Interface Double-Exchange Ferromagnetism in the Mn-Zn-O System: New Class of Biphase Magnetism

M. A. García,1,2 M. L. Ruiz-González,3 A. Quesada,1,2 J. L. Costa-Krämer,4 J. F. Fernández,5 S. J. Khatib,6 A. Wennberg,4 A. C. Caballero,5 M. S. Martín-González,4 M. Villegas,5 F. Briones,4 J. M. González-Calbet,1,3 and A. Hernando1,2,4

1Instituto de Magnetismo Aplicado (RENFE-UCM-CSIC), P. O. Box 155, 28230 Las Rosas, Madrid, Spain
2Departamento de Física de Materiales, UCM, 28040 Madrid, Spain
3Departamento de Química Inorgánica I, UCM, 28040 Madrid, Spain
4Instituto de Microelectrónica de Madrid, CNM-CSIC, Isaac Newton 8 PTM, 28760 Tres Cantos, Madrid, Spain
5Instituto de Cerámica y Vidrio, CSIC, Cantoblanco, 28049 Madrid, Spain
6Instituto de Catálisis y Petroquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

In this Letter, we experimentally show that the room temperature ferromagnetism in the Mn-Zn-O system recently observed is associated with the coexistence of Mn3+ and Mn2+ via a double-exchange mechanism. The presence of the ZnO around MnO2 modifies the kinetics of MnO2 → Mn2O3 reduction and favors the coexistence of both Mn oxidation states. The ferromagnetic phase is associated with the interface formed at the Zn diffusion front into Mn oxide, corroborated by preparing thin film multilayers that exhibit saturation magnetization 2 orders of magnitude higher than bulk samples.

Prompted by the need to understand the unusual magnetic properties recently observed in the Mn-Zn-O system, considerable work has been carried out. The first observation of room temperature (RT) ferromagnetism (FM) was reported by Sharma et al. [1] in low Mn content (10% MnO2–90% ZnO and 2% MnO2–98% ZnO) pellets annealed at 500 °C. The ferromagnetic behavior was first explained in terms of the formation of Mn-doped ZnO, which was previously predicted to be a dilute magnetic semiconductor with a Curie temperature above 300 K [2]. However, the origin of the reported ferromagnetic behavior is still a matter of controversy. Kundaliya et al. [3], based on thermogravimetric analysis (TGA) experiments, suggested an oxygen-vacancy Mn2–xZnxO3–δ phase as responsible for the observed RT FM. Moreover, recent studies evidence the absence of magnetic order in Mn-doped ZnO down to 2 K [4,5]. In a recent paper [6], RT FM was confirmed in samples prepared following Sharma et al. method, although differences concerning the structural characterization have been found. Actually, only a weak Zn diffusion into MnO2 grains is observed, whereas the presence of Mn into the ZnO matrix is never detected. In any case, the mechanism responsible for the RT FM has not been elucidated yet. In this sense, the aim of this work is focused on the study of the origin of the RT FM in the Mn-Zn-O system.

2% MnO2–98% ZnO and 10% MnO2–90% ZnO pellets were prepared following the method described by Sharma et al. [1,6]. Pure MnO2 samples were also studied for comparison purposes. These samples were annealed in air at different temperatures in the range 500 °C–800 °C for 12 h. After annealing at 500 °C, the ZnO-MnO2 samples exhibit RT ferromagnetic behavior, as previously reported [6].

The x-ray diffraction pattern shown in Fig. 1(a) and corresponding to the 10% MnO2–90% ZnO sample can be indexed on the basis of a mixture phase constituted by a majority one (ZnO), one minority, around 5% (Mn2O3), and traces of MnO2 and Zn2Mn3–xO4. This result can be understood taking into account that MnO2 can be partially reduced to Mn2O3 when treated at 500 °C, the temperature at which a total diffusion of Zn into Mn oxide grains is far from being reached. On the other hand, it is well known that x-ray diffraction (XRD) supplies average structural information. This means that if local diffusion of Mn in Zn has happened it could not be detected by this technique. In this sense, a transmission electron microscopy study linked with energy-dispersive x-ray spectroscopy (EDS) analysis has been performed to check if any local diffusion has succeeded. This information would be, indeed, very valuable in order to understand the observed magnetic properties. EDS analysis shows the presence of particles exhibiting different composition. The majority ones contain only Zn, while around 5% involves only Mn. A third type, in a very low ratio, comprising both cations, also appears. Selected area electron diffraction (SAED) patterns of the particles containing Mn and Zn separately can be, respectively, indexed on the basis of the ZnO and Mn2O3 unit cells, in agreement with the XRD study. On the other hand, particles containing both cations display Mn/Zn average ratios between 2.5 and 4. Moreover, inside each crystal changes in the Mn/Zn ratio are apparent. The SAED and the high resolution electron microscopy (HREM) study suggest that in each region containing Mn and Zn a spinel-like structure is stabilized. As a representative example, for a Mn/Zn = 2.5 ratio, a HREM image and its corresponding fast Fourier transform (FFT) along the [131] zone axis are displayed in Fig. 1(b).

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Changes in the microstructure were not found on particles having different Mn/Zn ratios, suggesting that a solid solution $\text{Zn}_x\text{Mn}_3\text{O}_4$ can be formed when MnO$_2$ and ZnO are heated up together. It is remarkable that the Zn content is never found to be $x \leq 1$; i.e., the spinel phase is always Mn rich. On the other hand, it is clear that the proportion of this phase is very low, in agreement with x-ray diffraction information. Evidence of Mn-doped ZnO was not detected.

Increasing the annealing temperature above 600°C gives rise to a decrease of the FM signal at room temperature that completely disappears after annealing at 800°C [Fig. 2(a)], in agreement with previous studies [1]. The XRD patterns of the annealed samples displayed in Fig. 2(b) indicate structural changes. Above 500°C, the very weak signal corresponding to MnO$_2$ disappears while the Mn$_2$O$_3$ peak intensity starts decreasing. In addition, new peaks characteristic of a spinel-like phase, $\text{Zn}_x\text{Mn}_3\text{O}_4$, appear and their intensities increase as the temperature is enhanced. The HREM study of the sample treated at 800°C confirms a Zn rich spinel structure, suggesting that heating has allowed further diffusion of Zn. The simultaneous increase of the $\text{Zn}_x\text{Mn}_3\text{O}_4$ phase and decrease of the ferromagnetic signal suggests that this phase is not responsible for the RT FM. Although there is some controversy about the magnetic properties of this spinel, it is well known that it exhibits paramagnetic behavior at RT [7]. For a further understanding, several samples in the $\text{Zn}_x\text{Mn}_3\text{O}_4$ system have been prepared and characterized. FM at RT was never observed in this solid solution.

Since no manganese oxides are ferromagnetic at room temperature, the observed FM must be related to the reaction of MnO$_2$ with ZnO prior to the final formation of the $\text{Zn}_x\text{Mn}_3\text{O}_4$ spinel. The kinetics of MnO$_2$ reduction is
modified by the presence of Zn. In this sense, TGA
[Fig. 3(a) and also Fig. 2(b) of Ref. [3]] shows that the
MnO \rightarrow Mn_2O_3 \text{ reduction process (}Mn^{4+} \rightarrow Mn^{3+}\text{)} is
very sharp and takes place between 500 °C and 600 °C.
However, in the presence of Zn, Mn^{4+} \rightarrow Mn^{3+} \text{ reduction
starts at lower temperature (about 200 °C) and there is a
progressive reduction up to 600 °C. Therefore, the
temperature range where Mn^{3+} and Mn^{4+} coexist is widen in
the presence of Zn.

In order to get more reliable information of manganese
oxidation states, Raman studies were performed. Raman
spectra of 2%MnO_2–98%ZnO and 10%MnO_2–90%ZnO, MnO_2,
Mn_2O_3, and ZnMn_2O_4,

![Raman spectra from 2%MnO_2–98%ZnO, 10%MnO_2–90%ZnO, MnO_2,
Mn_2O_3, and ZnMn_2O_4.](image)

FIG. 3. (a) TGA from pure MnO_2 and the component of MnO_2
in 2%MnO_2–98%ZnO. The latter was obtained by subtracting
the data for pure ZnO from the experimental results. (b) Raman
spectra from 2%MnO_2–98%ZnO, 10%MnO_2–90%ZnO, MnO_2,
Mn_2O_3, and ZnMn_2O_4.

spinel phase; the latter is related to an intermediate oxidation state [8], that is, local coexistence of Mn^{4+} and Mn^{3+}. In
our case, the presence of Zn seems to stabilize this mixture of oxidation states.

It is worth noting that the RT FM is found only for the
latter samples annealed in the temperature range where
Mn^{3+} and Mn^{4+} coexist, pointing to the simultaneous
presence of both oxidation states as responsible for the
observed RT FM. The coexistence of Mn^{4+} and Mn^{4+} is
known to be responsible for FM via the double-exchange
mechanism in different compounds [9,10], which usually
exhibits a large Curie temperature \((T_C)\) even above RT
[11]. Actually, the situation is similar to that found in
La_{1−x}Ca_{x}MnO_3. For \(x = 1\) the valence of Mn is 4+, whereas for \(x = 0\) the valence is 3+. None of those com-
ounds is FM, but the intermediate values of \(x\), which yield
to a mixture of Mn^{3+} and Mn^{4+}, give rise to the appearance
of FM with high \(T_C\).

It has not been described yet how the presence of Zn
modifies the kinetics of MnO_2 reduction. During the anneal-
ning process, Zn diffuses into MnO_2 grains favoring the
reduction to Mn_2O_3 and subsequent formation of the
Zn,Mn_{3−x},O_4. This is clearly observed by EDS micro-
analysis, since different areas of the same particle show
changes in the Mn/Zn ratio. The Mn^{3+} oxidation state
seems to be associated with phases containing Zn that
are doped Mn_2O_3 and Zn,Mn_{3−x},O_4, whereas Mn^{4+} is in
MnO_2. Therefore, it is expected that both Mn^{3+} and Mn^{4+}
coexist in the interface which separates regions with Zn
from those without Zn, that is, the Zn diffusion front into
Mn oxide grains. Figure 4 summarizes this situation. This
would explain the low saturation magnetization value re-
ported [1,3,6] in the RT ferromagnetic bulk systems, and
that the ferromagnetic phase is observed over a large
paramagnetic component but it has not been reported as
isolated: FM is not associated with a phase but with the
interface between nonferromagnetic phases.

In order to confirm this point, we have tried to increase
the MnO_2/ZnO interface (and therefore the surface of the
Zn diffusion front) by growing a thin film multilayer
sample consisting of 40 sequential ZnO/MnO_2 bilayers
by pulsed laser deposition onto a Si substrate. The ZnO
and MnO_2 individual layers are 7.5 and 1.5 nm thick, respec-
tively. The hysteresis loops of this sample are shown in
Fig. 4(b). The saturation magnetization is 1 emu/cm^2, 2
orders of magnitude larger than the highest \(M_s\) reported for
this system in bulk, and similar to the best value reported
for thin films [12], confirming that the FM is originated at
the interface. The coercive force for this sample [around
50 Oe at 5 K as shown in the inset of Fig. 4(b)] is smaller
than for bulk material (180 Oe at 5 K) [6]. Thereby, further
analysis of the anisotropy and technical magnetization pro-
cesses in these multilayers must be carried out. Despite
the small size of the magnetic entities, a noticeable contribu-
tion of superparamagnetic regions to the magnetization can
be disregarded since, in that case, the hysteresis loops at 5 and 300 K shown in Fig. 4(b) should be fairly different (both curves should overlap when represented as a function of \( H/T \)). The XRD patterns from this sample showed a clear signal from Mn$_2$O$_3$, confirming that this phase is involved in the interface that give rises to the ferromagnetic behavior. The composition of this interface could be similar to that proposed by Kundaliya et al. [3].

In summary, we showed that RT FM in the Mn-Zn-O system is due to the incorporation of Zn into the MnO$_2$ grains. The presence of Zn modifies the kinetics of thermal reduction Mn$^{4+} \rightarrow$ Mn$^{3+}$ during the annealing process, favoring the coexistence of both oxidation states, which gives rise to a double-exchange mechanism, responsible for the RT ferromagnetic behavior. Annealing above 500 °C increases Zn diffusion on manganese oxides, leading to spinel Zn$_x$Mn$_{3-x}$O$_4$ phases. The FM arises at the interface or Zn diffusion front, and it can be increased by maximizing the interface preparing multilayers. This is a new class of surface magnetism: double-exchange mechanism, at the interface between two compounds containing Mn atoms in different oxidation states.

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*Corresponding author.
Electronic address: ahernando@renfe.es