

Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides

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Room-temperature ferromagnetism has been observed in nanoparticles (7–30 nm diam) of nonmagnetic oxides such as CeO_2 , Al_2O_3 , ZnO , In_2O_3 , and SnO_2 . The saturated magnetic moments in CeO_2 and Al_2O_3 nanoparticles are comparable to those observed in transition-metal-doped wideband semiconducting oxides. The other oxide nanoparticles show somewhat lower values of magnetization but with a clear hysteretic behavior. Conversely, the bulk samples obtained by sintering the nanoparticles at high temperatures in air or oxygen became diamagnetic. As there were no magnetic impurities present, we assume that the origin of ferromagnetism may be the exchange interactions between localized electron spin moments resulting from oxygen vacancies at the surfaces of nanoparticles. We suggest that ferromagnetism may be a universal characteristic of nanoparticles of metal oxides.

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Integration of semiconductor with ferromagnetic functionality of electrons has been the focus of recent research in the area of spintronics because of the difficulties associated with the injection of spins into nonmagnetic semiconductors in conventional spintronic devices. Ferromagnetism in semiconductors and insulators is rare, the well-known ferromagnetic semiconductors being the chalcogenides EuX ($X=\text{O}, \text{S}$, and Se) ($T_C < 70$ K) and CdCr_2X_4 ($X=\text{S}$ and Se) ($T_C < 142$ K) with the rocksalt and spinel structure, respectively.^{1,2} Following the theoretical prediction of Dietl *et al.* that Mn-doped ZnO and GaN could exhibit ferromagnetism above room temperature,³ several studies have focused on films and bulk samples of metal oxides such as TiO_2 , ZnO , In_2O_3 , SnO_2 , and CeO_2 doped with Mn, Co, and other transition metal ions.^{4–8}

While the existence of ferromagnetism in transition-metal-doped semiconducting oxides remains controversial,⁹ thin films of the band insulator HfO_2 have been reported to exhibit ferromagnetism at room temperature in the absence of any doping.¹⁰ This is puzzling, since pure HfO_2 does not have any magnetic moment and the bulk sample is diamagnetic. Similar ferromagnetism has been reported in other nonmagnetic materials such as CaB_6 , CaO , and SiC where the origin of ferromagnetism is believed to be due to intrinsic defects.^{11–13} It has been suggested that ferromagnetism in thin films of HfO_2 may be related to anion vacancies.¹⁴ It has been reported very recently that thin films of undoped TiO_2 and In_2O_3 also show ferromagnetism at room temperature,¹⁵ the corresponding bulk forms of these materials being diamagnetic. Thin films of these oxides might have defects or oxygen vacancies that could be responsible for the observed ferromagnetism. *Ab initio* electronic structure calculations using density functional theory in HfO_2 have shown that isolated half-nium vacancies lead to ferromagnetism.¹⁶ Meanwhile, there is a conflicting report attributing the ferromagnetism in HfO_2 to possible iron contamination while using stainless-steel tweezers in handling thin films.¹⁷

In this Rapid Communication, we report the discovery of ferromagnetism at room temperature in nanoparticles of nonmagnetic oxides such as CeO_2 , Al_2O_3 , ZnO , In_2O_3 , and

SnO_2 . Our studies show that ferromagnetism is associated only with the nanoparticles while the corresponding bulk samples are diamagnetic. The origin of ferromagnetism in these materials is assumed to be the exchange interactions between localized electron spin moments resulting from the oxygen vacancies at the surfaces of the nanoparticles.

Nanoparticles of CeO_2 , Al_2O_3 , ZnO , In_2O_3 , and SnO_2 were prepared by the methods described in the literature.^{18–20} The preparation methods do not involve any magnetic element and therefore we rule out the possibility of contamination of magnetic impurities. For example, the nanoparticles of CeO_2 were prepared by the addition of hexamethylenetetramine to a solution of cerium nitrate [$\text{Ce}(\text{NO}_3)_3$] under constant stirring.¹⁸ The nanoparticles of all these oxides were annealed at temperatures between 400 and 500 °C in flowing oxygen to remove organic matter. In order to make bulk samples, these nanoparticles were sintered at high temperatures (1000–1400 °C). Powder x-ray diffraction (XRD) was used to identify the phase and its purity and to determine the grain size. The particle size and morphology were studied by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Magnetization measurements were carried out with a vibrating sample magnetometer in a physical property measuring system (PPMS, Quantum Design, San Diego, CA, USA).

XRD patterns of all the samples showed that they were monophasic with broad peaks characteristic of nanoparticles. The lattice parameters and the full width at half maximum of all the reflections were obtained from Rietveld refinement in the pattern matching mode using the program FULLPROF.²¹ The lattice parameters of the oxide nanoparticles were generally higher than those of the corresponding bulk forms. For example, the lattice parameter of the CeO_2 nanoparticles (7 nm) is 5.424(3) Å whereas that of the corresponding bulk sample is 5.413(1) Å. This is in agreement with an earlier report that the lattice expands in oxide nanoparticles.²² The increase of lattice with decreasing particle size might result from the oxygen vacancy associated with nanoparticles. Similar results were obtained for Al_2O_3 , ZnO , In_2O_3 , and SnO_2 samples. The average particle sizes of CeO_2 , Al_2O_3 ,

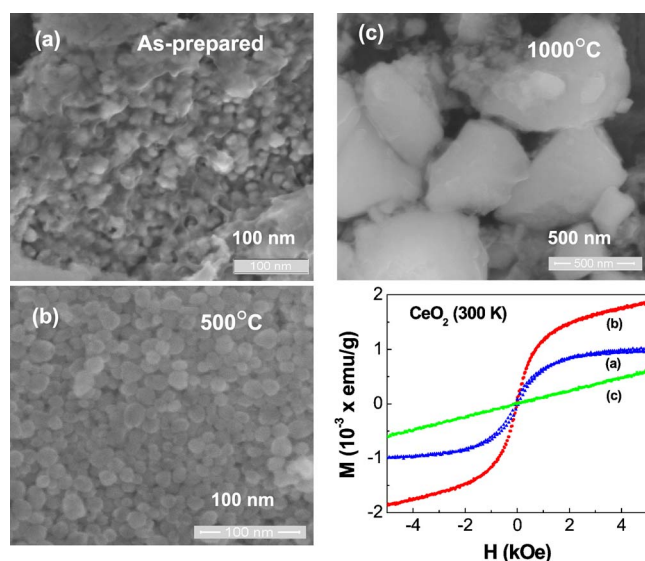


FIG. 1. (Color online) FESEM images of CeO_2 nanoparticles [(a) 7 nm, (b) 15 nm, (c) 500 nm] and their magnetization curves at 300 K. Note the absence of ferromagnetism in the 500 nm nanoparticles, in contrast to the 7 or 15 nm nanoparticles.

ZnO , In_2O_3 , and SnO_2 estimated by the Scherrer formula using all diffraction lines were 15, 4, 30, 12, and 20 nm, respectively.

In Fig. 1 we show the room-temperature magnetization-field curves of many CeO_2 samples: (a) as prepared (b) heated at 500 °C for 1 h and (c) heated at 1000 °C for 1 h. We have shown the FESEM images of these three samples in the figure. It can be seen that the as-prepared particles (7 nm) are covered by the organic coating used in the preparation of nanoparticles whereas the 500 °C heated particles (15 nm) are free from such coating. It is obvious from the $M(H)$ curves that the as-prepared and 500 °C heated nanoparticles show ferromagnetic behavior with coercivity ~ 100 Oe. This is surprising, since bulk CeO_2 is a band insulator with Ce^{4+} in the $4f^0$ electronic configuration. On the other hand, the ferromagnetism is suppressed in the 1000 °C sample with ~ 500 nm size particles and this sample exhibits a linear $M(H)$ behavior with low magnetic moment, a behavior close to diamagnetism as normally expected of CeO_2 .

A TEM image of Al_2O_3 nanoparticles obtained by heating $\text{Al}(\text{OH})_3$ at 500 °C is shown in Fig. 2(a). The $M(H)$ curves of these nanoparticles (0.0291 g) recorded at 300 and 390 K are shown in Fig. 2(b). These nanoparticles show ferromagnetism even at 390 K with clear hysteretic behavior. The saturation magnetic moment at 300 K is $\sim 3.5 \times 10^{-3}$ emu/g, comparable to that reported for Mn-doped ZnO .⁵ In order to verify that the room-temperature ferromagnetism is associated only with nanoparticles, the nanoparticles of the sample were pressed into a bar and sintered at 1400 °C for 1 h in air to obtain bulk samples with micrometer-sized particles. The magnetization of the bulk sample thus obtained is shown in Fig. 2(b). It is clear from this figure that the bulk sample is diamagnetic. Similarly, room-temperature ferromagnetism is observed in ZnO nanoparticles heated at 400 °C and diamagnetic behavior in the sample sintered at 1200 °C (Fig. 3).

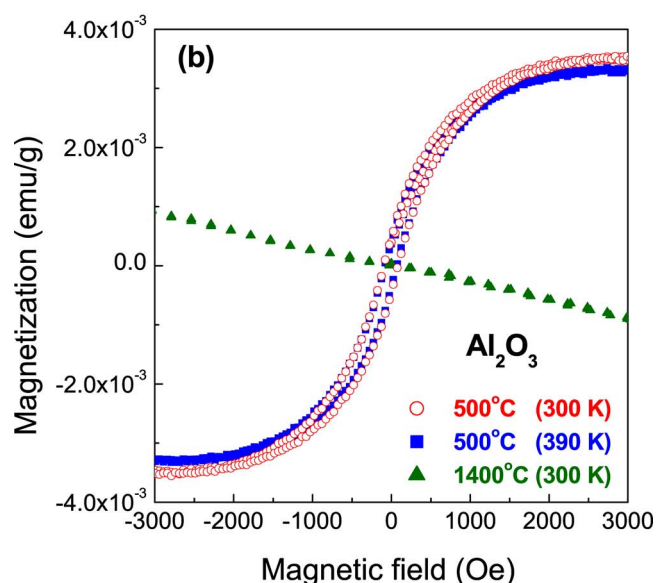
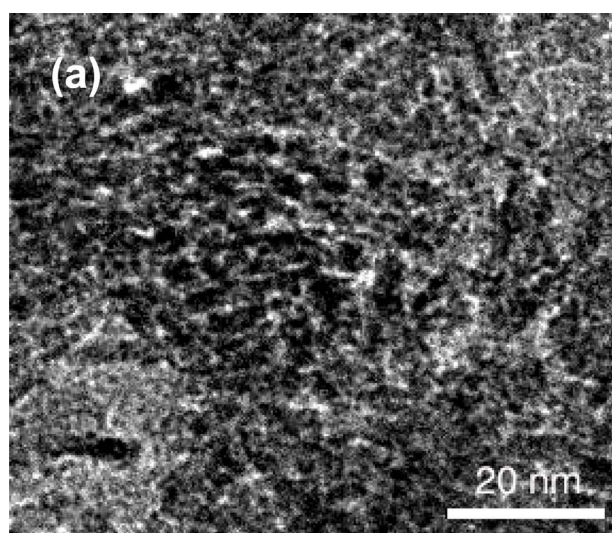


FIG. 2. (Color online) (a) TEM image of Al_2O_3 nanoparticles heated at 500 °C and (b) their magnetization curves showing ferromagnetism even at 390 K. Note that the nanoparticles sintered at 1400 °C exhibit diamagnetic behavior at 300 K.

Unlike CeO_2 , Al_2O_3 , and ZnO , which are insulators, In_2O_3 and SnO_2 are transparent conductors with a wide band gap (~ 3.6 eV). Magnetization data of In_2O_3 and SnO_2 nanoparticles are shown in Fig. 4. The magnetization behavior of SnO_2 is slightly different from that of the other oxides, but similar to that observed in thin films of Co-doped SnO_2 .⁷ It can be seen from this figure that there is a small hysteresis at low fields and that the magnetic moment increases linearly at higher field. The linear behavior may be due to magnetic moments associated with conduction electrons. This is consistent with the observation that the nanoparticles after sintering at 1200 °C show paramagnetic behavior. Though there may be slight differences in the magnetization behavior, nanoparticles of all the oxides studied exhibit room-temperature ferromagnetism. It should be noticed that the nanoparticles of paramagnetic metallic ReO_3 with low mag-

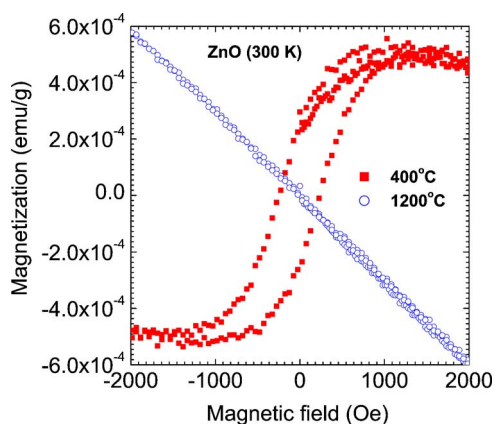


FIG. 3. (Color online) M versus H curves measured at 300 K for nanoparticles of ZnO heated at 400 °C and sintered at 1200 °C.

netic susceptibility are reported to show hysteresis at 5 K.²⁴ As the magnetic susceptibility of ReO_3 nanoparticles is relatively low, it may show ferromagnetism even at room temperature.

The origin of ferromagnetism in the nanoparticles of these nonmagnetic oxides seems to be similar to that in thin films of HfO_2 , TiO_2 , and In_2O_3 where the oxygen deficiency results from thin film growth conditions.^{10,15} In contrast to thin films, where the contamination of films by handling can vitiate the results, ferromagnetism in the oxide nanoparticles is robust and universal. We suggest that the unpaired electron spins responsible for ferromagnetism in the nanoparticles have their origin in the oxygen vacancies, especially on the surfaces of the oxide nanoparticles. The nature of exchange interactions between them is not clear at present. However, one may expect that electrons trapped in oxygen vacancies (F center) are polarized to give room-temperature ferromagnetism. This mechanism has been proposed to explain ferromagnetism in some transparent oxides.²³

In conclusion, we have shown that nanoparticles of metal oxides such as CeO_2 , Al_2O_3 , ZnO , In_2O_3 , and SnO_2 , exhibit room-temperature ferromagnetism whereas the corresponding bulk oxides exhibit diamagnetism. We assume that the origin of ferromagnetism may be the exchange interactions between unpaired electron spins arising from oxygen vacancies at the surfaces of the nanoparticles. We suggest that all metal oxides in nanoparticulate form would exhibit room-temperature ferromagnetism. The ferromagnetism assumed to be associated with oxygen vacancies gives a possible clue

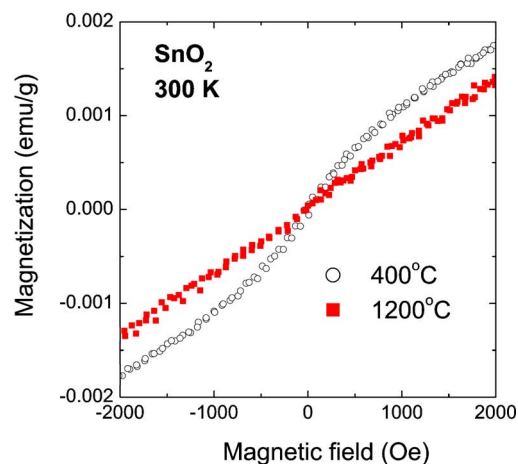
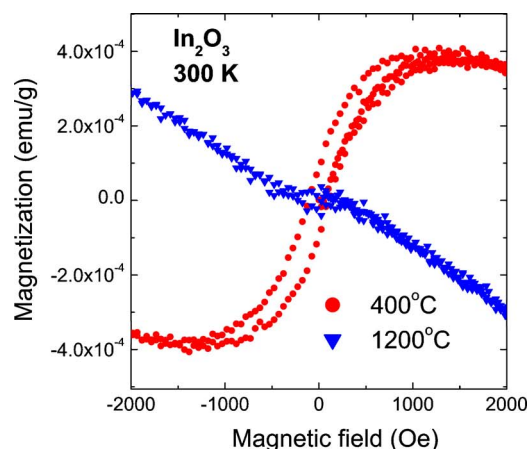


FIG. 4. (Color online) M versus H curves measured at 300 K for nanoparticles of In_2O_3 and SnO_2 heated at 400 °C and sintered at 1200 °C.

to understand some of the contradicting findings in the dilute magnetic semiconducting oxides.

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