Cu doped ZnO pellets: study of structure and Cu specific magnetic properties

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2012 J. Phys.: Condens. Matter 24 506001
(http://iopscience.iop.org/0953-8984/24/50/506001)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 84.221.235.254
The article was downloaded on 24/11/2012 at 13:42

Please note that terms and conditions apply.
Cu doped ZnO pellets: study of structure and Cu specific magnetic properties

Prashant S Vachhani1,2, Giusepe Dalba1, Raj Kumar Ramamoorthy1,3, Francesco Rocca4, Ondrej Šipr5 and Anil K Bhatnagar2,3

1 Department of Physics, University of Trento, 38123 Povo (Trento), Italy
2 School of Physics, University of Hyderabad, Hyderabad-500 046, India
3 School of Engineering Sciences and Technology, University of Hyderabad, Hyderabad-500 046, India
4 IFN-CNR, Institute for Photonics and Nanotechnologies, Unit ‘FBK-Photonics’ of Trento, 38123 Povo (Trento), Italy
5 Institute of Physics ASCR, v. v. i., Cukrovarnicka 10, CZ-162 53 Prague, Czech Republic

E-mail: vachhani_prashant@rediffmail.com

Received 10 July 2012, in final form 9 October 2012
Published 23 November 2012
Online at stacks.iop.org/JPhysCM/24/506001

Abstract
Cu doped ZnO polycrystalline pellets were synthesized with Cu concentrations varying from 2 to 10 wt% by a solid state reaction route (mixing of ZnO and CuO powders). Global magnetization measurements showed that all the samples were paramagnetic. Fitting the temperature-dependence of the magnetization to the Curie–Weiss law revealed the presence of an antiferromagnetic interaction between magnetic moments. Structural characterizations were carried out by x-ray diffraction and x-ray absorption spectroscopy (XAS) at the Cu K-edge. 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 Zn1−xCuxO solid solution. Element-specific magnetic measurements were carried out by x-ray magnetic circular dichroism (XMCD) and compared to the results of ab initio calculations. The XMCD signal at the Cu K-edge originates from magnetic moments localized at Cu sites and, by monitoring the magnetic field dependence, we concur that these moments are associated with a paramagnetic state.

(Some figures may appear in colour only in the online journal)

1. Introduction

Over the past 10 years, diluted magnetic semiconductors have attracted much attention from scientists owing to their potential application in spintronic devices [1]. In particular, transition metal doped ZnO has been predicted to show ferromagnetic behavior with a Curie temperature $T_C$ above room temperature [2]. A large number of reports showing or not-showing ferromagnetism in transition metal doped ZnO films as well as bulk have been published.

The overall scenario about room temperature ferromagnetism (RTFM) in Cu doped ZnO still remains controversial, though in most of studies the observed RTFM is considered as an intrinsic property of a sample [3].

The first report showing a large x-ray magnetic circular dichroism (XMCD) in Cu doped ZnO samples was presented by Ando et al in 2001 [4]. RTFM was also reported in Cu doped ZnO bulk samples prepared using the sol–gel method by Lee et al [5]; they claimed that the solubility of Cu was less than 5% using x-ray diffraction (XRD) and optical absorption measurements and showed a bulk magnetic ordering by magnetic measurements, whose physical mechanism remained uncertain. After that report, many other papers on Cu doped ZnO films attributed RTFM to either defect induced or carrier mediated mechanisms [6–11]. In particular, Herng et al studied the effect of N2O annealing on Cu doped ZnO films and investigated the films by high resolution transmission electron microscopy (HR-TEM) and x-ray photoelectron spectroscopy (XPS) [8]. Magnetic measurements were also done to show bulk magnetic ordering [10]. These studies indicated the Zn interstitial (Zn_i) as the essential point defect for the enhancement
of FM (and for the substitution of nitrogen dopants). Recently, Xu et al [11] studied the annealing effect on Cu doped ZnO nanowires in a Zn and O₂ enriched environment [11]. By correlating photoluminescence (PL) and magnetic measurements, they provided experimental evidence for the intrinsic Zn₂-, mediated high temperature ferromagnetism. Only in one report it has been argued that ferromagnetism in Cu doped ZnO may originate from the formation of a planar CuO nanophase, excluding the intrinsic character [12]. Recently, a microscopic indirect double exchange model was proposed by Herrg et al [13] to explain the observed RTFM in Cu doped ZnO films on the basis of theoretical calculations and measurements of soft XMCD: ferromagnetism emerges as due to Cu impurities coupled with the oxygen vacancies. Very recently, the importance of vacancies has been experimentally supported using EXAFS and XANES analysis by two independent groups either in Cu and Co doped ZnO films [14, 15], but without use of XMCD.

To get a deeper insight into the diverse properties of Cu doped ZnO, it would be desirable to study its structure and magnetism simultaneously on the same footing. This could be achieved in the modern synchrotron radiation facilities at the beamline ID12 of ESRF (Grenoble, France). In this paper, we apply x-ray absorption spectroscopy to investigate the intrinsic magnetic nature of Cu doped ZnO bulk polycrystalline samples. These polycrystalline pellets were successfully used to produce ferromagnetic films by pulsed laser deposition. After presenting the magnetization properties of the pellets, we will show results obtained by local structural techniques such as x-ray absorption spectroscopy (EXAFS and XANES analysis) and x-ray magnetic circular dichroism (XMCD). This element specific approach is quite useful in testing the local origin of magnetism, in parallel with the usual bulk magnetic characterization.

In order to investigate the element specific magnetic properties of Cu doped ZnO pellets within the bulk (and not only at surface as is usual for soft x-ray measurements) we have carried out for the first time XMCD measurements using hard x-rays at the K-edge of Cu. We have found that at low Cu content the most of Cu atoms substitute for Zn inside the ZnO wurtzite lattice, while at the higher Cu concentrations some unreacted CuO remains segregated from the solid solution. In agreement with magnetic measurements, XMCD studies on Zn₀.₉₈Cu₀.₀₂O and Zn₀.₉₅Cu₀.₀₅O pellets show that the magnetic moments at Cu atoms are paramagnetic, with the intensity of the signal decreasing as Cu content increases.

2. Experimental details

Polycrystalline pellets of Zn₁₋ₓCuₓO (x = 0.02, 0.04, 0.07, 0.10) were synthesized by mixing ZnO and CuO powders (purity 99.99%; Sigma Aldrich, USA) in stoichiometric proportions and calcinating the mixture at 400 °C for 12 h. The powders were then ground, pelletized and sintered at 1000 °C for 12 h. Magnetic measurements were carried out using a superconducting quantum interference device (SQUID) in the temperature range from 5 to 350 K. As usual, two different magnetization curves were measured: zero field-cooled (ZFC) and field-cooled (FC) [16]. The structural properties were studied by x-ray diffraction (XRD) using Cu Kα radiation. EXAFS and XANES spectra were carried out at the European Synchrotron Radiation Facility (ESRF), BM08-GILDA beamline, at 77 K. The analysis of the EXAFS spectra was performed by the FEFF8.0 code [17]. The XMCD (i.e. the difference between right and left circular polarized XANES spectra measured under a 3 T magnetic field) was recorded at 7 K at ID12 of ESRF, with pellets surface tilted to 16° with respect to the orbital plane of the synchrotron. The XMCD spectra were taken in an external magnetic field of ±3 T in order to minimize artifacts.

3. Computational method

Electronic and magnetic structure of Cu doped ZnO was calculated within a fully relativistic Korringa–Kohn–Rostoker Green’s-function (KKR-GF) formalism, using the SPRKKR code [18]. We assumed that there is a single Cu impurity in the whole system, positioned either at the Zn-substitutional or at the interstitial site of the underlying wurtzite structure. Computationally these impurities were treated within the self-consistent embedded Green’s function technique, meaning that—unlike in the super-cell approach—there is no spurious interaction between the impurities. We imposed the atomic sphere approximation (ASA) to the potential, with additional empty spheres inserted at the interstitial sites. Structural relaxation was not attempted. X-ray absorption and XMCD spectra were calculated for the ground state potential, i.e. the core hole was neglected. It was found earlier that this affects the intensities of some peaks in x-ray absorption spectra of ZnO and CuO [19, 20] but does not create or suppress new features.

4. Results and discussion

4.1. Bulk magnetic properties

To explore the magnetic nature of Zn₁₋ₓCuₓO pellets, we have carried out global magnetic measurements using a SQUID magnetometer. Figure 1(a) shows FC magnetization curves of Zn₁₋ₓCuₓO pellets obtained by applying a magnetic field of 500 Oe at 300 K. For clarity, we display only the FC curves, because they are almost indistinguishable from ZFC in most cases. In figure 1(b), we also show the hysteresis M(H) curves for two available samples x = 0.07 and 0.1 measured at room temperature. It is clear from these measurements that all the pellets are paramagnetic. To better interpret the magnetization data, we have fitted our results assuming two different sets of local magnetic moments (purportedly associated with Cu atoms): the first set includes independent moments with no interaction between them and the second set comprises interacting moments. In the first case the susceptibility should follow a simple Curie law \( \chi = C/T \). The second case would correspond to a system with ferromagnetic or antiferromagnetic interactions in a paramagnetic state and
the susceptibility can be expressed using the Curie–Weiss law \( \chi = C/(T - \Theta) \). So, we used an ansatz

\[
\chi = C_1/T + C_2/(T - \Theta)
\]

to fit our experimental curves. A good match with experimental data is obtained as can be seen in figure 1(a). Numerical results are presented in table 1.

The negative values obtained for \( \Theta \) indicate the presence of an antiferromagnetic (AFM) interaction between Cu atoms. This recalls the case of Co doped ZnO where the presence of an antiferromagnetic interaction between some Co impurities has been suggested [21–23]. For the 10% Cu sample, all the parameters shown in table 1 deviate from the monotonic trend and it is shown later that this can be correlated to the different local structure around Cu atoms in this compound.

The fact that the \( M(T) \) dependence cannot be fitted by a simple Curie or Curie–Weiss law, but rather by a two-term form as in equation (1), indicates that ZnO magnetization is of a more complicated nature. The obtained value of \( C_2 \) is about 10 times larger than that of \( C_1 \) (see table 1), meaning that the antiferromagnetically interacting local moments dominate over the paramagnetically interacting moments. The ratio \( C_1/C_2 \) is maximum for the 2% Cu doped sample; this may be connected with the fact that at higher doping the probability of having two Cu atoms nearby is higher and the interaction between their moments is enhanced, thus increasing the contribution from \( C_2 \). If we restrict ourselves to analyzing the antiferromagnetic moments, using a simple model of identical moments with antiferromagnetic interaction between the nearest neighbors only, and assuming that there is a localized magnetic moment associated with every Cu atom, the magnitude of such effective magnetic moments can be estimated from the \( C_2 \) constant (see, for example, equations (11.22) and (12.39) of [24]). In this way we get \( \mu_{\text{eff}} = 1.19 \mu_B, 1.54 \mu_B, 1.20 \mu_B \) and 0.82 \( \mu_B \) for Cu concentrations of 2, 4, 7 and 10%, respectively. One should, however, be cautious in interpreting these values because they were obtained by relying on a very simple model. For example, different kinds of Cu sites may be present, having their own magnetic interactions and with unknown relative content.

### 4.2. Structural properties

In the XRD measurements on \( \text{Zn}_{1-x}\text{Cu}_x\text{O} \) samples, only the peaks related to the wurtzite ZnO structure were observed up to 4% Cu concentration. When Cu content is more than 4%, some diffraction peaks attributed to CuO appear, as shown in figure 2. We will comment later on this evidence.

Figure 2 demonstrates the high crystallinity of all the pellets, independently of the Cu content. Using the Debye–Schererr formula, the particle size has been evaluated for all the samples: the obtained values are almost equal, giving an average size of 108 ± 5 nm.

The Zn K-edge XANES spectra taken at 300 K for all the pellets are almost identical for all the Cu concentrations and very similar to bulk ZnO, suggesting that the Zn environment changes only a little with Cu doping up to 10%. Figure 3 shows the normalized Cu K-edge XANES spectra along with its first derivative. All the spectra exhibit a pre-edge feature at \( 8977 \text{ eV} \) denoted by ‘a’, better seen from the inset of figure 3. For transition metal atoms in tetrahedral coordination, this pre-peak is mostly not due to the direct 1s \( \rightarrow 3d \) transition but to a dipole-allowed transition to the p component of the p–d hybridized orbital [25]. The intensity of the pre-edge peak for transition metal dopants in ZnO can thus be considered as direct evidence of substitutional incorporation of the transition

---

**Table 1.** Results of parameters obtained by best fitting equation (1) to the experimental \( M–T \) curves presented in figure 1(a).

<table>
<thead>
<tr>
<th>Samples</th>
<th>( C_1 ) ( (\text{K emu} \text{g}^{-1} \text{Oe}^{-1}) \times 10^{-4} )</th>
<th>( C_2 ) ( (\text{K emu} \text{g}^{-1} \text{Oe}^{-1}) \times 10^{-4} )</th>
<th>( \Theta ) ( (\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ZnO} )</td>
<td>0.18 ± 0.01</td>
<td>1.13 ± 0.01</td>
<td>−99 ± 5</td>
</tr>
<tr>
<td>( \text{ZnO-Cu}_{0.02} )</td>
<td>0.35 ± 0.01</td>
<td>3.73 ± 0.01</td>
<td>−219 ± 5</td>
</tr>
<tr>
<td>( \text{ZnO-Cu}_{0.04} )</td>
<td>0.35 ± 0.01</td>
<td>3.98 ± 0.01</td>
<td>−241 ± 5</td>
</tr>
<tr>
<td>( \text{ZnO-Cu}_{0.07} )</td>
<td>0.29 ± 0.01</td>
<td>2.67 ± 0.01</td>
<td>−182 ± 5</td>
</tr>
</tbody>
</table>

---

**Figure 1.** (a) FC magnetization curves of \( \text{Zn}_{1-x}\text{Cu}_x\text{O} \) pellets under an applied magnetic field of 500 Oe. Open circles show results of best fits with equation (1). (b) Enlarged region of the hysteresis \( M(H) \) curves for samples \( x = 0.07 \) and \( x = 0.1 \) measured at room temperature (the inset shows the whole measured range).
metals in Zn sites because, in that case, Cu is in tetrahedral coordination, meaning that the corresponding transition is dipole-allowed [26, 27]. In CuO, this pre-peak is due to quadrupole-allowed transitions and arises at a slightly higher energy [20]. In our case, the relative area of this pre-edge peak remains almost identical (0.076 ± 0.005 au) within the experimental error for 2% and 4% Cu doping, then decreases a lot (0.048 ± 0.005 au) for higher doping. The existence of a pre-edge peak confirms the substitution of Cu at the Zn site but its decrease with increasing $x$ suggests the presence of some Cu atoms in other than substitutional sites. The hump at 8985 eV (denoted by ‘b’) on the XANES spectra is much more noticeable for higher concentrations of Cu: it is typical of CuO, as can be seen from XANES and from the first derivative spectra presented in figure 3. This means that for Zn$_{0.93}$Cu$_{0.07}$O and Zn$_{0.90}$Cu$_{0.10}$O samples some part of the original CuO remains unreacted within the solid solution, in agreement with XRD results.

In figure 4, we report the EXAFS signals $k^2 \chi (k)$ at the Cu K-edge for the Zn$_{1-x}$Cu$_x$O pellets and for the reference CuO sample, together with that of ZnO (at the Zn K-edge). EXAFS oscillations for the Zn$_{1-x}$Cu$_x$O pellets are quite different from those for CuO, being very similar to oscillations observed for ZnO, particularly at low Cu content. The similarity of the EXAFS signal for the pellets and for pure ZnO is quite strong evidence in support of the presence of Cu in the substitutional Zn site.

The Fourier transforms (FT) of the EXAFS $k^2 \chi (k)$ signals are shown in figure 5 for Zn$_{1-x}$Cu$_x$O pellets along with the reference compounds ZnO and CuO. In ZnO, Zn is coordinated with four oxygen atoms at almost equal distances $R_{Zn-O}$ of 1.95 and 1.98 Å. This is very similar to nearest-neighbor distances around Cu in CuO, where Cu is coordinated with four oxygen atoms at $R_{Cu-O}$ of 1.95 and 1.96 Å. Therefore, it is clear why both ZnO and CuO show a similar first shell peak in the FT. The next nearest shells of Zn in ZnO are formed by 12 Zn atoms (six at 3.21 Å and six at 3.25 Å) corresponding to the peak with the maximum at
around 2.9 Å in figure 5. The second nearest neighborhood of Cu in CuO (corresponding to the broad three-hump structure which extends from 2.1 to 3.8 Å in figure 5) is more complex, being formed by two oxygens (2.78 Å) and by a series of copper shells: four atoms at 2.90 Å, four atoms at 3.08 Å and two atoms at 3.17 Å.

The qualitative analysis of FT for Zn$_{1-x}$Cu$_x$O pellets at increasing Cu concentration suggests a modification of the Cu environment from the one of Zn sites in ZnO to that of Cu in CuO. We note, however, that the peak at about 5.3 Å is present for all the Cu doped samples and is similar to that in ZnO. This provides further evidence that even in the 10% Cu doped pellet the long range crystalline structure around Cu dopants is that of ZnO, with a strong modification only for distances shorter than 6 Å.

To obtain quantitative structural information, EXAFS theoretical phase shifts and back scattering amplitudes were calculated by putting Cu as the photoabsorbing atom in a ZnO crystal, using the FEFF8.0 code. Since Cu and Zn atoms are close in the periodic table, Cu–Zn and Cu–Cu pairs are practically indistinguishable and can be simulated using Cu–Zn signals. The back Fourier transform was done in the range 0.7–3.5 Å. Three single-scattering paths were used for the fits, representing the nearest-neighbor Cu–O, the second-nearest-neighbor Cu–Zn and the third-nearest-neighbor Cu–O shells. Best fitting was done using EDAFIT software [28]: the results are presented in figure 6. EXAFS oscillations of Zn$_{0.98}$Cu$_{0.02}$O, Zn$_{0.96}$Cu$_{0.04}$O and Zn$_{0.91}$Cu$_{0.07}$O pellets are well reproduced. For the Zn$_{0.90}$Cu$_{0.10}$O sample, the fitting is not really satisfactory; we tried to best fit that signal also using the CuO geometry and the derived theoretical signals but the fit was not significantly improved, indicating a much more complex situation, difficult to model with only three shells. The main quantitative results obtained using nearest and next nearest neighbors are summarized in table 2. The first shell distance changes very little with Cu concentration, while the coordination number is around 4 for the pellet with 2% Cu, then decreases and reaches a value of 2.7 for 10% Cu doped sample. The analysis of the second shell shows an average distance as in ZnO, but a sharp decrease of coordination number starting at 7% Cu: this again indicates the presence of high static disorder, probably related to the remaining quantity of unreacted CuO segregated in nanoclusters within the solid solution.

![Figure 6](image_url)

**Figure 6.** Cu K-edge EXAFS $k^2\chi(k)$ functions of Zn$_{1-x}$Cu$_x$O pellets (lines) and simulations (dots), based on Cu central absorbing atom substitution of Zn in ZnO. The best fit range is 3–9 Å$^{-1}$.

### 4.3. XMCD: experiments and theory

Figure 7(a) shows the normalized XANES spectra and XMCD signals taken at Cu K edge at 7 K in an external magnetic field of 3 T. A clear dichroic signal is observed at the pre-edge feature of Cu. This signal is of the order of 0.3% with respect to the edge jump for the Zn$_{0.98}$Cu$_{0.02}$O sample and around 0.1% for the Zn$_{0.90}$Cu$_{0.10}$O sample. The decrease of the XMCD peak intensity with increasing Cu content $x$ can be plausibly associated with the formation of a CuO-like environment that takes place at Cu content higher than 4%. Namely, if the dichroic signal originates only from those Cu atoms that are substitutional on Zn sites, its intensity (calculated after edge jump normalization of the original spectra) should decrease.

This assignment is supported by results of *ab initio* calculations presented in figure 8. Here we show the XMCD Cu K-edge signal calculated for an isolated Cu impurity in a Zn-substitutional site. The theory predicts an XMCD peak at the same position and of the same shape as we have measured it. Note that the experiment was performed for non-oriented pellets while the calculated XMCD spectrum shown here assumes an oriented system; the XMCD signal

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bond type</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\beta$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.98}$Cu$</em>{0.02}$O</td>
<td>Cu–O</td>
<td>4.1 (±0.2)</td>
<td>1.948 (±0.001)</td>
<td>0.0031</td>
<td></td>
</tr>
<tr>
<td>Zn$<em>{0.96}$Cu$</em>{0.04}$O</td>
<td>Cu–O</td>
<td>3.7 (±0.2)</td>
<td>1.946 (±0.001)</td>
<td>0.0028</td>
<td></td>
</tr>
<tr>
<td>Zn$<em>{0.91}$Cu$</em>{0.07}$O</td>
<td>Cu–O</td>
<td>3.1 (±0.2)</td>
<td>1.945 (±0.001)</td>
<td>0.0036</td>
<td></td>
</tr>
<tr>
<td>Zn$<em>{0.90}$Cu$</em>{0.10}$O</td>
<td>Cu–O</td>
<td>2.7 (±1)</td>
<td>1.942 (±0.001)</td>
<td>0.0004</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Best fitting results of Zn$_{1-x}$Cu$_x$O ($x = 0.02, 0.04, 0.07$ and $0.10$). The errors on $N$ are estimated taking into account correlations with Debye–Waller factors.
Indeed, our calculations show that this p component is the orbital magnetic moment for the photoabsorbing site [29].

For a non-oriented system would correspond to the average of the oriented spectra, with the spectrum for the magnetization $M$ in the $ab$ plane being counted twice. We also performed calculations for Cu in an interstitial site—in that case, no magnetic moment forms. So putting all the pieces together, we have solid evidence that the observed XMCD signal truly arises from substitutional Cu.

Our calculations indicate a strong dependence of the calculated XMCD signal on the orientation of the magnetization with respect to the underlying crystal lattice. To understand this better, let us recall that the XMCD sum rules link the K-edge XMCD signal to the $p$ component of the orbital magnetic moment for the photoabsorbing site [29]. Indeed, our calculations show that this $p$ component is $-0.002 \, \mu_B$ if $M$ is parallel to the $c$-axis and $-0.005 \, \mu_B$ if $M$ is perpendicular to the $c$-axis, indicating more than 100% anisotropy. At the same time, these values are quite small in absolute terms indicating quite a low intensity of the XMCD signal. Interestingly, the total orbital magnetic moment (having its largest contribution from the $d$ electrons, which are not directly probed by the K-edge absorption spectra) does not display a large anisotropy: it is $\mu_{orb} = 0.14 \, \mu_B$ if $M$ is parallel to the $c$-axis and $0.15 \, \mu_B$ for the perpendicular orientation of $M$. The spin magnetic moment for substitutional Cu is calculated as 0.59 $\mu_B$. This means that the ratio of the orbital magnetic moment to the spin magnetic moment is 0.25, i.e., several times more than for bulk magnetic transition metals Fe, Co and Ni (where it is 0.044, 0.097 and 0.099, respectively [30]). This is probably because the electron states of the Cu impurity are quite localized; similar enhancement of $\mu_{orb}$ with respect to $\mu_{spin}$ is often observed for impurities or ad-atoms (cf [31] and references therein).

It should be stressed that the electronic structure calculations were performed for an isolated Cu impurity, so they cannot predict magnetic order. The calculated XMCD signal corresponds to a presupposed parallel alignment of the magnetic moments (e.g. forced by an external magnetic field). In reality, the ordering can be varied, depending on the nature of the exchange interaction between the moments. It is thus possible that—apart from formation of a ‘magnetically dead’ CuO-like environment—there is yet another cause for the experimentally observed decrease of the XMCD signal with increasing Cu content: namely, larger Cu concentration $x$ means a higher probability of having Cu–O–Cu quasilinear configurations, where Cu atoms may couple antiferromagnetically (analogously to Co impurities [21, 22]), thus not contributing to the XMCD signal. This is also in agreement with our previous discussion on the quantitative analysis of magnetization data in table 1.

To further clarify the type of magnetic contribution due to Cu in our samples, we examined the ‘hysteresis curves’ obtained by plotting the intensity of the XMCD signal measured at the energy of the pre-edge against the strength of the applied external magnetic field. The temperature was 7 K and the magnetic field was varied from $-6$ to $+6$ T and back. The curves are shown in figure 7(b). Neglecting the little modulations, attributed to reproducible non-linearity of magnetic field increase in the sample, only a linear trend can be recognized, without any measurable hysteresis or saturation. This indicates that the magnetic contribution which gives rise to Cu K-edge XMCD is only paramagnetic, both for the 2% and for the 10% Cu doped ZnO pellets.

This finding of ours can help in understanding the mechanism behind the exchange interaction in doped ZnO. In particular, as we have already pointed out, the dichroic signal is maximum at low doping. In that case, the Cu atoms are...
in Zn-substitutional positions (as follows from our XRD and EXAFS analysis), and consequently the host ZnO wurtzite lattice is not very distorted. There, we do not expect to have a large number of point defects or carriers. Thus, in agreement with some recent works that discussed the origin of ferromagnetism in Co doped ZnO bulk and films [15, 27, 32] as related to the presence of defects, the sample should exhibit only paramagnetism, as we have clearly measured.

5. Conclusions

In summary, we have synthesized Zn$_{1-x}$Cu$_x$O bulk samples with varying Cu concentration from $x = 0.02$ to 0.1. The XAFS analysis reveals that for a Cu concentration of 4% or less, most of the Cu atoms substitute Zn in the wurtzite lattice, while for higher Cu concentration, some of the Cu atoms remain segregated in unreacted CuO nanoclusters. Global magnetic measurements carried out on pellets show paramagnetic behavior for all the samples, with antiferromagnetic interaction between some magnetic moments. Local element-specific measurements based on the Cu K-edge XMCMD show that there are magnetic moments associated with Cu impurities and that these moments display paramagnetic behavior when the external magnetic field is varied.

Acknowledgments

This work has been carried out under the India-Trento program for advanced research (ITPAR) funded by the DST, New Delhi, India and the University of Trento, Italy. It was also supported by the common research project of AS CR and CNR ‘Interplay between structural and electronic properties of nanostructures’ and by project 108/11/0853 of the Grant Agency of the Czech Republic. The authors acknowledge the support of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) for the Proposals HE-3444 and 08-01-893. P S Vachhani is grateful to the University Grant Commission (UGC) for a Dr D S Kothari postdoctoral fellowship. One of the authors (AKB) also acknowledges support from the Indian National Science Academy (New Delhi, India). We would also like to thank A Rogalev and F Wilhelm for their fruitful discussions as well as for help in carrying out XANES and XMCD measurements at ID12 of ESRF. The authors are grateful to A Kuzmin for his cooperation in this Research Project.

References