PHYSICAL REVIEW B **73**, 193308 (2006)

Ferromagnetism and electrical transport in Fe-doped NiO

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(Received 18 January 2006; revised manuscript received 16 April 2006; published 16 May 2006)

We report Fe-doped NiO nanopowder, exhibiting room ferromagnetism mainly arising from the double exchange mechanism through the doped Fe ions and free charge carriers. Electrical measurements reveal that ac conductivity of the polycrystalline ceramics with Fe-doped NiO can be expressed as the sum of a frequency-independent conductivity σ_1 and a frequency-dependent one σ_2. The latter σ_2 can be represented by the frequency dispersion for the dielectric loss due to the hopping diffusion of charge carriers with a single effective staying time $\tau \sim 6.11 \times 10^{-10}$ s at a lattice site.

DOI: 10.1103/PhysRevB.73.193308 PACS number(s): 75.50.Tt, 75.10.Hk, 73.22.−f

Diluted magnetic semiconductors (DMSs) have been intensively studied in connection with their potential applications for the spintronic devices.[1] There have been considerable recent interest in the design of DMS with a particular focus on the exploration of different oxide-based semiconductor hosts (e.g., ZnO, TiO_2, SnO_2, perovskite $ATiO_3$, etc).[2] A lot of work on preparation and investigation of ferromagnetic (FM) mechanism of these systems with transition metal (TM) ions doped have been reported.[3]

Nickel oxide NiO is a strongly correlated material which exhibits insulating character and antiferromagnetic (AFM) order that remains even at rather high temperatures $T_N = 523$ K.[4] The measured optical gap of NiO is about 4.0 eV, clearly indicating that it behaves as an insulator with room-temperature conductivity less than 10^{-13} S/cm.[5] Although pure NiO is a Mott-Hubbard insulator at room temperature, an introduction of Ni^{2+} vacancies or doping with Li^+ will cause considerable increase in the conductivity of NiO.[6] In doped NiO, a lot of intensive investigations have been conducted for its great theoretical and technological importance due to the special electrical behaviors and related spin dynamics.[7]

The magnetic structure of NiO consists of ferromagnetic sheets of Ni^{2+} parallel to the (111) plane with opposite spin directions in neighboring sheets. No direct cation-cation exchange can take place in NiO since the t_{2g} orbitals are full, but 90° Ni-O-Ni interactions can occur via the oxygen $2s$ and $2p$ orbitals.[8] Recently, Kodama and his co-workers[9] observed anomalous large moments, coercivities, and loop shifts in NiO nanoparticles, and ascribed to a new finite size effect due to sublattice configurations. Janusz *et al.*[10] precluded the possibility of the ferromagnetic double-exchange coupling in the system $Li_xNi_{1-x}O$ $(x<0.3)$ and concluded the lack of magnetism. Goodenough *et al.*[11] proved that a FM phase along with a rhombohedral distortion of the lattice was observed for $x>0.3$. Battle *et al.*[12] investigated the structure of the antiferromagnet $Co_pNi_{1-p}O$ by the neutron diffraction, and found that the solid solutions undergo AFM ordering and that T_N is a linear function of composition. However, up to now, there are seldom reports on the ferromagnetism in the TM ion-doped NiO.

The present work is a sequel to an earlier brief publication,[13] in which the room-temperature FM behavior of the Fe-doped NiO nanoparticles was reported. Here we discuss the FM properties of the Fe-doped NiO, different from the finite size effect induced magnetism observed in nanosized NiO, and mainly report on the frequency and temperature dependence of the ac conductivity $\sigma(\omega, T)$ in NiO-based ceramics.

$Ni(NO_3)_2 \cdot 6H_2O$ (A.R.), $Fe(NO_3)_3 \cdot 9H_2O$ (A.R.), and NH_4HCO_3 (A.R.) were employed as starting raw materials. $Fe_xNi_{1-x}O$ $(x{:}\,0\text{–}0.02)$ nanoparticles, i.e., NiO (NFO-0), $Fe_{0.005}Ni_{0.995}O$ (NFO-1), $Fe_{0.01}Ni_{0.99}O$ (NFO-2), and $Fe_{0.02}Ni_{0.98}O$ (NFO-3) were synthesized by a chemical coprecipitation and postthermal decomposition method. The polycrystalline NFO ceramic samples with the above-mentioned composition were prepared by sintering the corresponding NFO nanopowders via a traditional ceramic processing.

X-ray diffraction (XRD) patterns were obtained at room temperature using Cu $K\alpha$ radiation to study the phase composition. The x-ray photoelectron spectroscopy (XPS) presented was recorded at room temperature using a Al $K\alpha$ source ($h\nu = 1486.6$ eV). The magnetic behavior was measured by a vibrating sample magnetometer equipped with a dewar for low temperature testing. The ceramic samples were polished, and electroded by sputtering gold. The ac conductivity of the specimens was measured using a HP4285 impedance analyzer over a frequency range from 100 Hz to 1 MHz and a temperature range from −50 to 200 °C, with an accuracy of ±0.1 °C.

The microstructure and phase composition of the particles and ceramics [see Fig. 1(a)] indicate that all NFO samples contain a single fcc NiO phase. Because the radius difference between the Ni^{2+} ion (0.69 Å) and the Fe^{3+} ion (0.64 Å) is not remarkable, Ni^{2+} ions in lattice structure can be replaced by Fe ions. The existence of the Fe ions in the present $Ni_{1-x}Fe_xO$ samples is verified by the XPS measurements [e.g., see Fig. 1(b)]. It can be seen that the spectrum consists of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks as well as their satellite structures, which is consistent with the previously reported data.[14] However, no metallic Fe^0 (binding energy $\sim$706 eV) was observed in our samples.

For the undoped NiO sample, it is AFM below the Néel

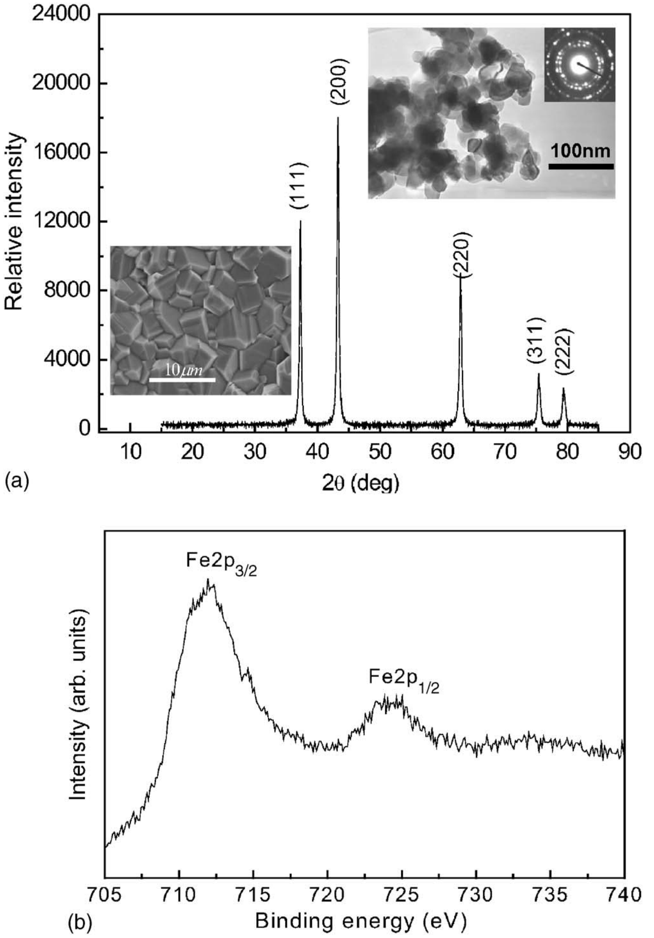

FIG. 1. (a) XRD pattern and (b) the core-level XPS spectra of Fe $2p$, for the NFO-3 sample. The insets in (a) show typical TEM and SAED patterns for the nanosized powder and SEM cross-section micrographs for the ceramic bulk sample.

temperature (573 K). By increasing the content of the Fe doping, the samples exhibit obvious FM properties at room temperature and the magnetization loops exhibit a remanent magnetization and characteristic FM hysteresis cycle. As shown in the inset of Fig. 2, a distinct FM hysteresis loop at room temperature and 100 K can be observed in the NFO-3 sample with a maximum magnetization of 0.575 emu/g ($\sim 0.38\mu_B$/Fe) at the applied field of 10 kOe and room temperature, which can be comparable to that reported for Mn-doped $\mathrm{Cu_2O}$,[15] and much larger than those other DMS systems such as Ni-doped ZnO aggregates,[16] Mn-, Co-, and V-doped ZnO films.[17] The FM behavior observed in NiO particles of smaller than 8 nm in diameter by Makhlouf *et al.*[9] showed less linear and larger magnetizations at 296 K, but the ferromagnetism disappeared for NiO particles of larger than 30 nm. However, the grain size in our samples is larger than 30 nm [Fig. 1(a)], and finite size effect cannot explain the origin of the magnetism. As previously reported,[18] in the Fe-doped oxide-based DMS systems, the possible presence of a secondary phase (e.g., metallic magnetic Fe particles) can also be the origin of ferromagnetism. As for our Fe-doped NiO samples, the origin of ferromagnetism can be ruled out by the secondary phase, as evidenced by the Fe $2p$ XPS spectra and XRD results (Fig. 1).

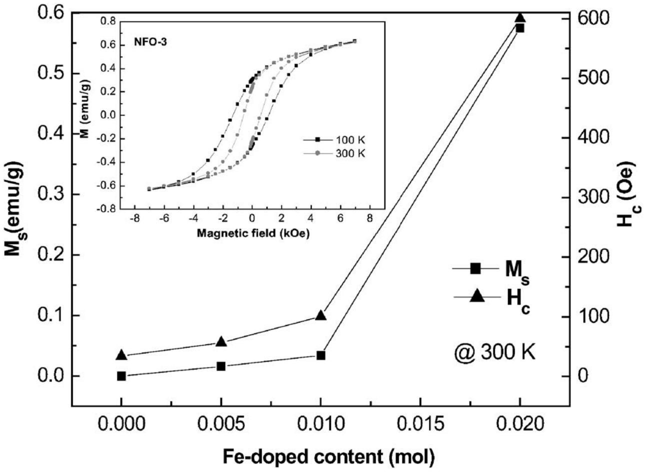

FIG. 2. Fe-doped concentration dependence of the magnetization and coercive field for various NFO samples; inset is a typical ferromagnetic hysteresis loop of the NFO-3 sample at 300 and 100 K.

Seebeck coefficient measurements illustrate that our undoped and Fe-doped NiO samples exhibit positive values and indicate that the holes are major carriers in the samples. In these p-type Fe-doped NiO samples, the Ni ions are partially substituted by the Fe ions, which are randomly localized over the host lattice. Thus, this kind of disorder certainly breaks the translation symmetry of the system and the original magnetic order in NiO grains is interrupted. The ferromagnetism in the Fe-doped NiO could be caused by the double exchange through the introduced magnetic Fe ions and the related defects (e.g., $\mathrm{Fe}_{\mathrm{Ni}}^{\bullet}$). An electron is weakly trapped in the $\mathrm{Fe}_{\mathrm{Ni}}^{\bullet}$ defect site, where the electron occupies an orbital which overlaps the d shells of both Fe neighbors. As shown in Fig. 2, it is noting that the maximum magnetization increased from 0.016 to 0.575 emu/g by increasing the Fe-doped concentration, which can be ascribed to the fact that the increase in the magnetic Fe ions and the $\mathrm{Fe}_{\mathrm{Ni}}^{\bullet}$ defects with the concentration of doped Fe ions increasing enhances the FM double-exchange interaction.

The ac conductivities of the Fe-doped and undoped NiO polycrystalline ceramics have been measured at various frequencies and temperatures. As shown in Fig. 3, above 320 K, the conductivity is independent of a frequency for 0.5% Fe-doped NiO ceramic samples. The observed values can be expressed as the sum of a frequency-independent conductivity σ_1 and a frequency-dependent one σ_2 shown in the inset of Fig. 3. It is of interest to note that the high-frequency conductivity is almost temperature-independent at low temperatures, and the total conductivity is nearly equal to σ_2. The similar phenomena are also observed in the other NFO ceramic samples.

As shown in Fig. 4, the temperature-independent conductivity σ_2 at low temperatures can be fitted with the frequency dispersion formula given for the dielectric loss due to the hopping diffusion of charge carriers around the defects by Pollak *et al.*,[19] with a staying time τ at a site, i.e.,

$$\sigma_2 - \sigma_{dc} \propto \omega^2\tau/(1+\omega^2\tau^2). \qquad (1)$$

The fitting of the data to Eq. (1) gives an effective staying time $\tau \sim 6.11\times10^{-10}$ s. This τ value is quite close to the

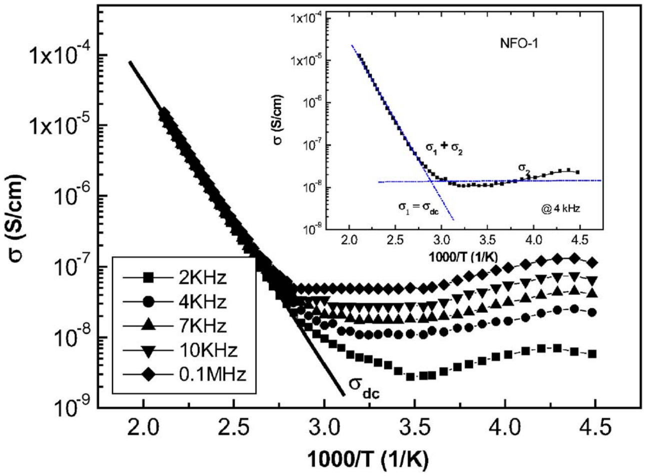

FIG. 3. (Color online) Temperature dependence of ac conductivity for the NFO-1 sample at several frequencies; inset is ac conductivities at 4 kHz.

single staying time of $\sim 2.22\times 10^{-10}$ s obtained in Li-doped NiO single crystals.[20]

As discussed previously,[13] the ferromagnetism observed in the Fe-doped NiO could be associated with the ferromagnetic nanoclusters due to possible composition inhomogeneities of both rich and lacking of Fe ions. Thus the effective staying time τ for the hopping of charge carriers (i.e., holes) could be attributed to different defect scattering mechanisms, e.g.,

$$1/\tau = 1/\tau_o + 1/\tau_c, \tag{2}$$

where τ_o is associated with the hopping of holes around a Ni vacancy, and the hole hopping is among the 12 equivalent positions surrounding the Ni vacancy as in Li-doped NiO single crystals.[20] Thus τ_o is in 10^{-10} s order of magnitude obtained in Li-doped NiO single crystals. Here τ_c is associated with mesoscopic inhomogeneities such as the ferromagnetic clusters (FM nanoregions), and is accounted for the cluster boundary scattering of holes. The relaxation time τ_c, to the first-order approximation, proportional to the nanocluster size, is larger than τ_o. Thus, $\tau \sim \tau_o$, i.e., the frequency dispersion yields a single effective staying time in the Fe-doped NiO, as in Li-doped NiO.[20]

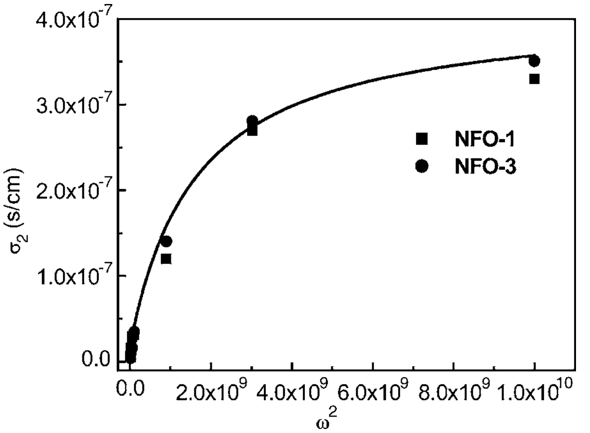

FIG. 4. Frequency dependence of ac conductivity σ_2 for the NFO-1 and NFO-3 samples in the low temperature range. The solid curve is the fitted line by Eq. (1).

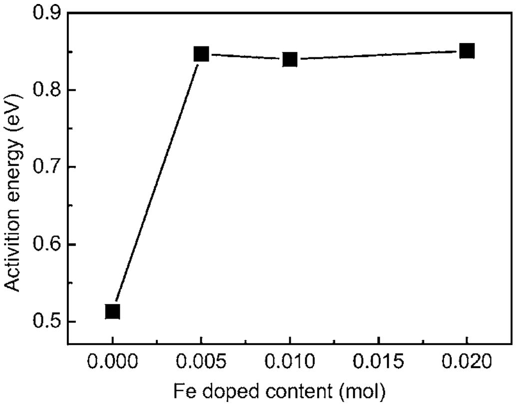

FIG. 5. The activation energy of various NFO polycrystalline ceramic samples.

According to the polaron theory, an expression for the temperature dependence of the dc conductivity of the doped NiO is, with a temperature-dependent prefactor, given by the following simple equation[21]

$$\sigma_{dc} \propto T^{-1}\exp(-E_g/k_B T), \tag{3}$$

where E_g, k_B, and T are the activation energy, Boltzmann constant, and absolute temperature, respectively. Using Eq. (3), we can get the activation energy E_g of these ceramic samples. As shown in Fig. 5, obviously, doped Fe ions lead to the increase of the activation energy (from ~0.51 to ~0.85 eV), like the case in the Ga^{3+}, In^{3+}, and Cr^{3+} doped NiO where the considerable increase in the activation energy was also observed.[22] In the Fe-doped NiO, the generation of $Fe^{\bullet}_{Ni}$ donor centers tend to raise the Fermi level (E_F), and they are incorporated with the formation of nickel vacancies, $[Fe^{\bullet}_{Ni}]=2[V''_{Ni}]$, with some holes left in the V''_{Ni} level, which is to be expected to be far away from the valence band. Therefore, the activation energy is increased. Of interest to note, the doping concentration of Fe has little influence on the activation energy in the measured temperature range (~0.85 eV) and the activation energy tends to be saturation, which is probably due to the solubility restrictions increasing with the doping concentration as in the Cr^{3+}-doped NiO specimens.[23]

It is generally believed that the long-range ferromagnetic exchange can be mediated by carriers in a spin-polarized band. The ferromagnetic properties in oxide-based DMSs stabilized or enhanced by the electron or hole doping have been predicted theoretically and confirmed by some experiments.[24] For our Fe-doped NiO samples, the activation energy is almost constant in the Fe-doped concentration range 0.005–0.02 mol, therefore, we can assume that the donor level stays approximately constant with respect to the valence band. However, the samples' conductivity (i.e., hole concentration) is obviously different from each other due to the compensation effect induced by the Fe-related defects, so are their magnetic properties. Quantitative evaluation of the effect of carrier concentration on the ferromagnetic properties is desirable, and further work is needed to reveal the relation between the temperature and doping dependence of conductivity and magnetic hysteresis.

In summary, room-temperature ferromagnetism observed in Fe-doped NiO samples is associated with ferromagnetic clusters from the doping Fe ions and the related defects. The ac conductivity of the Fe-doped NiO samples shows a strikingly dispersion at temperatures below 320 K, which can be expressed as the sum of a frequency-independent conductivity and a frequency-dependent one. The doping concentration of Fe has little influence on the activation energy of dc conductivity in the measured temperature range.

This work was financially supported by the Ministry of Sci & Tech of China through a 973-Project, under Grant No. 2002CB613303, NSF of China (Grant Nos. 50502024 and 50425721, and 10574078) and the Nova program of Beijing. Y. L would like to thank P. Mahadevan for her helpful discussions.

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