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著者	Tanabe Minemaru, Manabe Takuro, Kohiki Shigemi, Mitome Masanori, Yubuta Kunio
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Effects of $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$ matrix on magnetization of dispersed Fe_3O_4 nanocrystals

Minemaru Tanabe[1], Takuro Manabe[1], Shigemi Kohiki*[,1], Masanori Mitome[2], and Kunio Yubuta[3]

[1] Department of Materials Science, Kyushu Institute of Technology, Kitakyushu, Japan
[2] National Institute for Materials Science, Tsukuba, Japan
[3] Institute for Materials Research, Tohoku University, Sendai, Japan

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* Corresponding author: e-mail kohiki@che.kyutech.ac.jp, Phone: +81 93 884 3310, Fax: +81 93 884 3300

Solid solutions $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$ with x = 0 - 0.3 were synthesized to employ as dispersion matrix for oleic acid coated Fe_3O_4 nanocrystals. The x = 0.05 matrix exhibited a resistance minimum at a non-zero temperature in each temperature dependent resistivity with magnetic fields of 0 T and 1 T, and a negative magnetoresistance. The sample of oleic acid coated Fe_3O_4 nanocrystals dispersed in the x = 0.05 matrix showed enhanced spontaneous magnetization as the factor of ≈1.3 relative to as-synthesized oleic acid coated Fe_3O_4 nanocrystals.

1 Introduction Transparent conducting oxides doped with 3*d* transition metal elements exhibiting room temperature ferromagnetism (RT-FM) have been studied intensively for realizing spintronics devices [1-20]. Tin doped indium sesquioxide (ITO) exhibiting RT-FM is promising for practical device applications because ITO has been the most widely used transparent conducting oxide in electronic and semiconductor industry.

Magnetite (Fe_3O_4) is well known as a half-metal material accompanied with fully spin-polarized carriers due to the minority-spin of octahedrally coordinated Fe^{2+}. Spontaneous magnetization (*M*s) of Fe_3O_4 below 585 ºC, resulted from uncompensated majority-spin of octahedrally coordinated Fe^{2+}, is antiparallel to the spin of polarized carriers. Okada et al. [21] reported that pulsed-laser-deposited Fe_3O_4 nanocrystals (NCs) dispersed in a single-crystalline ITO film exhibited RT-FM and a negative magnetoresistance (MR) due to collinear arrangement of *M*s of the Fe_3O_4 NCs. Okada et al. [22] modified the matrix from ITO to $(Ho_xIn_{1-x})_2O_3$, and observed enlarged *M*s. If the spin of polarized carriers itinerating around the conduction band of $(Ho_xIn_{1-x})_2O_3$ is antiparallel to the magnetic moments of localized Ho^{3+} (10.6 μ_B), localized Ho^{3+} moments align parallel with *M*s of dispersed Fe_3O_4 NCs, and enlarge observed *M*s.

It is known as the Kondo effect for diluted magnetic conductors that antiparallel arrangement between the spin of carriers and the localized magnetic moments accompanies a resistance minimum at a non-zero temperature in temperature dependent resistivity (ρ-T). Therefore, it is of great interest to examine effects of matrix with and without a resistance minimum at a non-zero temperature on magnetization (M-H) of dispersed Fe_3O_4 NCs. We employed $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$ with x = 0 - 0.3 as dispersion matrix. Hereafter, we denote $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$ as Ho_xITO for convenience. The Ho_xITO matrix with x = 0.05 demonstrated a resistance minimum and a negative MR. We dispersed oleic acid coated (OA-) Fe_3O_4 NCs in Ho_xITO (x = 0 - 0.3) matrix, and examined changes in M-H with x. Carboxyl groups of OA were reported to combine with Fe atoms at surface of Fe_3O_4 NCs, and OA layer with thickness ≈3 nm was formed on the surface [23]. It is expected that spin-polarized carriers of Fe_3O_4 NCs tunnel into Ho_xITO matrix through insulating OA layer, and the carriers in the matrix facilitate parallelization of localized Ho^{3+} moments and *M*s of dispersed OA-Fe_3O_4 NCs if the matrix exhibits both a resistance minimum and a negative MR.

2 Experiment

2.1 Sample preparation Ho_xITO with x = 0 - 0.3 were synthesized from powders of Ho_2O_3 and In_2O_3 mixed

in accordance with x = 0, 0.025, 0.05, 0.1, 0.2, and 0.3, and SnO_2 powders weighed as [Ho + In] : [Sn] = [1.9] : [0.1] in molar ratio. The mixtures were heated at 1500 °C for 6 h in flowing O_2 gas, and then re-heated at 1200 °C for 2 h in flowing Ar gas.

OA-Fe_3O_4 NCs were synthesized from $Fe(acac)_3$ in a solution of dibenzylether mixed with OA [24]. $Fe(acac)_3$, dibenzylether, and OA, weighed with the molar ratio of [1] : [26] : [2], were mixed with vigorous stirring for 1 h at RT. The mixture was kept at 300 °C for half an hour. After cooling to RT, OA-Fe_3O_4 NCs were precipitated from the crude solution by adding toluene/hexane (1:1) followed by centrifugation. The precipitation was washed with anhydrous chloroform.

As-synthesized OA-Fe_3O_4 NCs were dispersed into Ho_xITO powders with the molar ratio of [Fe_3O_4] : [Ho_xITO] = [0.05] : [1]. The mixtures were heated at 900 °C for 1 h in flowing Ar gas.

2.2 Characterization X-ray diffraction (XRD) was measured with a Rigaku CN2013 diffractometer with Cu $K\alpha$ radiation at RT. For electrical measurement by four probes method, Ho_xITO powders were pressed into a coin-type pellet before heating at 1200 °C for 2 h in flowing Ar gas. Then, the pellet was cut into a bar-shaped sample. Pt electrodes were bonded by gold wires to a Quantum Design MPMS 5S system. Current-voltage (I-V) characteristics at various temperatures under H = 0 and 1 T were measured for all the samples and some selected samples, respectively. M-H curve at 300 K was recorded by using a Quantum Design MPMS 5S SQUID magnetometer.

3 Results and discussion

3.1 Ho_xITO matrix As shown in the lower panel of Fig. 1, Ho_xITO matrix showed diffraction peaks can be indexed only to the C-rare earth type cubic lattice. Both Ho_2O_3 and In_2O_3 are known to crystallize into the C-rare earth type cubic lattice, and the lattice constant a of Ho_2O_3 and In_2O_3 are 1.0606 nm (JCPDS 43-1018) and 1.0118 nm (JCPDS 06-0416), respectively. As shown in the upper panel of FIG. 1, the a value of Ho_xITO matrix varied linearly with x from 0 to 0.3, obeying the Vegard's law.

Temperature dependent resistivity at H = 0 T (ρ^0-T) for all the Ho_xITO matrices are shown in Fig. 2. The $x \leq$ 0.1 matrices were conductive (ρ^0 < 0.1 Ωcm), but the x > 0.2 matrices were rather resistive (ρ^0 > 1 Ωcm). The x = 0.05 matrix showed larger ρ^0 than the x = 0.025 and 0.1 matrices. ρ^0 of the x = 0.025 and 0.1 matrices were so close each other, and larger than the x = 0 matrix. In each ρ^0-T, the x = 0.025 and 0.05 matrices exhibited the resistance minimum respectively at ≈150 K and ≈125 K, while the x = 0 and 0.1 matrices indicated no resistance minimum. As known as the Kondo effect, the resistance minimum for diluted magnetic conductors accompanied with antiparallel configuration between spin of carriers and localized mag-

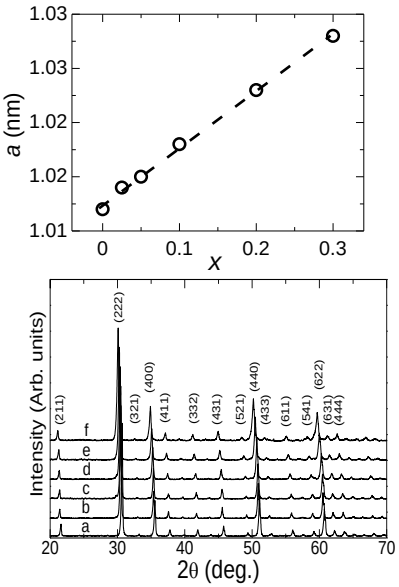

Figure 1 Lower panel: XRD pattern of the Ho_xITO matrix with x = 0 (a), 0.025 (b), 0.05 (c), 0.1 (d), 0.2 (e), and 0.3 (f). Upper panel: lattice constant a of the matrix with x. Straight line is a guide for eye.

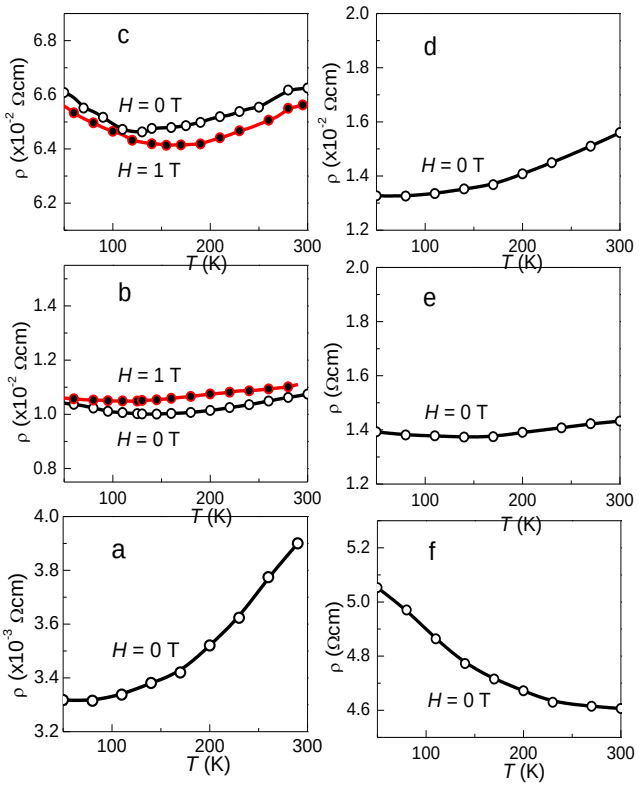

Figure 2 ρ^0 - T measured with H = 0 T for the Ho_xITO matrix with x = 0 (a), 0.025 (b), 0.05 (c), 0.1 (d), 0.2 (e), and 0.3 (f), shown by open circle. ρ^H - T measured with H = 1 T for the matrix with x = 0.025 (b) and 0.05 (c), shown by closed circle.

netic moments. Such antiparallel arrangement is expected to bring about MR = $(\rho^H - \rho^0)/\rho^0$ with a negative sign, here ρ^H represents ρ measured at $H \neq 0$. Figures 2b and 2c show also temperature dependent resistivity at H = 1 T (ρ^H-T) for the x = 0.025 and 0.05 matrices, respectively. For the x = 0.025 matrix, the resistance minimum disappeared in ρ^H-T, and ρ^H was larger than ρ^0. The x = 0.05 matrix demonstrated ρ^H-T with the resistance minimum at ≈175 K, and ρ^H smaller than ρ^0. Such a negative MR supports antiparallel arrangement between the spin of carriers and the localized magnetic moments of Ho^{3+} in the x = 0.05 matrix.

3.2 OA-Fe_3O_4 NCs XRD pattern and M-H curve of as-synthesized OA-Fe_3O_4 NCs are shown in Fig. 3. All the XRD peaks were attributable to the inverse spinel type Fe_3O_4 cubic lattice (JCPDS 19-0629). Crystallite size of ≈65 nm for the NCs was estimated from the (511) reflection by Scherrer's equation.

At 300 K, as-synthesized OA-Fe_3O_4 NCs demonstrated sigmoidal M-H curve almost saturated at H = 0.3 T. The small coercive field (Hc ≈27 Oe) indicates that OA prevented agglomeration of Fe_3O_4 NCs leading to larger second particle formation. Present M-H curve looks similar to those of reported OA-Fe_3O_4 NCs [23,25-27]. The magnetization at 1 T (M_{1T}) of ≈1 μ_B/Fe atom for present NCs is rather large than those reported (≈0.85 μ_B/Fe atom [23] and ≈0.82 μ_B/Fe atom [25]), and almost the same to that (≈0.95 μ_B/Fe atom) reported in ref. 26.

3.3 OA-Fe_3O_4 NCs/Ho_xITO matrix All the samples of OA-Fe_3O_4 NCs dispersed in the Ho_xITO matrix showed hysteresis loop at 300 K, as seen in Fig. 4. The M-H curve of the $x \leq 0.05$ samples almost saturated at H = 0.5 T, although the $x \geq 0.1$ samples showed no saturation below H = 1 T. Ms of the samples, derived from an intercept of a tangent line for each M-H curve, were larger than that of the as-synthesized NCs. As shown in Fig. 5, Ms of the samples normalized to that of the as-synthesized NCs, increased slightly with x from 0 to 0.025, peaked at x = 0.05, decreased at x = 0.1, and then slightly decreased with further increases in x to 0.3. The x = 0.05 sample showed enhancement of Ms as the factor of ≈1.3. Both $M_{0.5T}$ and M_{1T} behaved almost parallel to Ms for the $x \leq 0.05$ samples, while those for the $x \geq 0.1$ samples deviated from Ms. Increments in $M_{0.5T}$ and M_{1T} for the $x \geq 0.1$ samples reflect increases of thermally excitable Ho^{3+} paramagnetic moment at 300 K with x of the matrix.

Figure 6 shows ρ^0-T and ρ^H-T for the sample of OA-Fe_3O_4 NCs dispersed in the Ho_xITO matrix with x = 0.05. The resistance minimum in both ρ^0-T and ρ^H-T disappeared for the x = 0.05 sample. A positive MR ($\rho^H > \rho^0$) can arise from parallel configuration of localized Ho^{3+} moments with Ms of dispersed OA-Fe_3O_4 NCs.

As shown in Fig.7, Hc of the samples also varied with x, and peaked at x = 0.05. The x dependence of Hc looks similar to that of Ms for the samples. Enlarged Hc and enlarged Ms for the x = 0.05 sample suggest carriers facilitated parallelization of localized Ho^{3+} moments and Ms of dispersed OA-Fe_3O_4 NCs.

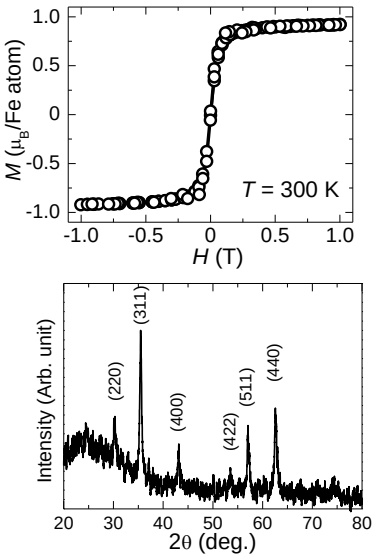

Figure 3 Lower panel: XRD pattern of as-synthesized OA-Fe_3O_4 NCs. Upper panel: M-H ($H \geq 1$ T) curve of as-synthesized OA-Fe_3O_4 NCs.

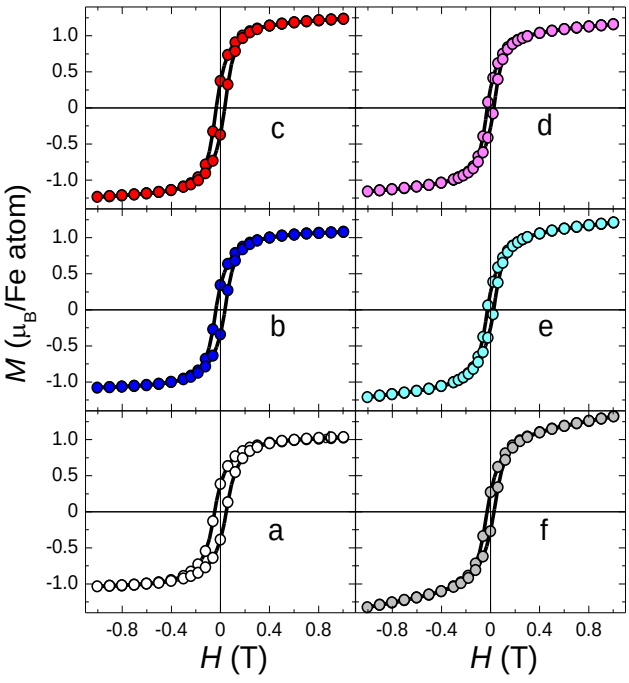

Figure 4 M-H curve for the samples of OA-Fe_3O_4 NCs dispersed in the Ho_xITO matrix with x = 0 (a), 0.025 (b), 0.05 (c), 0.1 (d), 0.2 (e), and 0.3 (f).

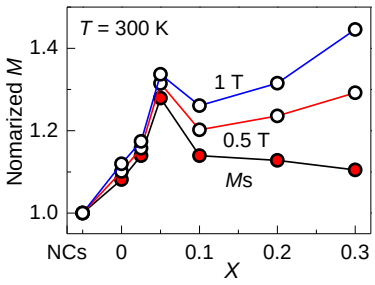

Figure 5 *M*s, $M_{0.5T}$ and M_{1T} for the samples with *x*. Values were normalized to those of as-synthesized OA-Fe_3O_4 NCs.

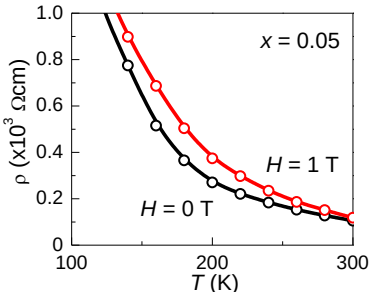

Figure 6 ρ^0 - *T* with *H* = 0 T and ρ^H - *T* with *H* = 1 T for the sample of OA-Fe_3O_4 NCs dispersed in the Ho_xITO matrix with *x* = 0.05.

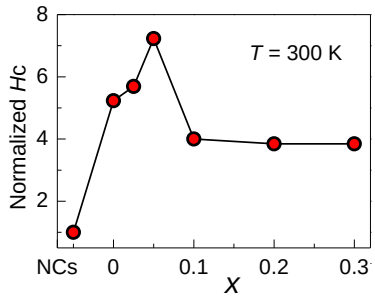

Figure 7 *H*c for the samples with *x*. Values were normalized to that of as-synthesized OA-Fe_3O_4 NCs.

4 Summary The Ho_xITO matrix with *x* = 0.05 exhibited both a resistance minimum at a non-zero temperature and a negative MR. The sample of OA-Fe_3O_4 NCs dispersed in the Ho_xITO matrix with *x* = 0.05 demonstrated enlarged *M*s as the factor of ≈1.3 relative to the as-synthesized NCs. In the sample of OA-Fe_3O_4 NCs dispersed in the Ho_xITO matrix with *x* = 0.05, the resistance minimum in both ρ^0-*T* and ρ^H-*T* disappeared, and the sign of MR turned from negative to positive. Similar behavior in *M*s and *H*c with *x* also supports that the enlarged *M*s for the *x* = 0.05 sample arose from parallel configuration of localized Ho^{3+} moments in the Ho_xITO matrix to *M*s of dispersed OA-Fe_3O_4 NCs.

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