Local structure and magnetism of Cu-doped ZnO via Cu K-edge XAS and XMCD: theory and experiment

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Abstract. We investigate theoretically the sensitivity of Cu K-edge XANES and XMCD of Cu-doped ZnO (Cu:ZnO) to the local structure. We find that the sensitivity is high enough to enable to distinguish between geometries conceivable for Cu:ZnO. However, one cannot distinguish between Cu and Zn in further coordination shells. Likewise, presence of oxygen vacancies in the ab plane does not alter XANES or x-ray linear dichroism (XLD). By analysing experimental XANES and EXAFS signals of Cu:ZnO pellets (which are paramagnetic) and Cu:ZnO films (which are ferromagnetic) we find that for the pellets, Cu is in Zn-substitutional sites while for the films, the coordination of Cu is as in CuO. Cu K-edge XMCD measurements were performed for both types of samples but detectable signal was obtained only for the pellets. The theory confirms that this XMCD signal originates from magnetic moments localised at Cu atoms located in Zn-substitutional sites.

1. Introduction

Magnetism of wurtzite ZnO doped by transition metal atoms still evades a consistent explanation [1]. Numerous results on structure and magnetism of pure and doped ZnO were obtained but a coherent picture is difficult to obtain. One of the problems is that it is hard to study magnetism and structure simultaneously “on the same footing”. X-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) spectroscopy is a very useful tool in this respect.

In this paper we investigate the potential of XAS and XMCD to investigate Cu-doped ZnO (Cu:ZnO). Our main focus is on theory but to put this work in context, we also present some new experimental data which will be analysed in a greater detail elsewhere.

2. Computational framework

Electronic structure was calculated within a fully relativistic KKR Green’s-function formalism, using the sprKKR code [2]. The Cu impurities were treated within the embedded Green’s function technique, meaning that — unlike in the super-cell approach — there is no interaction between the impurities. The Cu impurity is located either at the Zn-substitutional (Cu_{Zn}) or
at the interstitial site (Cu\textsubscript{i}) of the underlying wurtzite structure. To simulate vacancies, which have attracted a lot of attention lately [3], we substituted O atoms by empty sites (V\textsubscript{O}) in some cases. Structural relaxation was not attempted (substituting Cu\textsubscript{Zn} for Zn changes the distances by less than 0.01 Å [4]).

We imposed the atomic sphere approximation (ASA) to the potential, with additional empty spheres inserted at the interstitial sites. Most of the spectra were calculated for the ground state potential. Namely, simple ways of incorporating the core hole used in XAS such as the final state approximation or the transition state approximation seem to be unsuitable for XMCD [5, 6]. However, to assess the core hole effect at least approximatively, we did some calculations also using the transition state potential.

3. Experiment

We investigated spectra of Cu:ZnO pellets and of oriented Cu:ZnO thin films. Polycrystalline targets of Zn\textsubscript{1-x}Cu\textsubscript{x}O were synthesized by mixing ZnO and CuO powders and calcinating the mixture at 400°C. To get polycrystalline pellets, the powders were ground, pelletized and sintered at 1000°C. To get oriented Zn\textsubscript{1-x}Cu\textsubscript{x}O thin films of thickness of about 300 nm, we used pulsed laser deposition (PLD) to deposit the targets material onto c-cut sapphire substrate. The Cu concentration \(x\) was 2\%, 4\%, 7\% or 10\%.

XAS was measured at the ESRF at the BM08-Gilda beamline. The x-ray linear dichroic (XLD) spectra were recorded as a difference between XAS for two perpendicular linear polarisations at the ID12 beamline. The XMCD spectra were recorded at 7 K at the ID12 beamline, in an external magnetic field of ±3 T.

More detailed description of the sample preparation and a thorough analysis of our measurements will be published elsewhere.

4. Results and discussion

4.1. Magnetic properties

Magnetic measurements were carried out using SQUID in the temperature range from 5 to 350 K. The polycrystalline pellets samples were paramagnetic, with signatures of antiferromagnetic interaction between local moments (obtained by fit to the Curie-Weiss law). The oriented thin films were all ferromagnetic at room temperature [7, 8].

4.2. Sensitivity of XANES to structure type

To be able to analyse XAS properly, it is desirable to know the structural sensitivity of the spectra for our specific situation. Therefore, we calculated Cu K-edge x-ray absorption near-edge structure (XANES) for Cu in a number of structures: Cu\textsubscript{Zn} and Cu\textsubscript{i} in ZnO, CuO, and also hypothetic Cu metal with structure of ZnO. Apart from orientationally-averaged XANES for polycrystals, we calculated also the XLD as the difference between the spectra of monocrystals for two perpendicular orientations of the x-rays polarisation vector. The results are shown in figure 1. There are clear differences between XAS and especially XLD for Cu in different environments, one can thus distinguish between Cu\textsubscript{Zn} and Cu\textsubscript{i} and also between CuO or Cu clustering. It does not matter in this respect whether the core hole is included in the calculations or not.

Our calculations further show that Cu and Zn are practically interchangeable as concerns their photoelectron scattering properties. That means that one cannot distinguish by XAS whether Cu is surrounded by Zn or Cu in more distant shells. We calculated also Zn K-edge XAS and XLD and found that there is practically no difference whether Zn is in pure ZnO or whether it is close to a Cu impurity. And finally we found that if there is V\textsubscript{O} in the \(ab\) plane next to the Cu impurity, both XAS and XLD look very similar to spectra without vacancies.
Figure 1. Cu $K$-edge XAS (left) and XLD (right) for Cu$_{Zn}$ in ZnO, CuO, hypothetic Cu with structure of ZnO and for Cu$_i$ in ZnO. Full grey lines correspond to calculations for ground state potential, dash-dotted lines lines to transition state potential.

(similar conclusions were reached by Ciatto et al. [3]). We do not show the spectra here for brevity.

4.3. Structure of Cu:ZnO pellets and films
Experimental Cu $K$-edge XANES of Cu:ZnO pellets and films differ quite a lot (figure 2 left): spectrum of the pellets generally resembles spectrum of ZnO while spectrum of the films resembles spectrum of CuO. Moreover, a pronounced pre-peak for the pellets looks like a signature of Cu in a tetrahedral environment [9] while a faint pre-peak at a bit higher energy for the films reminds the quadrupolar pre-peak observed in CuO [10]. This suggests that Cu is incorporated as Cu$_{Zn}$ in the wurtzite lattice in the pellets while it segregates as CuO in the films.

We measured also the Cu $K$-edge EXAFS, in order to have a more accurate and reliable information about the structure. The Fourier-transforms of $k^2$-weighted EXAFS signals $k^2 \chi(k)$ for the $x=7\%$ samples are shown in the right panel of figure 2. For other concentrations, the situation is similar. Together with a quantitative analysis that will be published elsewhere, this confirms that Cu occupies the Zn-substitutional site in Cu:ZnO pellets while it is in a CuO-like environment in Cu:ZnO films.

4.4. Cu $K$-edge XMCD spectra
By calculating electronic structure of Cu impurities in ZnO, we found that Cu$_i$ is nonmagnetic, while Cu$_{Zn}$ is magnetic. We calculated also the magnetic structure for Cu$_{Zn}$ with vacancies, with V$_O$ either in the first or in the second shell of O atoms in the $ab$ plane of the wurtzite structure (the Cu–V$_O$ distance is 1.98 Å and 3.80 Å, respectively). Table 1 summarises the results for spin magnetic moments $\mu_{\text{spin}}$ and orbital magnetic moments $\mu_{\text{orb}}$ evaluated within the atomic
Figure 2. Experimental Cu K-edge XANES (left) and Fourier-transformed EXAFS (right) of Zn_{0.93}Cu_{0.07}O films and pellets (solid grey lines) compared to experimental data for Cu K-edge of CuO and to Zn K-edge of ZnO, respectively (dashed blue lines). The Zn K-edge XANES of ZnO was shifted in energy to be aligned with the Cu K-edge spectra. Vertical shift was added between XANES of Cu:ZnO and reference materials for clarity.

Table 1. Magnetic moments and numbers of holes for Cu\textsubscript{Zn} in ZnO with no vacancies and with V\textsubscript{O} in the ab plane, either in the 1\textsuperscript{st} or in the 2\textsuperscript{nd} shell of O atoms. The unit is $\mu_B$.

|                  | $\mu_{\text{spin (tot)}}$ | $\mu_{\text{spin (Cu)}}$ | $\mu_{\text{orb (Cu)}}$ | $\mu_{\text{orb (Cu)}}^{(p)}$ | $n_h^{(p)}$ (Cu) | $n_h^{(d)}$ (Cu) |
|------------------|--------------------------|---------------------------|--------------------------|-------------------------------|------------------|------------------|
| no vacancy       | 1.70                     | 0.59                      | 0.14                     | −0.0016                       | 5.52             | 0.98             |
| vacancy in 1\textsuperscript{st} shell | 0.54                     | 0.18                      | 0.06                     | −0.0005                       | 5.60             | 0.88             |
| vacancy in 2\textsuperscript{nd} shell | 1.18                     | 0.52                      | 0.30                     | −0.0096                       | 5.52             | 0.95             |

sphere around Cu (its radius is 1.30 Å). We show also the total spin magnetic moment in the whole system, which demonstrates that the polarisation cloud extends quite far away from the Cu atom. Magnetic moments for the nearest neighbours of Cu\textsubscript{Zn} are 0.19 $\mu_B$ for the three O atoms in the ab plane and 0.09 $\mu_B$ for the apical O atom. The Cu K-edge XMCD probes the \( p \) component of $\mu_{\text{orb}}$, therefore we show it in table 1 as well. Finally, we present also the numbers of holes in the \( p \) and \( d \) band of Cu\textsubscript{Zn} as these quantities are of interest when utilising the XMCD sum rules [11].

Theoretical Cu K-edge XMCD of Cu\textsubscript{Zn} evaluated either for the ground state or for the transition state potential is shown in the left panel of figure 3. XANES is shown as well so that peak positions in XAS and in XMCD can be compared (note that the XMCD signal was multiplied by 100). A prominent XMCD peak appears at the pre-edge. Its intensity strongly depends on the orientation of the magnetic field \( \mathbf{M} \) with respect to the wurtzite lattice. This anisotropy as well as the average XMCD peak intensity depends on how the core hole is treated.

To investigate the effect of vacancies, we calculated XMCD also for Cu\textsubscript{Zn} with V\textsubscript{O} in the first
Figure 3. Left: Calculated Cu K-edge XMCD for Cu$_{Zn}$ in single-crystal ZnO, with $\mathbf{M}$ parallel or perpendicular to the $c$ axis, for the ground state and the transition state potential. XANES for Cu$_{Zn}$ in polycrystalline ZnO for the ground state potential is also shown. Right: Calculated Cu K-edge XMCD for Cu$_{Zn}$ in ZnO without or with O vacancies in the $ab$ plane, for ground state potential, with $\mathbf{M} \parallel c$ (three lower curves) together with experimental Cu K-edge XMCD for Zn$_{0.98}$Cu$_{0.02}$O and Zn$_{0.90}$Cu$_{0.10}$O pellets.

or in the second shell of oxygens in the $ab$ plane. The results are shown in the right panel of figure 3 ($\mathbf{M} \parallel c$, ground state potential). Presence of a vacancy next to Cu$_{Zn}$ nearly suppresses the sharp XMCD pre-edge feature while a more distant vacancy affects the “fine XMCD structure” in the energy region corresponding the the main XANES peak.

Experimental Cu K-edge XMCD was measured both for paramagnetic Cu:ZnO pellets and ferromagnetic Cu:ZnO films. Detectable signal was found only for the pellets and it is shown in the top of the right panel of figure 3 (scaled so that experimental and theoretical XANES intensities match). We investigated also the magnetic-field-strength dependence of the XMCD intensity and found that it exhibits a paramagnetic pattern. For the Cu:ZnO films, the Cu K-edge XMCD is zero (within the limit of the noise).

5. Discussion

By measuring XAS and XMCD at the same edge we can unambiguously connect local geometric and magnetic structure. Use of the $K$ edge makes it possible to exploit the EXAFS data to find that Cu:ZnO materials can indeed have quite different local structures; this may be the reason why divergent results on properties of Cu:ZnO were obtained in the past [12, 13, 14, 15].

Our XMCD measurements show that, surprisingly, Cu atoms are not magnetic in ferromagnetic Cu:ZnO films. This is consistent with the emerging picture that ferromagnetism of doped ZnO is not directly connected to the magnetism of dopant atoms [16]. Paramagnetic character of Cu atoms in Cu:ZnO pellets, where Cu is substitutional, reminds similar situation found earlier for Co-doped ZnO [17]. Another point to mention is that our calculations show that oxygen vacancies do not suppress magnetism of substitutional Cu, even though they affect it significantly.

Our embedded impurity calculations give larger total magnetic moments around Cu$_{Zn}$ than supercell calculations [4, 18, 19] — this indicates that in supercell calculations the impurities
still interact. Relatively large theoretical $\mu_{orb}/\mu_{spin}$ ratio obtained for CuZn is consistent with analogous situations for ad-atoms and impurities [20]. Finally, our calculations suggest that the core hole may affect the XMCD spectra significantly, stressing the need to have a practically manageable formalism for including the core hole also in XMCD calculations, where the final state or transition state approximations are inappropriate [5, 6].

6. Conclusions
Cu K-edge XANES and XLD of Cu in different environments is sufficiently different to distinguish between geometries conceivable for Cu:ZnO. However, because of similar scattering properties of Cu and Zn, XAS is not able to tell these two atoms one from another if the structure is otherwise the same.

Local environments of Cu atoms in paramagnetic Cu:ZnO pellets and in ferromagnetic Cu:ZnO films are quite different: for the pellets, Cu is in Zn-substitutional sites while for the films, the coordination of Cu is as in CuO. Copper atoms in paramagnetic pellets are magnetic. For ferromagnetic films, copper atoms are non-magnetic. This suggests that ferromagnetism of transition metal doped ZnO is not directly linked to magnetism of the dopant but rather is connected with structural changes induced by these dopants.

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