

Defect-Related Origin of the Ferromagnetism in ZnO:Co

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In recent years transition metal ion doped ZnO has been the focus of intense scientific enquiry. ZnO:Co is by far the most studied member of this family. However, despite the many experimental claims for ferromagnetism, a definitive theoretical explanation for long range magnetic interaction has so far been lacking. Here we present a mechanism which describes not only the origin of this previously inexplicable magnetism but also explains the experimental findings to date and in addition, suggests a recipe for tailoring the magnetic properties. We demonstrate that the magnetism originates from a Co^{2+} oxygen vacancy pair with a partially filled level close to the ZnO conduction band minimum. The long range coupling then occurs via conduction electrons at moderate n doping. This however is not sufficient for room temperature ferromagnetism due to the prohibitive concentrations of O vacancies needed. The experimental findings may then be explained by a combination of our proposed mechanism and the formation of blocked superparamagnetic clusters.

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1. Introduction

ZnO doped with small quantities of transition metal ions has been found to exhibit magnetic properties and has emerged as a promising candidate for use as a functional dilute magnetic semiconductor [1]. However, the literature on magnetically doped ZnO is vast and highly controversial [2]. In particular, the microscopic origin of the ferromagnetism in a system where the magnetic ions are at concentrations two orders of magnitude smaller than those of traditional magnets is unclear. Nor there is a general consistency amongst experimental results, with many reports indicating room temperature ferromagnetism and others failing to find any clear evidence of such in similar experimental conditions. In this work we investigate the case of ZnO:Co.

The main experimental findings are: (1) spectroscopic analysis shows that Co^{2+} substituting for Zn is the source of all the different magnetic phases, including the room temperature ferromagnetism (RTF); (2) RTF is always inferred from magnetometry (SQUID) or dichroism with the magnetic hysteresis considered as a sufficient indicator of RTF; (3) the coercive field is typically small (≈ 100 Oe) as well as the saturation magnetization (M_s) and the remanence (M_r); (4) the magnetic state is highly dependent upon the growth conditions, sample morphology and intrinsic defects; (5) exposure to Zn vapors enhances RTF; (6) recent experimental and theoretical evidence suggest that exposure of ZnO to Zn promotes oxygen vacancy (V_O) formation. These are the main source of oxygen deficiency but not of free carriers, which are instead attributed to unintentional H-doping. The promotion of RTF arising from Zn vapor exposure is then likely to be due to an increase in V_O and not of free carriers. (7) Electron paramagnetic resonance (EPR) in-

dicates the presence of two magnetic centers related to Co^{2+} .

2. Results

2.2. The two-site model

An extensive study over many candidate mechanisms for ferromagnetism was conducted [2] with density functional theory incorporating approximated self-interaction corrections [3]. It was found that exchange coupling between Co^{2+} ions is only short ranged and with a sign that depends on the crystalline direction. Likewise when intrinsic defects are present Co^{2+} can couple mostly ferromagnetically and extremely strongly but still at very short range only. This alone is still insufficient for RTF, since it requires a concentration of Co^{2+} and eventually defects equal to or greater than the percolation limit ($\approx 20\%$ for the fcc lattice).

We then turned our attention to looking for possible defect complexes capable of sustaining long range magnetic interaction. We found that $\text{Co}^{2+}-V_O$ pairs (CoV) form a spin-polarized defect band just at the top of the ZnO conduction band. Its occupation can be tuned with additional n doping resulting in a carrier-mediated long range magnetic interaction. This persists quite strongly to third nearest neighbors (NN), pushing the percolation limit to only 7%.

The results presented in this work are primarily concerned with the thermodynamic properties of a model system conforming to the picture presented above. We explain the phenomenology of ZnO:Co by considering two different Co-related magnetic centers: Co^{2+} and CoV [4]. CoVs interact ferromagnetically at long range amongst each other (the coupling strength is 50 meV, 15 meV and

5 meV at 1st, 2nd, 3rd NN, respectively), while simple Co^{2+} 's can sustain only NN antiferromagnetic interaction (15 meV). Finally, Co^{2+} and CoV strongly couple ferromagnetically but only at NN (50 meV). The chosen parameters for the model are representative, although conservative, of our density functional theory results. The Hamiltonian is thus given by

$$H = \sum_{\langle i,j \rangle}^{\text{Co,CoV}} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\langle i \rangle}^{\text{Co,CoV}} D(\mathbf{S}_i \cdot \hat{\mathbf{n}})^2, \quad (1)$$

where the last term in the Hamiltonian represents the hard-axis easy-plane anisotropy ($|\hat{\mathbf{n}}| = 1$). It should also be noted that doping of the CoV impurity band is implicitly assumed and the NN ferromagnetic component of the Co^{2+} - Co^{2+} interaction neglected (along some particular direction). Monte Carlo calculations are then performed for a classical Heisenberg Hamiltonian ($|\mathbf{S}_i| = 1$). Our two species model percolates for CoV concentrations x^{CoV} of about 7%. This is quite large since one needs an equal concentration of V_O . Thus, our two-center model, as currently proposed, would appear to exclude the possibility of RTF in experimentally examined samples. However, experimental results can be accounted for with an alternative explanation involving blocked superparamagnetic clusters.

2.2. Blocked superparamagnetic regime

Below the percolation threshold, well separated nanoclusters may still form. These clusters, although locally magnetic, will have no magnetic correlation between each other. Thus the problem becomes whether or not these nanoclusters are sufficiently large to individually overcome the superparamagnetic limit. The important point is that the magnetization blocking in a superparamagnet may result in a magnetometry response indistinguishable from that of a ferromagnet. Since hysteresis at room temperature is usually the smoking gun for RTF, this hypothesis must be investigated. The size required for a cluster to be blocked is estimated by considering its anisotropy energy barrier. For a coherent rotation of a uniaxial single domain magnet this is $DN_b S^2$, where D is the zero field splitting, N_b is the number of magnetic ions in the cluster, and S is the Co spin. Taking D from EPR measurements [5], we estimate $N_b = 800$ for a blocking temperature of 300 K.

Clusters of this size should be detectable experimentally and would have a very large coercive field. However, this is most probably an overestimate. In granular magnets random dipolar interaction, random magnetic anisotropy or spinodal decomposition can push the blocking temperature to values considerably larger than those predicted for single particle coherent rotation (up to a factor of 5). By such arguments we can reduce our estimate for N_b to more reasonable 250 magnetic ions. So all we require, in order to observe a superparamagnetic blocking at room temperatures are clusters of 250 ions. Such clusters percolate locally within the cluster. Below we show a typical cluster distribution for our two

center model and demonstrate that this is indeed easily achieved. Figure 1 shows the cluster distribution $P(N)$ as a function of the cluster size N for various concentrations of Co^{2+} and CoV. These plots were constructed by randomly filling a very large wurtzite lattice ($\approx 10^6$ sites) with magnetic ions and counting the size of the percolating magnetic clusters generated. The size of the clusters are then normalized with respect to the total number of magnetic ions in the system. Let us note that in these simulations we do not bias the distribution of the Co^{2+} and CoV towards clustering, although density functional theory calculations suggest that clustering is indeed expected.

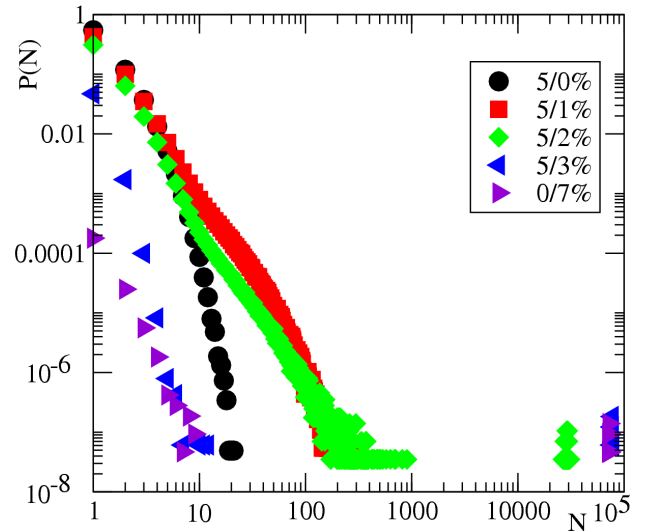


Fig. 1. Cluster distribution $P(N)$ as a function of the number N of magnetic ions in the cluster for different x^{Co} (first %) and x^{CoV} (second %).

The distribution becomes bimodal as x increases above $x^{\text{CoV}} > 6\%$. The most important result here is that concentrations which are feasible experimentally are capable of producing clusters large enough to be superparamagnetically blocked, thus yielding a ferromagnetic signature in magnetometry measurement at room temperatures.

2.3. Cluster correlation

What remains to be established is whether or not the large magnetically coupled clusters, which may in principle exist, are robust enough to survive as the system temperature approaches the ambient level. Here we study this problem by exploring the correlation between magnetic ions. This will determine both the degree of magnetic coupling and act as a criterion for deciding whether a given atom may be considered to be sufficient strongly coupled to another atom for both atoms to be considered to exist within the same magnetic cluster.

The spin-spin correlation of an atom with its neighbors is defined as follows:

$$C(\mathbf{R}, T)_i = \sum_j^{\mathbf{R}} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle. \quad (2)$$

The correlation function provides a measure of the degree to which one atom is coupled to another. It is both dependent on the temperature and a radius \mathbf{R} . Spins \mathbf{S}_j lying at a distance larger than \mathbf{R} from \mathbf{S}_i are not taken into consideration in the evaluation of the correlation function. In order to examine the viability of the superparamagnetic blocked cluster argument of the previous section an examination of the size of magnetically

correlated clusters was performed over many random configurations at varying concentrations of Co^{2+} and CoV. An atom was considered to belong to a cluster if the strength of the correlation between the atom and any member of the cluster was greater than a certain value. This value was varied in fixed steps between 0 (no correlation) and 1 (complete correlation). We find that the correlation between two atoms in a system close to the critical temperature and composed of a homogeneous distribution of CoV at a concentration of 7%, is 0.3. This value is then used as the cutoff for inclusion in a given cluster.

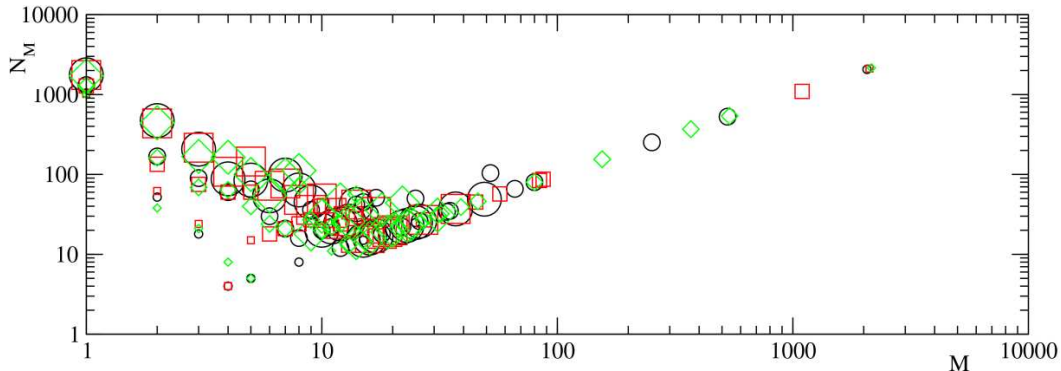


Fig. 2. N_M is the number of atoms existing in a given cluster of size M for concentrations 3% Co^{2+} and 3% CoV. The different symbols represent 5 different random configurations. The largest symbols are for $T = 250$ K, the medium symbols are $T = 100$ K, the smallest symbols are for 30 K.

Using this value a representative set of cluster distributions is shown in Fig. 2. In general, one may note that the average size of clusters which show correlation comparable to that of a percolating system close to the Curie temperature decreases as the temperature increases. In practice our figure traces the “melting” of strongly correlated regions of our diluted system. Importantly large clusters are found to exist up to quite high temperatures. For some systems clusters exceeding 200 atoms are shown to be in abundance at temperatures as high as 100 K. Even approaching 250 K still a considerable number of atoms exist in clusters with size of the order of 10 atoms. It should be remarked again that the parameters used in this model are highly conservative and the distributions shown represent effectively the lower bounds on the cluster sizes.

In conclusion, we have discussed the magnetism in ZnO:Co in terms of a two-center model with parameters extracted from density functional theory. We have argued that RTF can be mimicked by large blocked superparamagnetic clusters. By means of a statistical analysis of the two-spin correlation functions we have investigated the “melting” of such clusters as a function of the temperature.

Acknowledgments

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