High Pressure X-Ray Absorption Spectroscopy on Zn$_{1-x}$Mn$_x$O (x=0.25 and x=0.05) at the Mn K Edge

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Abstract. X-ray absorption measurements have been performed on Zn$_{1-x}$Mn$_x$O (x=0.25 and x=0.05) at the Mn K edge under pressure. Mn is in substitution of Zn whatever the composition or the structure. A phase transformation from wurtzite to rocksalt is observed close to 8 GPa for both compositions. The local compressibility around the Mn atom is similar to the bulk one, in the wurtzite and in the rocksalt phases. The transition is reversible for x=0.05 but irreversible for x=0.25.

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INTRODUCTION

The diluted magnetic semiconductor Zn$_{1-x}$Mn$_x$O is the subject of increasing interest since ferromagnetic behavior was predicted [1] in such material. Thin films of this material, deposited on sapphire have been reported to keep the wurtzite structure for Mn atomic proportions up to 30%[2] or 35%[3] There have been a few reports on ferromagnetic behavior at low temperature (45 K) [4] and at room temperature[5,6] but the subject remains controversial as some authors report spin-glass[7] or paramagnetic behavior[3]; Some authors attribute the ferromagnetic behavior to the presence of Mn nanoclusters, while EXAFS measurements indicate that Mn atoms are in substitution of Zn atoms[4,8].

In this context, EXAFS and XANES experiments under pressure are relevant as they would give very valuable information about the site configuration of Mn atoms at different pressures and in different crystalline phases (wurtzite and rock-salt).

EXPERIMENTAL

High pressure X-ray absorption has been performed on the LUCIA beamline[9] of SLS (PSI, Villigen, Switzerland) at the Mn K edge on Zn$_{1-x}$Mn$_x$O in transmission (x=0.25) or in fluorescence mode (x=0.05). Details on the sample preparation are given elsewhere[10]. The absorption of the diamonds has been reduced using fully or partially hollowed diamonds[11,12] (Figure 1). For the experiments in transmission, the total thickness of the diamonds is 1mm while in the fluorescence mode, the x-ray beam has to go through 0.2 mm of diamond and the fluorescence beam through 1.2 mm of Be.

FIGURE 1. (Left) fully hollowed diamonds with small (0.5mm thick) anvils. In this case the x-ray beam goes through the diamonds. (Right) partially hollowed diamonds (remaining wall 0.2 mm). In this geometry the incoming beam goes through one diamond while the fluorescence beam goes through the Be gasket.

In order to minimize the force on the table of the thin diamonds, small culets (200 μm) have been used in order to obtain pressure above 10 GPa. An 80 μm hole has been drilled in the center of the inconel or Be gasket and the sample has been loaded in this hole with silicon oil as pressure transmitting medium. The pressure has been calibrated inside the experimental chamber using the ruby optical fluorescence technique.

Because of the small size of the sample, it is necessary to use a well focused beam as is the case on the LUCIA beamline (the beam spot was smaller than 10 x 20 μm², full print).
RESULTS AND DISCUSSION

Figure 2 shows the evolution with pressure of the X-ray absorption spectra of \( \text{Zn}_{0.95}\text{Mn}_{0.05}\text{O} \) at the Mn K edge. The spectrum at room pressure shows clearly that Mn is in substitution of Zn and that no evidence of Mn clusters is observed. Above 7.3 GPa a strong modification of the spectra occurs. Both pre-edge part and XANES become different. The intensity of the pre-edge decreases strongly as shown in Figure 3.

The XANES features change and are in good agreement with the spectra simulated in the rocksalt structure using the ab initio full multiple scattering FEFF8\[12\] code (Figure 4), showing that Mn is still in substitution to Zn in the high pressure phase. Similar results are obtained for \( \text{Zn}_{0.75}\text{Mn}_{0.25}\text{O} \) at increasing pressure.

The first neighbor distances, Mn-O, have been obtained for both composition as a function of pressure. They are similar in the low pressure phase and differ slightly in the high pressure one, where the distance increases with the Mn concentration. In all cases they are slightly larger than the Zn-O distance in pure ZnO[14]. The local compressibility around the Mn atom is identical to the bulk compressibility and does not depend on the concentration.

As shown in Figure 2, the transition is fully reversible for the 5% Mn concentration. The spectrum labeled 0d, which corresponds to the spectrum after pressure releasing, is identical to the 0 pressure one. This is not the case for the 25% Mn content. The high pressure structure remains stable when pressure is released (Figure 5).
CONCLUSION

We have shown that Mn atoms are in substitution of Zn atoms, whatever the Mn concentration (at least up to 25%) and the structure. For both Mn content (5 and 25%) we observe a pressure induced phase transformation from the initial wurtzite structure to the rocksalt one close to 8 GPa. The Mn-O distance is the same for both Mn concentrations in the low pressure phase but differs in the high pressure one. The local compressibility around the Mn atoms does not depend on the concentration and is similar to the bulk one obtained for pure ZnO although the first neighbor distances Mn-O are slightly larger than the Zn-O distance.

Moreover we have shown that thanks to the high focusing and high stability of the LUCIA beamline combined with high pressure cells with specific anvil and gasket design, x-ray absorption spectroscopy is feasible at lower energy than the Fe K edge, even for diluted species. Access to lower Z elements, like Cl, S, P and eventually Si edges under high pressure will be possible in the future and will open new opportunities for high pressure research.

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REFERENCES