Magnetization Process in Dilute Magnetic Oxides

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Thin films of dilute magnetic oxides often exhibit high-temperature ferromagnetism with magnetization curves of the form $M \approx M_s \tanh(H/H_0)$; the curves are practically anhysteretic and temperature-independent below room temperature. The absence of temperature-dependent coercivity indicates that the magnetization process is dominated by magnetic dipole interactions, not by magnetocrystalline anisotropy. In a model of ferromagnetic grain boundaries, $H_0 \approx 0.14 M_0$, where M_0 is the magnetization of the ferromagnetic regions. Quantitative analysis of more than 200 films of different oxides reveals that only a few percent of the volume of these films is magnetically ordered.

Index Terms—**Anisotropy, dilute magnetic oxides, magnetization.**

I. INTRODUCTION

NONMAGNETIC oxides doped with a few percent of $3d$ transition-metal cations which show signs of high-temperature ferromagnetism remain the most controversial, and possibly the most significant group of new magnetic materials under investigation at present. The samples are often in the form of thin films on a substrate. Both conducting (SnO_2, ITO), semiconducting (ZnO) and insulating (TiO_2, HfO_2) oxides are reported to exhibit the ferromagnetic effect. A wide variety of $3d$ dopants has been implicated, but there are also some reports of ferromagnetic behavior in undoped films, and in nanoparticles or nanocrystalline ceramics [1]. A recent review of transition-metal doped ZnO films [2], for example, cites a thousand references.

There is much evidence to suggest that ferromagnetism in transition-metal doped ZnO is unambiguously correlated with structural defects, which depend on the substrate temperature and oxygen pressure used during film deposition [2], [3]; the charge carriers are byproducts of these defects. Ney *et al.* [4] have demonstrated that highly perfect Co-doped epitaxial films, for example, are purely paramagnetic, with cobalt occupying zinc sites and no sign of anything other than weak antiferromagnetic Co-O-Co nearest-neighbour superexchange. Droubay *et al.* [5] show that Mn-doped epitaxial films are paramagnetic, with Mn substituting for Zn, and no moments on either oxygen or zinc. Barla *et al.* [6] demonstrated that the cobalt in ferromagnetic Co-doped ZnO films was actually paramagnetic, and that there was no magnetic moment on the zinc. A study by Tietze *et al.* [7] who investigated 5% Co-doped films produced by PLD which exhibited a moment of $\approx 1 \mu_B$/Co, corresponding to a magnetization of ≈ 35 kA m^{-1} came to a remarkable conclusion; extensive XMCD measurements on the Co and O edges with a very good signal/noise ratio showed only the signatures of paramagnetic cobalt and oxygen. There is no sign of any element-specific ferromagnetism. By a process of elimination, only electrons trapped in oxygen vacancies or other defects remained as the possible intrinsic source of the ferromagnetism
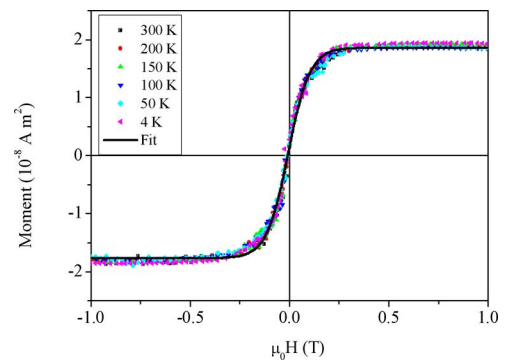
Fig. 1. Ferromagnetic magnetization curves of a thin film of indium-tin oxide (ITO) doped with 5% Mn, at different temperatures [10].

observed in the ZnO films. However, other studies did provide evidence for intrinsic ferromagnetism in XMCD studies of individual nanoparticles of the same material [8]. A data mining exercise on Mn-doped ZnO nanocrystalline ceramics has shown that the ferromagnetism in doped, and even undoped ZnO, is correlated with the grain-boundary volume, leading to the image of a ferromagnetic grain-boundary foam [9]. Magnetic order at temperatures far above room temperature is incompatible with the weak Mn-Mn exchange interactions in this material [5].

All these results beg the question: Are the ferromagnetic dilute magnetic oxides uniformly magnetized?

II. RESULTS

Here we are able to answer the question by examining a basic and characteristic feature of these unusual materials, their practically anhysteretic magnetization curve, which shows little or no temperature dependence in the range from 4 K to 300 K, This is the temperature range where most of the magnetization measurements on the thin films and nanoparticles or nanocrystalline ceramics have been made. Whenever temperature-dependent hysteresis does appear, it is usually a sign of phase segregation in the sample. A secondary ferromagnetic impurity phase is responsible. Samples of this type are not considered further.

Some representative data are shown in Fig. 1 [10]. The film here is indium tin oxide (ITO) doped with 5% manganese, but many other materials behave in the same way. We refer to these curves as 'practically anhysteretic' although they exhibit a coercivity of a few kA m^{-1}, and a remanence ratio of about 5%. The

TABLE I
AVERAGE PARAMETERS DEDUCED FROM THE MAGNETIZATION CURVES OF FERROMAGNETIC FILMS AND NANOPARTICLES

	H_0 (kA m^{-1})	M_0 (kA m^{-1})	M_s (kA m^{-1})	M_s/M_0 (%)
ZnO	86 (47)	614 (335)	61	9.9
SnO$_2$	75 (30)	535 (214)	10	1.9
TiO$_2$	161 (115)	1150 (821)	8	0.7
Fe (np)	275 (40)	1964 (286) 1710*	0.003	2 10^{-4}

* spontaneous magnetization of iron
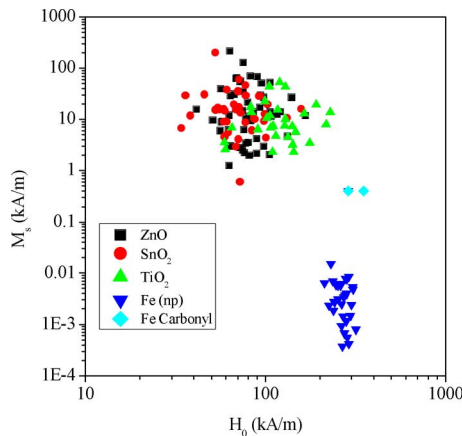
Fig. 2. Plot of sample magnetization versus H_0 for 200 anhysteretic ferromagnetic films.

Fig. 3. Magnetization curves of ferromagnetic iron particles which have a vortex structure.

point is that these values do not increase at low temperature. The high-field slope of the magnetization curves, due to the substrate and the contribution of mangaese ions, which are paramagnetic, is set to zero. When corrected in this way, the curves measured at different temperatures superpose. All the curves were first fitted to the empirical expression

$$M = M_s \tanh(H/H_0) \qquad (1)$$

where M_s is the saturation magnetization, and H_0 is a constant effective field that impedes saturation. It is readily estimated by extrapolating the slope at the origin, which reaches the saturation magnetization when $H = H_0$. This magnetic behavior bears no relation to superparamagnetism, where the quantity H_0 would have to be proportional to temperature. We have re-examined a great many magnetization curves measured in our laboratory on thin films and nanoparticles of the transition metal oxides ZnO, SnO$_2$, HfO$_2$ and TiO$_2$, undoped or doped with transition-metal cations. We have also looked at the magnetization curves of iron metal micro- and nanoparticles for comparison. The field applied to the thin films is usually in-plane.

Fig. 2 shows a scatter plot of M_s versus H_0 for more than 200 samples. For clarity, the same units of kA m^{-1} are used on both axes. Some conclusions can be immediately drawn from these data:

i) The lack of any temperature-dependent coercivity suggests that the magnetization process in these materials is unrelated to magnetocrystalline anisotropy, but controlled by dipolar fields, which scale with M_0, the local spontaneous magnetization of the ferromagnetic regions.
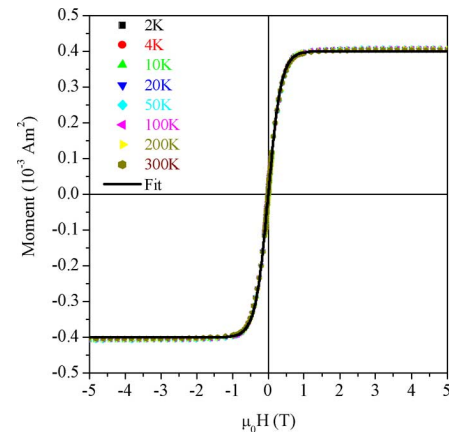
The dipolar field may be written as $H_d = -N_{\text{eff}}M_0$, where $1 < N_{\text{eff}} < 0$ is a local demagnetizing factor.

ii) The samples are *not* uniformly magnetized. If they were, the magnetiztion of the thin films would approach saturation in fields of a few kA m^{-1}, which are less than the saturation magnetization M_s

iii) The values of H_0 for the different oxides show overlapping, but distinct distributions, with average values of H_0 of order 100 kA m^{-1}, which are given in Table I.

iv) The magnetization curves of iron metal micro- and nanoparticles fall in a different region of the diagram, with $H_0 = 275 \pm 40$ kAm^{-1}

III. DISCUSSION

A first approach to analysing these materials is to treat them as wandering axis ferromagnets. This means that the ferromagnetic axis in different parts of the material points in a different direction, as a result of minimizing the dipolar interactions.

The magnetization curves are practically independent of temperature below room temperature. Well-separated soft ferromagnetic particles with a vortex structure show magnetization curves of this type. The example of dispersed iron microparticles is shown in Fig. 3. The demagnetizing factor here is not 1/3, because the particles are not collinear ferromagnetic single domains. The magnetization curves of iron partlcles with micron and submicron dimensions can be fitted to (1) with $H_0 = 274$ kA m^{-1}. The spontaneous magnetization of iron is $M_0 = 1710$ kA m^{-1}, so $H_0/M_0 = 0.16$.

A ferromagnetic grain-boundary foam can be modelled by assuming that the local easy axis lies in a grain boundary, and
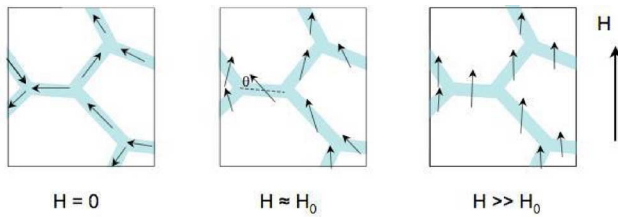
Fig. 4. Schematic magnetization process for a wandering axis ferromagnet where the magnetization is confined to the grain boundaries.

is randomly-oriented with respect to the direction of a uniform applied field (Fig. 4). The local demagnetizing field is $M_0 \sin \theta$, oriented normal to the grain boundary, where θ is the angle between the applied field and the plane of the grain boundary. Numerical analysis of this model gives an approach to saturation similar to (1) with $H_0 \approx 0.14 M_0$. Hence, it is possible to deduce the magnetization M_0 of the ferromagnetically-oriented regions in the samples, which are listed in Table I.

The ratio of M_s to M_0 directly gives the fraction of the sample volume which is occupied by the ferromagnetic regions. Hence, we deduce that the volume fraction for the oxide thin films is 1–10%. The iron nanoparticles, which were dispersed on an etched silicon surface, occupy 2 ppm of the sample volume [11]. In this case, the analysis could be checked by direct observation of the sample surface.

Similar analysis of the magnetization curves of weakly ferromagnetic nanoparticles or nanocrystalline ceramics [12] gives ferromagnetic volume fractions of order 1 part per million.

The inference that only a small fraction of the volume of these dilute magnetic oxides is actually ferromagnetic is rather robust. There is little difference in H_0 when the field is applied parallel or perpendicular to the plane of the film, so the ratio H_0/M_0 is unlikely to exceed 0.33. The two cases we considered, a curling vortex in micron-size iron particles and the grain boundary foam, gave 0.16 and 0.14 respectively. In the first case, the result is based on experiment; in the second it comes from the simulation.

Finally, it should be pointed out that the results could be compatible with contamination of the samples by scattered particles of a high-temperature ferromagnetic contaminant with $M_s \approx 500 \, \text{kA m}^{-1}$ (but not iron, or an iron or cobalt based alloy which has a greater magnetization). The only plausible candidate we can think of is airborne magnetite, but the variations with oxide type, and the absence of a signal when the materials we investigated are undoped would be hard to understand in this case. We

found no evidence for magnetite particles in the films. We seem to be dealing with sparse regions of intrinsic high-temperature ferromagnetic order in the dilute magnetic oxides.

IV. CONCLUSION

We conclude that the dilute ferromagnetic oxides are never uniformly magnetized, and that only a small fraction of the volume of the films is ferromagnetically ordered. The results are not consistent with any model of a uniformly magnetized diluted magnetic oxide. They are consistent, however, with a model where high-temperature wandering axis ferromagnetism is associated with grain boundaries, surfaces or interfaces [13].

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