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Appearance of Variable-Range-Hopping Conduction and Enhanced Spin Dependent Transport by Low Temperature Heat Treatment for Magnetite Nanoparticle Sinter

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1. Introduction

Although present electronics mainly depends on the control of a charge of electrons, spintronics is aimed at controlling of spin of electrons as well as an electronic charge. Therefore a half-metal, such as magnetite (Fe_3O_4), chromium dioxide (CrO_2) and $La_{2/3}Sr_{1/3}MnO_3$, is the most promising candidate material for spintronics devices. A half-metal is characterized by the presence of an energy gap in the majority spin band and no gap in minority spin band at the Fermi level. It is considered that a half-metal has completely spin-polarized conduction electrons. Magnetite nanoparticle sinter (MNPS) is the colossal assembly of magnetite nanoparticles and we can expect large effects on spin-dependent transport, because this system has enormous magnetic domains with spatially random spin orientation. As the spin orientation can be ordered by an applied magnetic field, we can anticipate a large change of magneto-resistance. Decreasing the diameter of a magnetite particle, it has been reported that a single magnetic domain is formed below ~100nm. In addition, the magnetite particle is considered to show the super-paramagnetic behavior below ~20nm. The combination style between magnetite nanoparticles of the MNPS is very sensitive for the method of the heat treatment, especially the temperature and the gas atmosphere. In this paper, we present the studies on the electrical conduction mechanism and the spin dependent transport of the MNPS made by low temperature HT through the electrical and magneto-resistance measurements.

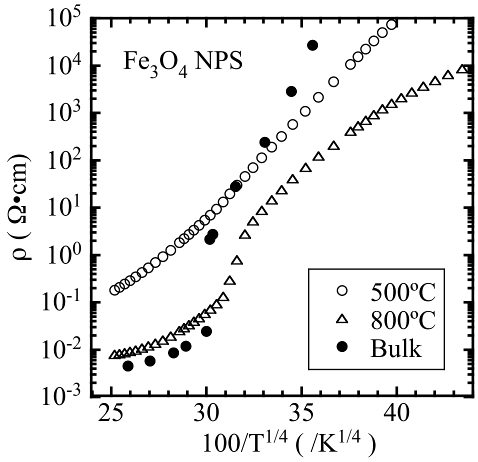

Fig. 1 Temperature dependence of the electrical resistivity of the MNPS for 500ºC and 800ºC samples.

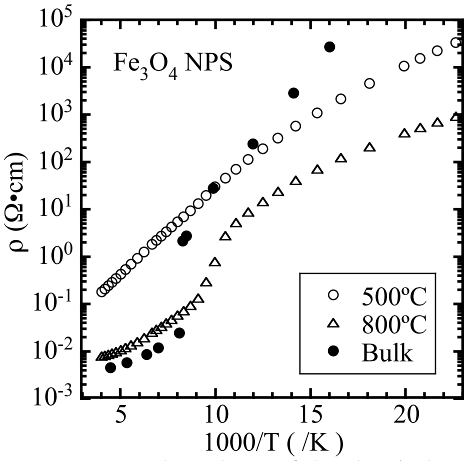

Fig. 2 Temperature dependence of the electrical resistivity of the MNPS for 500ºC and 800ºC samples (Arrhenius plot).

2. Experimental Procedures

The magnetite nano-particles (MNP's) were prepared by the chemical wet synthesis, and the average diameter of those is ~10nm. The MNP's were compacted by use of the hydraulic press-machine with the pressure of 3t/cm^2. The MNPS were made from the compacted MNP's by the HT at 500ºC and 800ºC for 5 hours in the atmosphere of Ar(90%)/H_2(10%). The MNPS were cut to a rectangular shape, 3x8x1mm^3, by use of the low speed diamond wheel saw. The four electrodes were attached to the rectangular shaped MNPS for 4-probe resistivity measurement. The MNPS were set to the closed-cycle He-refrigerator and the temperature was varied between 4K and 250K. The magnetic field was applied to the MNPS up to 0.7T by utilizing the electromagnet.

3. Experimental Results and Discussion

Magnetite (Fe_3O_4) is a mixed-valence iron oxide and the octahedral 6-coordinated B-site is occupied by Fe^{3+} and Fe^{2+}. The electrical conduction is caused by the hopping of a conduction electron with the minority spin from Fe^{2+} to Fe^{3+} in B-site. Magnetite shows a temperature-induced metal-insulator transition, which is called the Verwey transition [1]. The electrical resistivity (ER) of magnetite single bulk crystal abruptly increases by 2 orders of magnitude at ~123K, which is called the Verwey temperature, with decreasing temperature. Figure 1 shows the temperature dependence of the ER of the MNPS for 500ºC and 800ºC samples. The horizontal axis is given by

100/T$^{1/4}$ with the temperature T. For the comparison, the ER for the bulk single crystal is also shown in this figure. Regarding the MNPS for a 500ºC sample, the distinct jump of the ER has not been observed and the ER gradually varies with the temperature. However the magnetization indicates a slight jump at ~110K [2], which is near the Verwey temperature of a bulk single crystal. On the other hand, the ER of the MNPS for an 800ºC sample shows an abrupt change at ~110K by one order of magnitude. In strong disorder systems, Mott's variable range hopping (VRH) conduction is considered to occur in low temperature regions. The electrical resistivity by the VRH conduction is expressed as $\rho(T)=\rho(\infty)\exp\{(T_0/T)^{1/4}\}$. As seen in this Fig. 1, the ER of the MNPS for a 500ºC sample obeys the VRH expression below ~110K. On the contrary, the VRH dependence of the ER for an 800ºC sample cannot be observed in whole temperature regions of measurements. This indicates that the MNPS for a 500ºC sample corresponds to a stronger disordered system than that of an 800ºC sample. Figure 2 shows the temperature dependence of the ER of the MNPS for 500ºC and 800ºC samples by use of the Arrhenius plot. The ER of the MNPS for a 500ºC sample obeys the nearest neighbor hopping (NNH) expression, $\rho(T)=\rho(\infty)\exp(T_1/T)$, above ~110K. The NNH dependence of the ER for an 800ºC sample cannot be observed. The electrical conduction for an 800ºC sample is considered to follow the other conduction mechanisms. We consider that the MNPS for a 500ºC sample includes the large region of amorphous-like grain-boundary. The electrical conduction is inferred to be mainly dominated by the grain-boundary conduction (GBC), as compared with the inter-grain conduction (IGC). In this model, localized spin-orientation in grain-boundary region is regarded to be relatively random. In the absence of magnetic field, the conduction electron in the amorphous-like grain-boundary region should change the spin-orientation of that whenever the conduction electron hops to another site with different spin-orientation. By the application of magnetic field, the orientation of localized-spin approaches the direction of the magnetic field. As a consequence, the negative differential magneto-resistance (ND-MR) can be observed for the MNPS. Figure 3 shows the change of magneto-resistivity of the MNPS for 500ºC and 800ºC samples at 150K. The solid and dotted lines are the experimental and theoretical results, respectively. Here $\Delta\rho(B)$ means $\rho(B)-\rho(0)$ with the resistivity $\rho(B)$ at the magnetic field B. $\Delta\rho(B)/\rho(0)$ is proportional to $M(B)^2$ at low magnetic field, where $M(B)$ is the magnetization. If we assume that the magnetization $M(B)$ is expressed by the Langevin function $L(\beta)=\coth(\beta)-1/\beta$, we get

$$\Delta\rho(B)/\rho(0)=\alpha(T)L^2[\gamma(T)B]. \quad (1)$$

Here $\alpha(T)$ and $\gamma(T)$ are the temperature dependent parameters. As seen in Fig. 3, we find a good agreement between the experimental and theoretical results. Figure 4 shows the temperature dependence of $\Delta\rho(B)/\rho(0)$ at 0.7T of the MNPS for 500ºC and 800ºC samples. It is found that $\Delta\rho(B)/\rho(0)$ at 0.7T shows the maximum (4% for a 500ºC sample at ~110K and 2.3% for an 800ºC sample at ~100K). For the bulk single crystal, the sharp peak of $\Delta\rho(B)/\rho(0)$ has been observed at the T_V. $\Delta\rho(B)/\rho(0)$ at 1T and 290K for the bulk single crystal is ~0.1% [3].

4. Conclusions

With respect to the magnetite nanoparticle sinter (MNPS) for a 500ºC sample, we have observed the Mott's variable range hopping conduction below ~110K and the nearest neighbor hopping above ~110K. In addition, we have obtained a large enhancement of the magneto-resistance on the spin dependent transport of the MNPS for a 500ºC sample, as compared with those of the bulk single crystal and an 800ºC sample. From these experimental results, we consider that the MNPS for a 500ºC sample corresponds to a strong disordered system.

References

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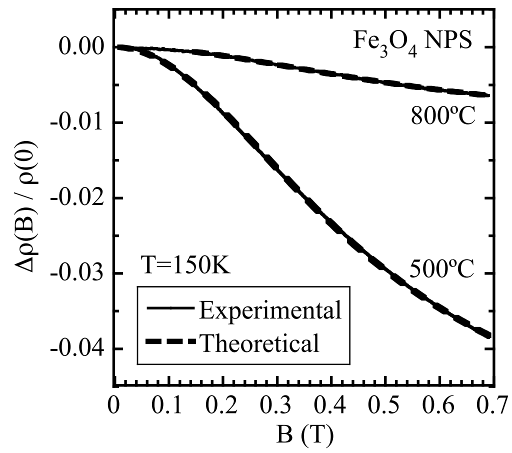

Fig. 3 The change of magneto-resistivity of the MNPS for 500ºC and 800ºC samples at 150K. The solid and dotted lines are the experimental and theoretical results, respectively.

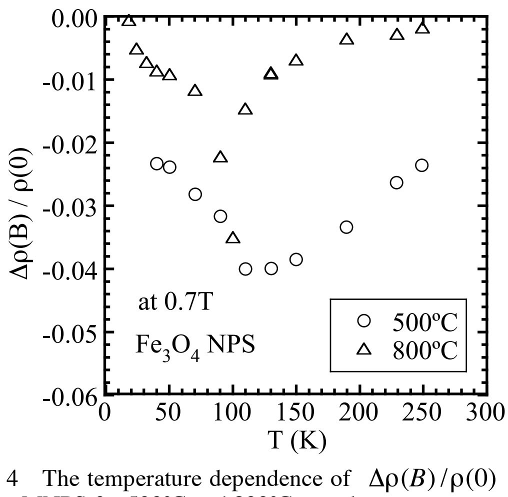

Fig. 4 The temperature dependence of $\Delta\rho(B)/\rho(0)$ at 0.7T of the MNPS for 500ºC and 800ºC samples.