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Tunneling Magneto-Resistance Effect of Fe_4N with MgO Barrier

Yoshihide Kimishima, Koki Homma, Masatomo Uehara and Ryota Taninoki

Department of Physics, Faculty of Engineering, Graduate School of Yokohama National University,
Tokiwadai 79-5, Hodogaya, Yokohama 240-8501, Japan
Fax: +81-45-339-4182, e-mail: kimi@ynu.ac.jp

γ'-Fe_4N is the ferromagnetic material with high Curie temperature and relatively high electrical conductivity. First principle calculation showed that the γ'-Fe_4N was a half-metal by 100% spin polarized conduction electrons with minority spins. So we expected large tunneling magneto-resistance effect in the Fe_4N/MgO/Fe_4N junctions. γ'-Fe_4N was prepared by sintering Fe_3O_4 nanoparticles in the atmosphere of NH_3/H_2 gas mixture at 673 K . Then MgO was added to the γ'-Fe_4N powder and sintered at about 473 K in pure Ar gas. Magneto-resistance was measured by 4-terminals method for x=0-0.8 samples of $(MgO)_x(Fe_4N)_{1-x}$, and magneto-resistance ratios of -1.2~-1 % were observed for x=0.3~0.6 samples at 300K. It is the first observation of tunneling magneto-resistance effect for γ'-Fe_4N granular system.

Key Words : γ'- Fe_4N, MgO, magnetization, magneto-resistance, TMR

1. INTRODUCTION

Perovskite-type iron nitride γ'- Fe_4N is a ferromagnet with a large magnetic moment below the Curie temperature T_c of 761 K [1], and has been considered as a promising material for magnetic recording media. The electronic structure of this compound has been calculated [2, 3], and a recent result for the spin polarization coefficient P [4] showed that this compound was a perfectly spin-polarized material with $P = -1$ at the Fermi level E_F. Here P was defined by $(\sigma_\uparrow - \sigma_\downarrow)/(\sigma_\uparrow + \sigma_\downarrow)$, and $\sigma_\uparrow$ and $\sigma_\downarrow$ were the conductivities of up and down spin electrons, respectively. Thus Fe_4N is a candidate of spintronics material for magnetic random access memory (MRAM) *etc.*

Powder specimens of γ'-Fe_4N have been prepared in atmospheres of NH_3+H_2 mixed gases from the precursors of Fe [5], $FeCl_2$ [6], Fe_2O_3 [7] and Fe_3O_4 nano-particles [8]. In particular, Wu *et al.* [8] revealed the gradual conversion of Fe_3O_4 into γ'-Fe_4N by reduction and nitriding in NH_3+H_2 mixed gases between 673 K and 973 K. They reported the measured results of magnetization and permeability of four kinds of samples, which were sintered at 673 K, 773 K, 873 K, and 973 K, but did not report any magneto-resistance data.

In the previous studies, highly oriented or single-crystalline MgO was revealed as a good tunneling barrier for the polarized conduction electrons [9]. Therefore, the present authors are interested in the magneto-resistive behaviors of the Fe_4N/MgO granular system, and describe their experimental results for the magnetization, resistivity, and magneto-resistance in this paper.

2. SAMPLE PREPARATION

First, the precursors of Fe_3O_4 nano-particles were prepared from a mixed aqueous solution of $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ with the mole ratio of 1:2. When an aqueous ammonium solution (NH_4OH) was dripped onto the above mixed solution, Fe_3O_4 nano-particles with a diameter of about 10 nm were precipitated [10-12]. Washed and dried Fe_3O_4 nano-particles were pressed to form pellets with a diameter of 10 mm, and sintered in the NH_3+H_2 mixed gases for 12 hours at 673 K. Then the mixtures of prepared γ'-Fe_4N specimen and MgO powder were sintered at 473K for 3 hours in air.

Powder Cu$K\alpha$ X-ray diffraction (XRD) patterns of $(MgO)_x(Fe_4N)_{1-x}$ samples are shown in Fig. 1, where x is the mol ratio of MgO. The crystal structure of γ'- Fe_4N is a cubic perovskite with the lattice parameter of a = 0.379 nm [13], while MgO has a NaCl structure with a = 0.4211 nm [14].

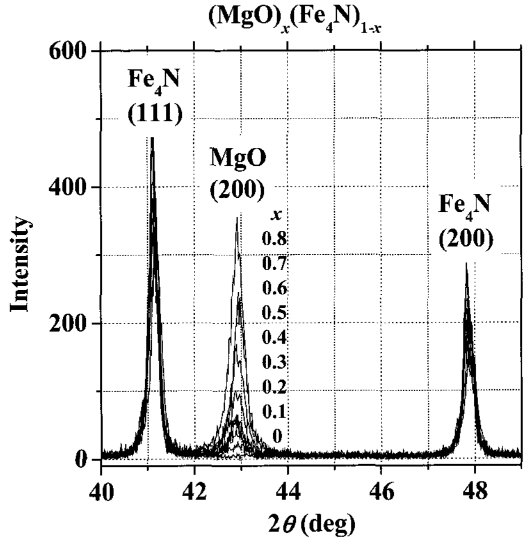


Fig. 1 XRD patterns of $(MgO)_x(Fe_4N)_{1-x}$ samples from x=0 to 0.8.

From the half width of each diffraction peak, the mean diameter d of Fe_4N and MgO particles were estimated by Sherrer's formula as about 80 nm and 30 nm, respectively.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Magnetization

The magnetization M was measured by means of a vibrating sample magnetometer (VSM) between 77 K and 300 K. Fig. 2 shows the temperature dependence of M at 5 kOe. The magnitude of M monotonically decreases with the mole ratio x of MgO.

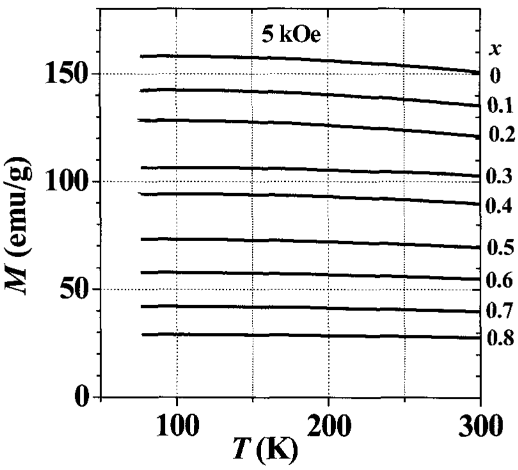


Fig. 2 Temperature dependence of the magnetization at 5 kOe, where x is the mole ratio of MgO.

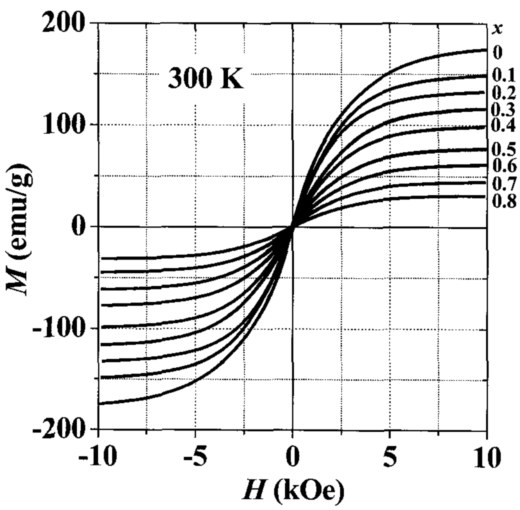


Fig. 3 Field dependence of the magnetization at 300 K, where x is the mole ratio of MgO.

Field dependences of magnetization M at 300 K are shown in Fig. 3. The saturation magnetization M_s at 77 K and 300 K were 189 emu/g and 179 emu/g, respectively for the $x = 0$ sample of pure γ'-Fe_4N, as shown in Fig.4. These values are considered to be reasonable when compared with data in the preceding literature [8, 15, 16].

The values of M_s decrease almost linearly with increasing x, obeying the relation of

$$M_s(x) = (1-x)\, M_s(0) \qquad (1).$$

It shows that non-interactive coexistence of γ'-Fe_4N and MgO phase is realized in each sample. The coercive fields H_c's were about 50 Oe and 90 Oe at 300 K and 77 K, respectively, for all of the samples.

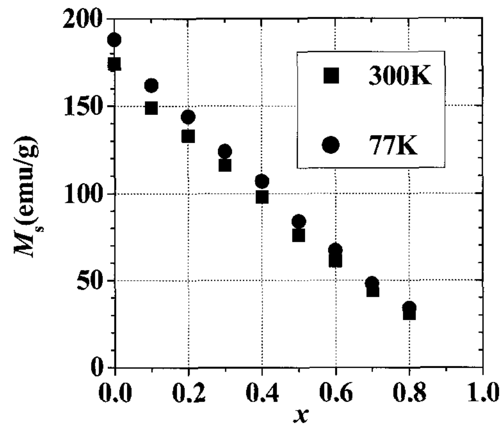


Fig. 4 x-dependence of the saturation magnetization at 300 K and 77 K.

3.2 Resistivity

Resistivity ρ was measured by the four-terminals dc method between 77 K and 300 K. The $T^{-1/2}$ dependences of ρ are plotted in Fig. 5 by means of a semi-logarithmic scale.

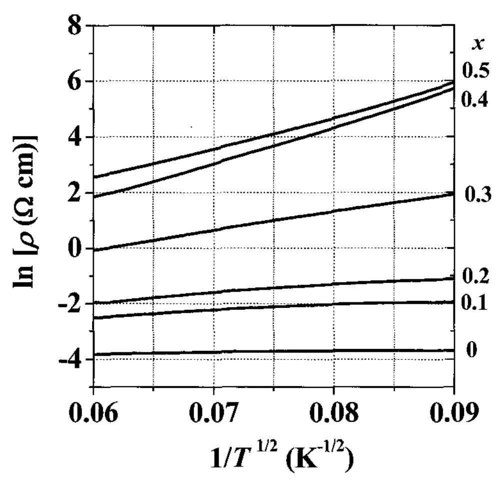


Fig. 5 $T^{-1/2}$ dependences of ρ plotted by means of a semi- logarithmic scale.

For an $x = 0$ sample of pure γ'-Fe_4N, weakly semi-conductive behavior appears in the ρ (T)-curve. It was assumed that the magnitude of ρ monotonically increased with x, because MgO was an insulator with very high ρ. As shown in Fig. 5, ρ drastically increased with increasing x. In addition, the linearity of $\ln \rho$ to $T^{-1/2}$ appears for the sample above $x = 0.1$. The tunneling magneto-resistance (TMR) theory [17, 18] gives the following expression for the resistivity of a granular system.

$$\rho = \frac{\rho_0}{1+P^2m^2}\exp\left(\sqrt{\frac{\Delta}{T}}\right) \quad (2),$$

where ρ_0 and Δ are constants, P is the spin polarization coefficient of conduction electrons, and m is defined by M/M_s. The parameter Δ is defined by $8\kappa C$, where C= sE_c=const. and $\kappa = \sqrt{2m^*(V-E_F)/\hbar^2}$. The parameter m^* is the effective mass of electrons, V is the barrier potential, E_F is the Fermi energy, s is the barrier thickness, and E_c is the charging energy.

The linear dependence of $\ln \rho$ on $T^{-1/2}$ shows that the MgO grains form good TMR barriers, and the increasing gradient of $\ln \rho$ vs. $T^{-1/2}$ curve means that the barrier potential is enlarged by the increasing of Mg content x.

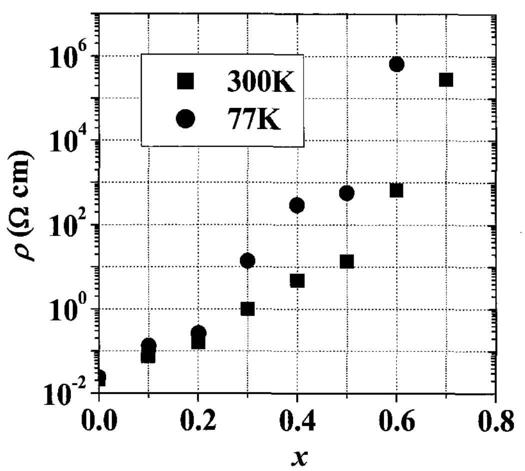
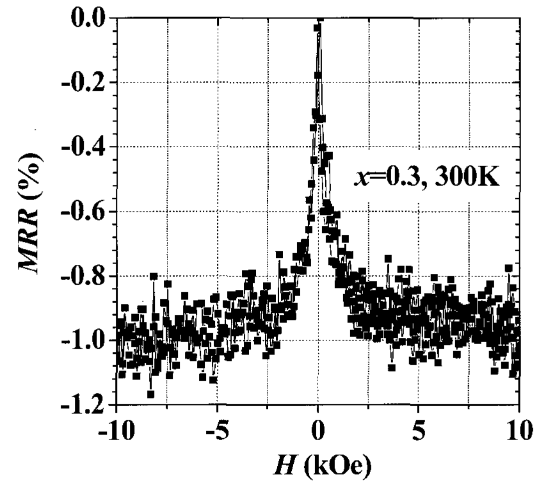


Fig. 6 x-dependence of the resistivity ρ at 300K and 77K.

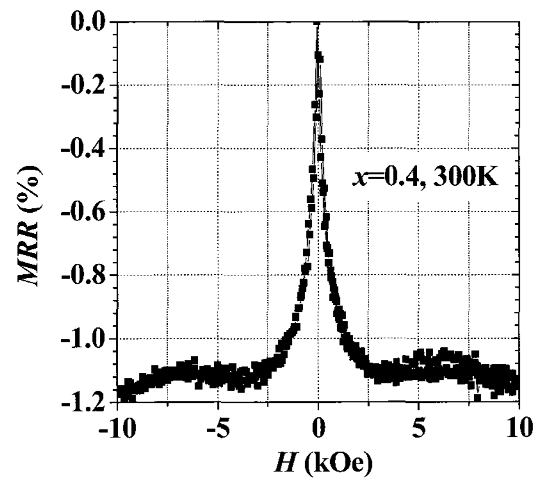
The x-dependences of ρ at 300 K and 77 K are shown in Fig. 6 by a semi-logarithmic scale, where ρ rapidly increases above x = 0.3. If x reaches near the percolation threshold [19, 20], the conducting paths of γ'-Fe_4N begin to disconnect from end to end of the sample. Therefore we can assume that the percolation threshold x_c is above 0.3. In this x-region, the connectivity of γ'-Fe_4N grains becomes very weak and the MgO grains with high resistivity between γ'-Fe_4N particles play an important role. The present system, including optimum tunneling barriers of MgO, should exhibit large TMR, since the linear change of $\ln \rho$ with $T^{-1/2}$ supports the notion that good TMR junctions are formed.

3.3 Magneto-resistance

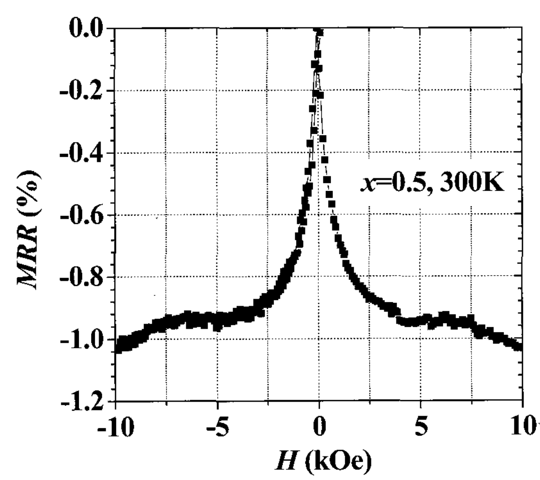
The field dependence of the resistivity $\rho(H)$ was measured between −10 kOe and 10 kOe at 300 K and 77 K, and the experimental results of the magneto-resistance ratio (MRR) are shown in Fig. 7(a)-(d) for x = 0.3, 0.4, 0.5 and 0.6 samples. Here the MRR is defined by



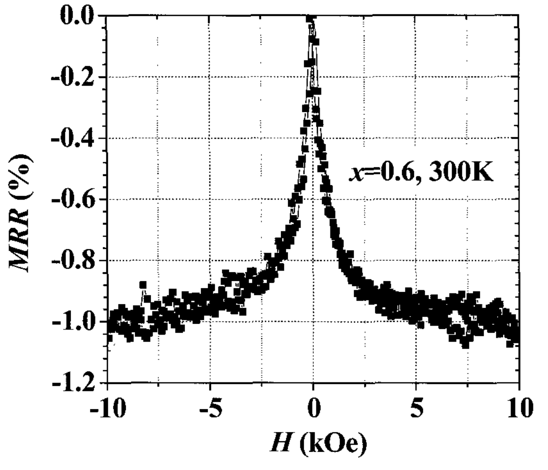
(a)



(b)



(c)



(d)

Fig. 9 Field dependence of the magneto-resistance ratio *MRR* at 300 K for $x = 0.3$ (a), $x = 0.4$ (b), $x = 0.5$ (c), $x = 0.6$ (d).

$[\rho(H) - \rho(H_P)] / \rho(H_P)$, where H_P is the peak field at which $\rho(H)$ becomes maximum. In the case of TMR, the H_P is generally consistent with coercive field H_c of ferromagnetic parts.

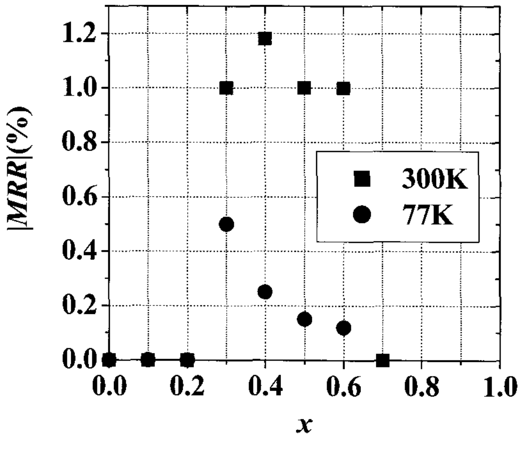


Fig.8 x-dependences of *MRR* at 300 K and 77 K.

The x-dependences of *MRR* at 300 K and 77 K are shown in Fig. 8. The *MRR*'s were apparently observed only for x=0.3-0.6 samples, where the values of $|MRR|$ are 1-1.2 % at 300 K, and 0.2-0.5 % at 77 K. The value of $|MRR|$ at room temperature may be due to the tunneling barriers of MgO at the inter-grain part between γ '-Fe_4N grains. It is the first observation of TMR effect for γ '-Fe_4N granular system. Peak values of $|MRR|$ near the percolation threshold has also been reported for half-metallic CrO_2 with TiO_2 [21] and polymer barriers [22] at 77 K.

4. CONCLUSION

Mixtures of $(MgO)_x(\gamma\text{'-}Fe_4N)_{1-x}$ were prepared from commercial MgO and γ '-Fe_4N from Fe_3O_4 nano-particles in NH_3+H_2 mixed gases. The magnetization M and the saturation magnetization of M_s could be explained by the non-interactive co-existence of γ '-Fe_4N and MgO phase in each sample. The temperature and field dependence of the resistivity showed that good TMR junctions were formed at x = 0.3-0.6 near the percolation threshold. Relatively large $|MRR|$ values of 1-1.2 % were observed at room temperature, which may be due to the effective TMR barriers of MgO in the grain boundaries between γ '-Fe_4N particles. It is the first observation of TMR effect for γ '- Fe_4N granular system.

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