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Structure, Spin Glass, and Spin State in Perovskite $\text{GdCo}_{1-x}\text{Mn}_x\text{O}_3$ ($x \leq 0.5$)

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Perovskite $\text{GdCo}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4, 0.5$) compounds have been prepared by solid-state reaction. Structures were characterized using X-ray diffraction and Rietveld Refinement method. The compounds crystallized in orthorhombic with $\text{P}1\text{m}1$ space group. Crystal lattices decreased with the increase of Mn doping level. DC magnetization and ac susceptibility were studied over a wide temperature range and different frequencies. A typical spin glass state was observed in all samples around the same temperature of 122 K where the compounds turned from paramagnetic to ferromagnetic states. For $x < 0.5$, secondary transitions were observed both in dc and ac measurement which were independent of frequency but depended on doping level. The valences of Co or Mn with possible spin states were estimated.

Index Terms—Ferromagnetism, magnetization, perovskite, spin glass, spin state.

I. INTRODUCTION

IN magnetic systems, frozen spins in random alignment causes the spin glass state. The spin glass state has been observed in spinels, amorphous materials, and mostly in diluted magnetic alloys. Spin glass could arise from paramagnetic state in disordered systems or from paramagnetic to ferromagnetic states. In the latter case, the spin glass co-exists with ferromagnetism. Recently, spin glass states have also been widely observed in a number of REMO_3 perovskite ($\text{RE} = \text{rare-earth}$, $\text{M} = 3\text{d}$ transition metal) compounds whose structures and magnetic properties are sensitive to the doping effect on either RE or M sites. In particular, $\text{REMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ perovskites exhibited very interesting paramagnetic, meta-magnetism [1], and ferromagnetism depending on the size [2]–[6]. Very recently, a typical spin glass behavior has been observed in perovskite $\text{GdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ with very sharp transition width of 1 K at 115 K [7] and also observed in $\text{YbMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ [8] and $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ [9] compounds. The determination of valences of Co and Mn and their spin states are important issues in clarifying the magnetism in the $\text{REMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ system. In this paper we presented our studies on the structures, ferromagnetism, spin glass and spin states of Co and Mn in $\text{GdCo}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4, 0.5$). We observed spin glass state and two peak features in dc and ac susceptibility. The valences of Co or Mn changed from $2+$ or $4+$ to $3+$ when Co amount increases and possible spin state transformation of Co and Mn was also suggested.

II. EXPERIMENTAL PROCEDURE

Polycrystalline samples of $\text{GdCo}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4, 0.5$) were prepared by conventional solid state reaction. High purity Gd_2O_3 , MnCO_3 , and CoCO_3 were well-mixed according to desired atomic ratios. These powders were then palletized with 10 mm diameter and 1 mm thickness. Palettes were then

sintered in two steps in air: first sintered at 900°C for 12 h, then they were crushed, mixed and re-palletized, and re-sintered at 1200°C for another 12 h.

The samples phases were studied by powder X-ray diffraction. Structures were refined using the Rietveld refinement program.

Using commercial Physical Property Measurement System (PPMS), zero-field cooled (ZFC) and field cooled (FC) magnetization measurements were carried out in 50 Oe and 2000 Oe over a wide temperature range of 5 K–340 K and ac susceptibility was also measured at different frequencies of 21, 217, and 2000 Hz.

III. RESULTS AND DISCUSSIONS FINAL STAGE

XRD results showed that all samples are single phase. Structure refinement was done based on the structure of $\text{GdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The refinement results revealed that all the samples were phase pure, orthorhombic crystallized with space group $\text{P}1\text{m}1$. Fig. 1 shows the result of Rietveld refinement of the XRD pattern of $\text{GdCo}_{0.6}\text{Mn}_{0.4}\text{O}_3$ measured at room temperature. Calculated results fit well with experimental data.

A variation of lattice parameters with x is shown in Fig. 2. It can be seen that increasing the doping level of Mn from 0.2 to 0.5, lattice parameters increased monotonically, a increased from 5.24 to 5.31 Å, b from 5.49 to 5.57 Å, and c from 7.49 to 7.54 Å.

DC magnetization carried out in a field of 50 Oe is shown in Fig. 3. It can be seen that the all samples showed a ferromagnetic transition at temperature around 122 K. However, below this temperature a secondary transition started to appear and decrease from about 117, 105 to 75 K when x decreased from 0.4 to 0.2. It should be noted that all the samples are single phase as determined from XRD. This implies that the presence of the secondary transition for $x < 0.5$ below the first ferromagnetic transition at 122 K is the intrinsic property of the compounds and is believed to be due to the magnetic interaction among Co, Mn, and Gd ions in this system. The contribution mainly from

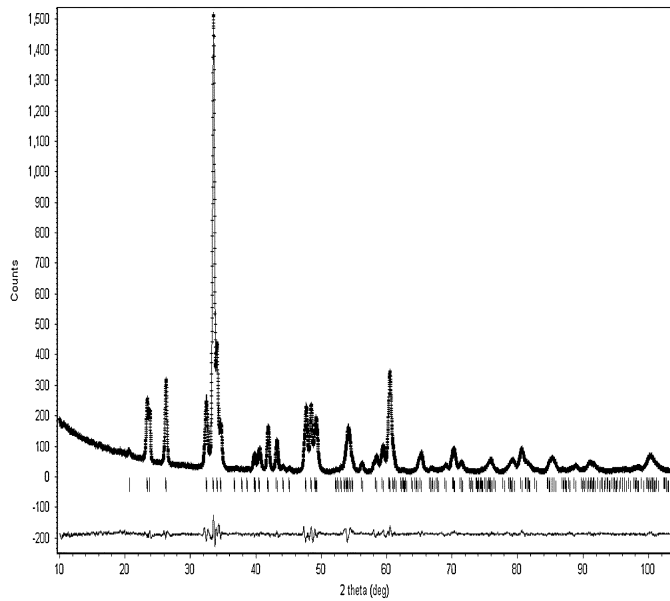


Fig. 1. The observed (crosses), calculated (solid), difference diffraction profiles at 300 K with peak markers for $GdCo_{0.4}Mn_{0.6}O_3$.

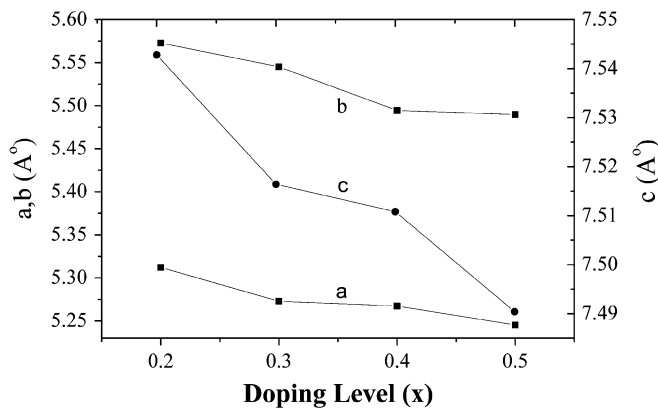


Fig. 2. Variations of lattice parameters with doping level x .

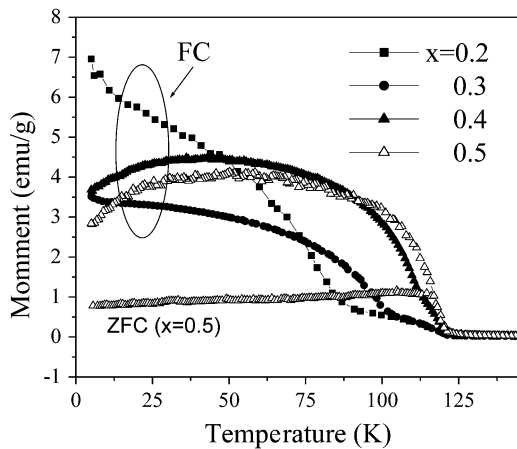
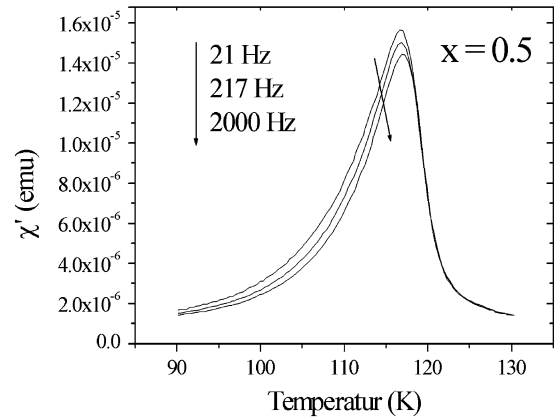


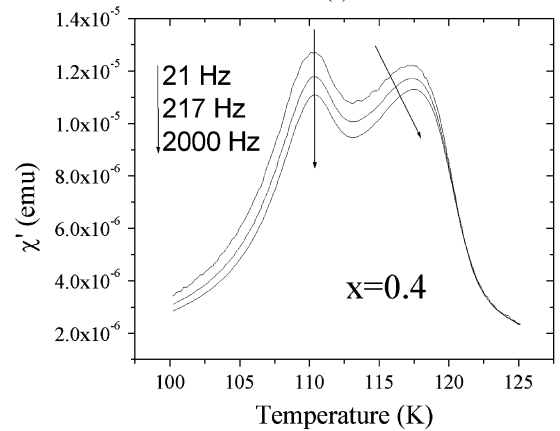
Fig. 3. Temperature dependence of moment measured in dc field of 50 Oe.

Co ions seems to be responsible for the secondary transition because the amount of Co ions increases when the x decreases.

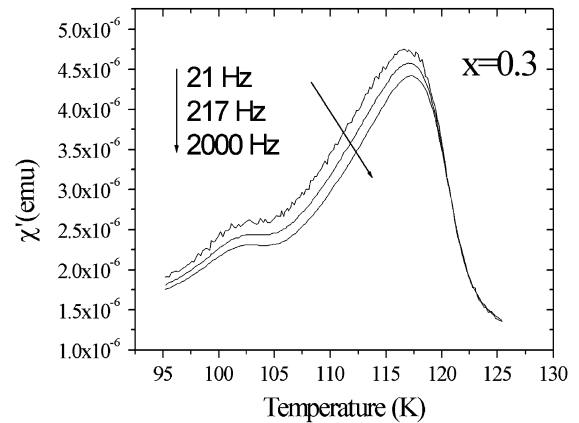
A decrease of magnetization in the FC were observed at 50 and 42 K for $x = 0.5$ and $x = 0.4$ samples, respectively. This



(a)



(b)



(c)

Fig. 4. Temperature dependence of real part of ac susceptibility measured at different frequencies.

might indicate an antiferromagnetic transition from these two samples below these temperatures. However, no such decrease of magnetization was observed in $x = 0.2$ and 0.3 samples.

The ac susceptibility as a function of temperature is shown in Fig. 4. A spin glass state around first transition at 122 K is clearly seen for all the samples. For $x = 0.5$ samples, only one peak at 122 K is seen in the real part of the ac susceptibility, which shifts to high temperature with increase of frequency, which is marked with an arrow in the direction of the peak shift.

When x decreases, in addition to the first peak, a secondary peak appeared and shifted to low temperatures, in agreement

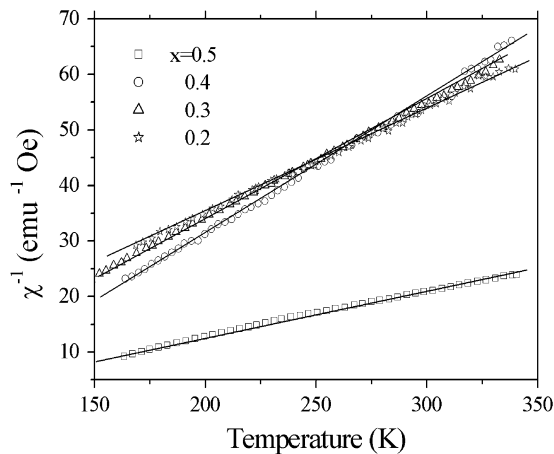


Fig. 5. Temperature dependence of inverse molar susceptibility, χ^{-1} , measured at a magnetic field of 2 kOe. Solid lines show linear fittings.

with what has been seen in dc magnetization measurements. It should be noted that all the secondary peaks in the ac susceptibility are independent of frequency and therefore indicates no relations with spin glass transitions.

The spin states observed at 122 K for all the samples were also reflected from cusps in the ZFC magnetization which is also a signature of spin glass transition. It is believed that the spin glass occurs due to a competition of spins when the system turned from paramagnetic and ferromagnetic [7].

The field cooled magnetization was also measured at a high field of 2 kOe to obtain the inverse molar susceptibility, χ^{-1} , as plotted against temperature in Fig. 5. The χ^{-1} data above 100 K can be well fitted to the Curie-Weiss law as shown in Fig. 5.

Obtained μ_{eff} from Curie-Weiss law fitting indicated that μ_{eff} per magnetic ion (Co, Mn, Gd) decreased from 7.11 to $5.70\mu_B$ when Mn decreased from 0.5 to 0.4. Then, μ_{eff} increased up to $6.72\mu_B$ as Mn decreased down to 0.2. As the Gd^{3+} contributes half of $7.94\mu_B$, both Co and Mn ions could only contribute about 1.7 – $3.1\mu_B$ /magnetic ions (Co, Mn, Gd). As the valences of Co and Mn is very complicated in the system, we can only roughly estimate the possible combination of spin states of Co and Mn which could give rise a value of $\mu_{\text{eff}}/(\text{Co, Mn, Gd})$ that is close to observed μ_{eff} from fitting. For $x = 0.5$ sample, a combination of high spin ($s = 2$) only for both Co^{3+} and Mn^{3+} plus $1/2 \text{Gd}^{3+}$ ($(0.5\mu_{\text{eff}}(\text{Gd}^{3+})^2 + 0.25\mu_{\text{eff}}(\text{Co}^{3+}(\text{HS}))^2 + 0.25\mu_{\text{eff}}(\text{Mn}^{3+}(\text{HS}))^2)^{0.5}$) $6.60\mu_B$, close to the μ_{eff} determined for $x = 0.5$ samples ($7.11\mu_B$). For $x = 0.4$, a combination of low spin of both Co^{2+} and Mn^{4+} ($(0.5\mu_{\text{eff}}(\text{Gd}^{3+})^2 + 0.2\mu_{\text{eff}}(\text{Co}^{2+}(\text{LS}))^2 + 0.3\mu_{\text{eff}}(\text{Mn}^{4+}(\text{LS}))^2)^{0.5}$) $= 5.75\mu_B$ resulting in an excellent agreement with observed $5.70\mu_B$. However, we cannot make a convincing estimate of the spin states of the Co and Mn, as both of them might take various valences as x changes. However,

it is possible that as x increases, the Co might have changed from $2+$ to $3+$ while Mn may change from $4+$ to $3+$, and the presence of multivalence of both Co and Mn is highly possible, making the system very complicated. A possible combination of high spin state of Co^{2+} and Mn^{4+} ($\sim 6.24\mu_B$) and high spin states of both Co^{3+} and Mn^{3+} ($6.53\mu_B$) led to a best fitting to observed μ_{eff} of 6.22 or $6.72\mu_B$ for $x = 0.3$ and 0.2 samples.

IV. CONCLUSION

Perovskite $\text{GdCo}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4, 0.5$) compounds crystallized in orthorhombic with Plmn space group. Crystal lattices decreased with the increase of Mn doping level. A typical spin glass state was observed in all samples around the same temperature of 122 K where the compounds turned from paramagnetic to ferromagnetic states. A secondary transition independent of frequency but dependent on doping level is also observed. The spin states and valences of both Co and Mn are likely to change with different amounts of Mn.

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REFERENCES

- [1] C. Marsh and C. Clark, "Metamagnetism in the perovskite compound $\text{Gd}_2\text{CoMnO}_7$," *Philos. Mag.*, vol. 19, p. 449, 1969.
- [2] N. Cornei and M.-L. Craus, "Metamagnetism in the perovskite compound $\text{Gd}_2\text{CoMnO}_7$, influence of the rare earth cation (Ln = La, Nd, Sm) on the properties of the $\text{Ln}_{0.44}\text{Ho}_{0.11}\text{Sr}_{0.45}\text{MnO}_{3\pm\delta}$ manganite oxides," *J. Alloys Comp.*, vol. 368, p. 58, 2004.
- [3] U. Voskoboinik, "Anomalous Field Dep. of Blocking Temperature of Natural Horse-Spleen Ferritin," *Acta. Phys. Pol.*, vol. S-43, A 92 Supplement, 1997.
- [4] I. O. Troyanchuk, N. V. Samsonenko, and E. F. Shapovalova, "Synthesis and characterization of $\text{Ln}(\text{Bo}_{0.5}\text{Mn}_{0.5})\text{O}_{0.3}$ (Ln-LANTHANOID; B = Ni, Co) perovskites," *Mater. Res. Bull.*, vol. 32, no. 1, p. 67, 1997.
- [5] S. K. Park, T. Ishikawa, and Y. Tokura, "Variation of charge-ordering transitions in $\text{R}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ (R = La, Pr, Nd, Sm and Gd)," *Phys. Rev. B*, vol. 60, no. 15, p. 10788, 1999.
- [6] H. Masuda, T. Fujita, T. Miyashita, M. Soda, and Y. Yasui, "Transport and Magnetic Properties of $\text{R}_{1-x}\text{AxCoO}_3$," *J. Phys. Soc. Jpn.*, vol. 72, no. 4, p. 865, 2003.
- [7] X. L. Wang, J. Horvat, H. K. Liu, A. H. Li, and S. X. Dou, "Spin glass state in $\text{Gd}_2\text{CoMnO}_6$ perovskite manganite," *Solid State Commun.*, vol. 118, p. 27, 2001.
- [8] X. L. Wang, M. James, J. Horvata, F. Gao, A. H. Lia, H. K. Liua, and S. X. Dou, "Structure and spin glass behavior in nonmetallic $\text{Yb}_2\text{CoMnO}_6$ perovskite manganite," *J. Magn. Magn. Mater.*, vol. 246, p. 86, 2002.
- [9] X. L. Wang, M. James, J. Horvat, and S. X. Dou, "Spin glass behavior in ferromagnetic $\text{La}_2\text{CoMnO}_6$ perovskite manganite," *Supercond. Sci. Technol.*, vol. 15, p. 427, 2002.