured at 300 K.

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