



## Room-temperature ferromagnetism observed in Fe-doped NiO

Jianfei Wang, Jingnan Cai, Yuan-Hua Lin, and Ce-Wen Nan

Citation: Applied Physics Letters **87**, 202501 (2005); doi: 10.1063/1.2130532 View online: http://dx.doi.org/10.1063/1.2130532 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/87/20?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Room-temperature ferromagnetism in epitaxial Mg-doped SnO2 thin films Appl. Phys. Lett. **100**, 182405 (2012); 10.1063/1.4711220

Structural and room-temperature ferromagnetic properties of Fe-doped CuO nanocrystals J. Appl. Phys. **107**, 113908 (2010); 10.1063/1.3436573

Exchange bias and the origin of room-temperature ferromagnetism in Fe-doped NiO bulk samples J. Appl. Phys. **103**, 023906 (2008); 10.1063/1.2832437

High resolution transmission electron microscopy and Raman scattering studies of room temperature ferromagnetic Ni-doped ZnO nanocrystals Appl. Phys. Lett. **90**, 052505 (2007); 10.1063/1.2435606

Temperature dependence of solubility limits of transition metals (Co, Mn, Fe, and Ni) in ZnO nanoparticles Appl. Phys. Lett. **89**, 144105 (2006); 10.1063/1.2360176



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 155.33.16.124 On: Wed, 26 Nov 2014 11:58:08

## Room-temperature ferromagnetism observed in Fe-doped NiO

Jianfei Wang, Jingnan Cai, Yuan-Hua Lin, and Ce-Wen Nan<sup>a)</sup>

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

(Received 3 June 2005; accepted 20 September 2005; published online 8 November 2005)

Here we report a kind of diluted magnetic semiconductor (DMS) system, i.e., Fe-doped NiO. Monophase Ni<sub>1-x</sub>Fe<sub>x</sub>O (x=0-0.02) was synthesized by using a chemical coprecipitation method and post-thermal decomposition processing. Pure NiO without Fe doped is antiferromagnetic. The results demonstrated the samples with Fe doped were ferromagnetic at room temperature, which is stronger than most DMS oxide systems, e.g., Mn or Ni-doped ZnO, and Co-doped TiO<sub>2</sub> reported recently. The effect of Fe doping was discussed and relevant mechanism was proposed, by comparing with previous studies of finite size effect in NiO nanoparticles and other DMS systems. © 2005 American Institute of Physics. [DOI: 10.1063/1.2130532]

Diluted magnetic semiconductors (DMS) are a new kind of materials for spintronic application,<sup>1</sup> especially those whose curie temperatures are above room temperature.<sup>2</sup> Since the discovery of room-temperature ferromagnetism in cobalt-doped TiO<sub>2</sub> thin films,<sup>3</sup> more reports on high-Curietemperature ferromagnetic DMS have appeared, including ZnO,<sup>4–8</sup> TiO<sub>2</sub>,<sup>3,9,10</sup> SnO<sub>2</sub>,<sup>11</sup> ZnTe,<sup>12</sup> In<sub>2</sub>O<sub>3</sub>,<sup>13</sup> Cu<sub>2</sub>O<sup>14</sup> based DMS. Among these, ZnO-based *n*-type DMS have attracted more and more interest. Several kinds of elements, such as Mn,<sup>4</sup> Co,<sup>5,6</sup> Ni,<sup>7</sup> and V,<sup>8</sup> have been doped into ZnO, in which magnetism has been observed beyond room temperature. However, few *p*-type DMS have been reported.

Stoichiometric NiO, which is known as an antiferromagnetic Mott-Hubbard insulator, could be semiconducting after the introduction of Ni<sup>2+</sup> vacancies or doping with other cations and thus become a *p*-type semiconductor.<sup>15,16</sup> The magnetic properties of NiO nanoparticles (31.5 nm in diameter) have recently been studied by Kodama *et al.*<sup>17</sup> They found that due to finite size effect the NiO nanoparticles could exhibit anomalous magnetic properties, such as large moments and coercivities and loop shifts at low temperatures. These features are absent in NiO of larger size at room-temperature.<sup>18</sup>

In this letter, we report the magnetic properties of Fedoped NiO, which are different from nanosize effect induced magnetism observed in nanosized NiO.<sup>17,18</sup> Remarkable room-temperature magnetism, comparable with most DMS systems reported so far, has been observed in Fe-doped NiO.

Pure Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and NH<sub>4</sub>HCO<sub>3</sub> were employed as starting raw materials. Nominal amounts of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were weighed and dissolved into distilled water. The hydroxycarbonate precursor was chemically precipitated by slowly adding an aqueous ammonium bicarbonate NH<sub>4</sub>HCO<sub>3</sub> solution whose pH was ~8 at 295 K, accompanying magnetic stirring. The resultant gels were washed several times with distilled water and ethanol until free of nitrate ions, filtrated and dried in air at 353 K. Afterwards, dried gels were calcined at 873 K for 4 h in air to obtain the resultant Fe-doped NiO samples.

X-ray diffraction (XRD) patterns were obtained at room temperature using Cu  $K\alpha$  radiation to study the phase com-

position. Step mode around high angle peaks was also used to reveal the effect of Fe doping on the NiO grain size. Scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectrometer (EDX) was employed to study the microstructure and composition of the samples. The magnetic behavior was measured by a vibrating sample magnetometer equipped with a dewar for low temperature testing.

Figure 1 shows the XRD patterns of the Ni<sub>1-x</sub>Fe<sub>x</sub>O samples. Because the radius difference between Ni<sup>2+</sup> ion (0.69 Å) and Fe<sup>3+</sup> ion (0.64 Å) or Fe<sup>2+</sup> (0.74 Å) is not remarkable, Ni<sup>2+</sup> ions in lattice structure can be replaced by Fe ions. The XRD analysis shows that these samples with  $x \le 0.02$  remain a single phase, i.e., NiO face-center-cubic (fcc) phase. However, the solubility of Fe in NiO is limited.<sup>19</sup> As x=0.05, a trace of Fe<sub>2</sub>O<sub>3</sub> appears in the XRD pattern of the sample. As x increases further, the samples become a mixture phase constituted by NiO, Fe<sub>2</sub>O<sub>3</sub>, and NiFe<sub>2</sub>O<sub>4</sub> ferrite. Next we will focus on the Fe-doped NiO samples with a single fcc phase.

Table I shows the effect of Fe dopant on the crystal size of NiO particles, which is calculated from three high angle peaks, i.e., (331), (420), and (422), using the common Scherrer formula after taking out the instrumental broadening. It can be seen from the results that the crystal grains are around 35–60 nm in diameter and become a little smaller as Fe dopant content increases, indicating that Fe ions could disturb the NiO crystal lattice and obstruct the crystal growth.



FIG. 1. XRD patterns of the  $Ni_{1-x}Fe_xO$  samples.

0003-6951/2005/87(20)/202501/3/\$22.50

Leuse of AIP content is subject to the terms at: http://scitati 87,202501-1 155 33 16 124 09: West 26 New 2014 11-58-08

<sup>&</sup>lt;sup>a)</sup>Electronic mail: cwnan@tsinghua.edu.cn

<sup>© 2005</sup> American Institute of Physics

TABLE I. Fe dopant dependence of the grain size of  $Ni_{1-x}Fe_xO$  (unit: nm).

(hkl)	NiO	Ni <sub>0.995</sub> Fe <sub>0.005</sub> O	Ni <sub>0.99</sub> Fe <sub>0.01</sub> O	Ni <sub>0.98</sub> Fe <sub>0.02</sub> O
(331)	58.6	48.6	48.7	43.1
(420)	53.1	44.6	44.9	36.6
(422)	60.8	45.0	47.4	38.1

SEM analysis (not presented here) indicates the particle sizes of all samples are around 100–200 nm. Thus the aggregations of grains and particles occur. The distribution of Fe element in NiO is uniform at by EDX map analysis.

Figure 2 illustrates the magnetic properties of  $Ni_{1-r}Fe_rO$ measured at room temperature. The inset is an enlarged part. It can be clearly seen that the moment of pure NiO shows a linear dependence on the extrinsic magnetic field, which is a characteristic of common antiferromagnetic NiO. When the Fe dopant content increases, the curve exhibits a distortion towards ferromagnetism. For example, the sample containing 1 mol% Fe becomes magnetic, while for 2 mol% Fe, a distinct ferromagnetic hysteresis loop can be observed, with a maximum magnetization of about 0.575 emu/g (~0.38  $\mu_B$ /Fe) at the maximum applied field of 10 kOe. This value is comparable with that reported for Mn-doped Cu<sub>2</sub>O,<sup>14</sup> and much larger than those for other DMS systems such as Ni-doped ZnO aggregates,<sup>7</sup> Mn,<sup>4</sup> Co,<sup>5,6</sup> and V<sup>8</sup> doped ZnO films.

Such ferromagnetic behavior has been observed in nanosized NiO.<sup>17,18</sup> According to Makhlouf et al.,<sup>18</sup> small NiO particles of < 8 nm in diameter would show less linear and larger magnetizations at 296 K, but for NiO particles of larger than 30 nm, no finite-size-effect induced magnetism could be observed. Although the grain size in our samples is several tens of nanometers (see Table I), it is still too large to result in ferromagnetism at room temperature. Kodama et al.<sup>17</sup> studied the hysteresis loops of NiO nanoparticles (31.5 nm in diameter) at 5 K. They found that even up to 70 kOe, the moment was unsaturated and the loop was open, which showed very different characteristics from our Fedoped NiO particles having the similar grain size. Moreover, for all samples the average particle size obtained via SEM is about 100-200 nm, suggesting that the grain aggregation exists, which might strongly weaken the finite size effect in our samples.

Shown in Fig. 3(a) is temperature dependence of the magnetization and coercivity of  $Ni_{0.98}Fe_{0.02}O$ . The magnetization of the sample is nearly independence of the tempera-







FIG. 3. (a) Temperature dependence of  $M_s$  and  $H_c$  of Ni<sub>0.98</sub>Fe<sub>0.02</sub>O sample, and (b) the loop shift as function of temperature for the sample Ni<sub>0.98</sub>Fe<sub>0.02</sub>O. The inset shows the hysteresis loops obtained at different temperatures.

ture over the testing range from 78 K to room temperature, which indicates that the Curie temperature is over the room temperature. However, the coercivity increases linearly when the temperature decreases. Of interest to note is the hysteresis loop shift observed in the sample. The loop shift could be enhanced greatly through decreasing temperature, reaching a large amount of 307 Oe at 78 K as shown in Fig. 3(b).

For the undoped NiO sample, it is antiferromagnetic below the Neel temperature (573 K), which can be seen in Fig. 2 and understood through the ordinary two sublattice model. As doped by magnetic Fe ions, defects could be introduced into NiO, i.e.,

$$Fe_{2}O_{3} \xrightarrow{\text{NiO}} 2Fe_{\text{Ni}}^{\bullet} + V_{\text{Ni}}'' + 3O_{o}$$
$$Fe_{\text{Ni}}^{\bullet} \leftrightarrow Fe_{\text{Ni}}^{\times} + h.$$

Thus the magnetic order in NiO grains would be interrupted, which causes relatively weak coupling between the sublattices and gives rise to ferromagnetism by double exchange through the introduced magnetic Fe ions and free charge carriers.

The ferromagnetism observed in the Fe-doped NiO could be associated with the ferromagnetic clusters in the samples. The ideal situation is that the doped Fe ions disperse uniformly in the NiO matrix. But for most cases there exists some composition inhomogeneity due to the limitation of the sample preparation process. Thus regions of both rich and lacking of Fe ions would co-exist, corresponding to the ferromagnetic and antiferromagnetic regions, respectively. Meiklejohn and Bean<sup>20,21</sup> had discovered the exchange anisotropy and referred it to the properties of exchange coupled ferromagnetic/antiferromagnetic materials. The effect is remarkable most simply by an offset of the field-cooled hysteresis loop from zero on the field axis. For our Fe-doped NiO at higher temperatures, the coupling between the ferromagnetic and anti ferromagnetic regions is weakened by thermal disturbance and thus the hysteresis loop is symmetrical. As the temperature decreases, the exchange interaction between the above two types of regions becomes stronger, resulting in the loop shift which becomes more prominent at lower temperature.

In conclusion, a room-temperature ferromagnetism has been observed in Fe-doped NiO. A maximum magnetization of about 0.575 emu/g (~0.38  $\mu_B$ /Fe) has been measured at 10 kOe in Ni<sub>0.98</sub>Fe<sub>0.02</sub>O. Finite-size-effect cannot explain the origin of the magnetism due to the much larger size and the aggregation of the crystal grains. The observed roomtemperature ferromagnetism and the large loop shift at low temperature could be associated with ferromagnetic clusters and ferromagnetic/anti ferromagnetic coupling due to the composition inhomogeneity. This would stimulate further interest in this area.

This work was supported by the NSF of China, the Ministry of S & T of China through a 973-Project under Grant No. 2002CB613303, and National High-Tech Research and Development Program of China under Grant No. 2003AA302120.

- <sup>1</sup>S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
- <sup>2</sup>T. Dietl, H. Ohno, F. Matsukure, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
- <sup>3</sup>Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science **291**, 854 (2001).

- <sup>4</sup>P. Sharma, A. Gupta, K. V. Rao, F. J. Owens, R. Sharma, R. Ahuja, J. M. Osorio Guillen, B. Johansson, and G. A. Gehring, Nat. Mater. **2**, 673 (2003).
- <sup>5</sup>D. A. Schwartz and D. R. Gamelin, Adv. Mater. (Weinheim, Ger.) **16**, 2115 (2004).
- <sup>6</sup>K. Rode, A. Anane, R. Mattana, J.-P. Contour, O. Durand, and R. LeBourgeois, J. Appl. Phys. **93**, 7676 (2003).
- <sup>7</sup>P. V. Radovanovic and D. R. Gamelin, Phys. Rev. Lett. **91**, 157202 (2003).
- <sup>8</sup>H. Saeki, H. Tabata, and T. Kawai, Solid State Commun. **120**, 439 (2001).
- <sup>9</sup>S. R. Shinde, S. B. Ogale, S. Das Sarma, J. R. Simpson, H. D. Drew, S. E. Lofland, C. Lanci, J. P. Buban, N. D. Browning, V. N. Kulkarni, J. Higgins, R. P. Sharma, R. L. Greene, and T. Venkatesan, Phys. Rev. B **67**, 115211 (2003).
- <sup>10</sup>S. R. Shinde, S. B. Ogale, J. S. Higgins, H. Zheng, A. J. Millis, V. N. Kulkarni, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **92**, 166601 (2004).
- <sup>11</sup>S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **91**, 077205 (2003).
- <sup>12</sup>H. Saito, V. Zayets, S. Yamagata, and K. Ando, Phys. Rev. Lett. **90**, 207202 (2003).
- <sup>13</sup>J. He, S. Xu, Y. K. Yoo, Q. Xue, H. Lee, S. Cheng, X. D. Xiang, G. F. Dionne, and I. Takeuchi, Appl. Phys. Lett. **86**, 052503 (2005).
- <sup>14</sup>M. Wei, N. Braddon, D. Zhi, P. A. Midgley, S. K. Chen, M. G. Blamire, and J. L. MacManus-Driscoll, Appl. Phys. Lett. 86, 072514 (2005).
- <sup>15</sup>Y. Nakamura, H. Ogawa, T. Nakashima, A. Kishimoto, and H. Yanagida, J. Am. Chem. Soc. **80**, 1609 (1997); J. Wu, C.-W. Nan, Y. Lin, and Y. Deng, Phys. Rev. Lett. **89**, 217601 (2002).
- <sup>16</sup>O. Bidault, M. Maglione, M. Actis, and M. Kchikech, Phys. Rev. B 52, 4191 (1995).
- <sup>17</sup>R. H. Kodama, S. A. Makhlouf, and A. E. Berkowitz, Phys. Rev. Lett. **79**, 1393 (1997).
- <sup>18</sup>S. A. Makhlouf, F. T. Parker, F. E. Spada, and A. E. Berkowitz, J. Appl. Phys. **81**, 5561 (1997).
- <sup>19</sup>M. Kurzawa and A. Blonska-Tabero, J. Therm Anal. Calorim. **77**, 65 (2004).
- <sup>20</sup>W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956); **105**, 904 (1957).
- <sup>21</sup>W. H. Meiklejohn, J. Appl. Phys. **33**, 1328 (1962).