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# Effects of Chemical Pressure on Rare-Earth Oxide GdNIn<sub>0.7</sub>Co<sub>0.3</sub>O<sub>3</sub> with Nonmagnetic Element Substitution

メタデータ	言語: eng 出版者: PHYSICAL SOC JAPAN 公開日: 2020-12-08 キーワード (Ja): キーワード (En): 作成者: バオ, ジンファ, OHSUGI, Shunsuke, KUNITA, Hiroki, 雨海, 有佑, 桃野, 直樹, 高野, 英明 メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/10258/00010324">http://hdl.handle.net/10258/00010324</a>

# Chemical Pressure Effects of Non-Magnetic Element Substitution on Rare Earth Oxide $\text{GdMn}_{0.7}\text{Co}_{0.3}\text{O}_3$

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Chemical pressure effects were studied for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$  ( $R$ = non-magnetic rare-earth element) with  $y = 0.1, 0.3$  and  $0.5$ . Substitution of Gd with La, Y or Lu in orthorhombic  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{1-x}\text{Co}_x\text{O}_3$  induced a systematic unit-cell volume change. Our results reveal that increasing or decreasing the average ionic radius of the rare-earth elements in the compounds affects the magnetic ordering temperature  $T_C$ . The reduction in the proportion of Gd due to substitution by non-magnetic elements weakens the spin reversal effect.

## 1. Introduction

ABO<sub>3</sub>-type perovskites with the formula  $RMnO_3$  ( $R$ : rare-earth element) have been investigated extensively as multiferroic materials.<sup>1-14)</sup> When Mn is replaced with other 3d transition metal elements, the magnetic and electrical properties are closely related to the  $Mn^{3+}/Mn^{4+}$  ratio, but other factors may also influence the magnitude and nature of the magnetic interactions. For instance, the ionic size of A site or B site cations may affect some geometrical parameters (i.e., the unit-cell volume, the B-O-B bond angle, or the tolerance factor).<sup>8-14)</sup> Previous studies on the structural and magnetic properties of  $GdMn_{1-x}Co_xO_3$ ,<sup>13,14)</sup> which is orthorhombic for  $0 \leq x \leq 1.0$ , have shown that substitution of Mn with other transition metal elements such as Co, Ni, and Cu causes a transformation of  $Mn^{3+}$  to  $Mn^{4+}$ . For  $x \geq 0.25$ , at the canted magnetic ordering temperature  $T_C$ , the field-cooled magnetization ( $M_{FC}$ ) shows a rapid increase, which results from canting of the Mn and Co moments. In particular, for  $x=0.3$ ,  $M_{FC}$  shows a maximum value at about 40 K, and then decreases rapidly with decreasing temperature and shows a negative magnetization value below the compensation temperature  $T_{comp} \sim 20$  K.<sup>14)</sup> This spin reversal phenomenon can be explained by the antiferromagnetic orientation of the Gd spin relative to the Mn and Co moments.<sup>14,15)</sup>

In this work, a systematic study of  $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$  with  $R=La, Y,$  and  $Lu$  is presented, using a solid-state reaction under ambient pressure as the synthesis method. Moreover, the effect of chemical pressure on the structure and magnetic properties is discussed.

## 2. Experimental Procedure

The samples were prepared by a solid-state reaction method at ambient pressure. High-purity (99.9%) powders of  $Gd_2O_3$ ,  $La_2O_3$ ,  $Y_2O_3$ ,  $Lu_2O_3$ ,  $Mn_2O_3$ , and  $Co_3O_4$  were weighed in appropriate proportions to obtain the desired nominal compositions of  $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$ . The mixtures were calcined twice. The first sintering process was performed by heating from room temperature to 1150 °C in 8 h, holding for 4 h, and then cooling to room temperature. The second calcining temperature was 1350 °C with a holding time of 8 h; the final sample was obtained after cooling. The samples were characterized by X-ray powder diffraction (XRD) using a diffractometer

(MiniFlex300, Rigaku) with Cu  $K_\alpha$  radiation and a Ni  $K_\beta$  filter. The structural parameters were obtained from Rietveld refinement of the XRD data using the RIETAN-FP program.<sup>16)</sup> The  $M_{FC}$  measurements were performed with a SQUID magnetometer (MPMS, Quantum Design).

### 3. Result and discussion

#### 3.1 Structure

Figures 1(a), 1(b), and 1(c) show XRD patterns for  $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$  with substitution by the non-magnetic elements La, Y and Lu, respectively. These are referred to as the La, Y and Lu series, respectively, hereafter. There were no detected impurity phases, and the patterns indicated that all samples were single-phase with a Perovskite-type orthorhombic structure (space group:  $Pnma$ ). The lattice parameters  $a$ ,  $b$ ,  $c$  and the unit-cell volume  $V$  are indicated in Table I. In the La substitution system,  $b$  and  $c$  increase greatly with substitution, reflecting the fact that the unit-cell volume  $V$  greatly increases, and the increase ratio is about 3% when the substitution amount  $y$  increases from 0.0 to 0.5. On the other hand,  $b$  and  $c$  decrease in the Y and Lu substitution systems, and  $V$  decreases by about 1.3% in Y substitution systems and by about 2.5% in Lu substitution systems. These changes are considered to be due to the differences in the ionic radii of La, Y, and Lu with respect to Gd. Figures 2(a) and 2(b) show  $a$ ,  $b(b/\sqrt{2})$ ,  $c$ , and  $V$ , respectively, as a function of the average ion radius  $\langle r_A \rangle = (1-y)r_{Gd} + yr_R$  ( $La^{3+} = 1.216\text{\AA}$ ,  $Gd^{3+} = 1.107\text{\AA}$ ,  $Lu^{3+} = 1.032\text{\AA}$ ,  $Y^{3+} = 1.075\text{\AA}$ ). The parameters  $a$ ,  $b(b/\sqrt{2})$ , and  $c$  change as a function of  $\langle r_A \rangle$ , and appear to become closer to each other with increasing  $\langle r_A \rangle$ . This indicates that  $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$  approaches the cubic perovskite structure with increasing  $\langle r_A \rangle$ . On the other hand, it seems that  $V$  is linearly related to  $\langle r_A \rangle$ , and is independent of the substituted ions. This volume change represents the chemical pressure effect.

#### 3.2 Magnetic properties

In Fig. 3, we show the temperature dependence of  $M_{FC}$ . It shows a rapid increase at  $T_C$  with decreasing temperature, which results from canting of the Mn and Co moments.  $T_C$  increases rapidly

with increasing concentration  $y$  for the La series, decreases with increasing  $y$  for the Y series, and decreases rapidly with increasing  $y$  for the Lu series. These changes in  $T_C$  correspond to the increase and decrease of the unit-cell volume  $V$  as shown in Fig. 4, where both  $V$  and  $T_C$  increase almost linearly as  $\langle r_A \rangle$  increases.

The inverse magnetic susceptibility  $\chi_{FC}^{-1}=H/M_{FC}$ , shown in Figs. 5(a), 5(b), and 5(c) for the La series, Y series, and Lu series, respectively, can be fitted above about 200 K using the Curie-Weiss law:

$$\chi = \frac{M_{FC}}{H} = \frac{C}{T-\Theta} \quad (1)$$

where  $C$  is the Curie constant, and  $\Theta$  is the Weiss temperature. We can obtain the effective number of Bohr magnetons via

$$P_{\text{eff}} = \sqrt{\frac{3Ck_B}{N\mu_B^2}} \quad (2)$$

where  $N$  is the number of  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$  formula units per gram,  $k_B$  is the Boltzmann constant, and  $\mu_B$  is the Bohr magneton. In Fig. 6, we plot  $P_{\text{eff}}$  as a function of the  $R$  concentration  $y$ . Assuming that the electronic states of the ions in the samples are  $\text{Gd}^{3+}(S=7/2)$ ,  $\text{Mn}^{4+}(S=3/2)$ ,  $\text{Mn}^{3+}(S=2, \text{high spin [HS]})$ , and  $\text{Co}^{2+}(S=3/2, \text{HS})$ , and there is no change in valence on substituting for Gd, the effective number of Bohr magnetons  $P_{\text{cal}}$  is estimated by the following equation:

$$P_{\text{cal}} = \sqrt{(1-y)P_{\text{Gd}^{3+}}^2 + 0.4P_{\text{Mn}^{4+}}^2 + 0.3P_{\text{Mn}^{3+}}^2 + 0.3P_{\text{Co}^{2+}}^2} \quad (3)$$

where  $P_{\text{Gd}^{3+}}$ ,  $P_{\text{Mn}^{4+}}$ ,  $P_{\text{Mn}^{3+}}$ , and  $P_{\text{Co}^{2+}}$  are 7.94, 3.87, 4.90, and 3.87, respectively.  $P_{\text{eff}}$  and  $P_{\text{cal}}$  are indicated by colored symbols and a broken line in Fig. 6, respectively.  $P_{\text{eff}}$  almost corresponds to  $P_{\text{cal}}$  in spite of the elemental substitution. We then considered that the substitution of Gd by nonmagnetic elements in this system changes the strength of the interaction between Mn and Co without changing the valence of Mn and Co.

In order to explain the decrease in  $M_{FC}$  below about 40 K, the so-called spin reversal phenomenon, we adopt the two-sublattice model used in studies of other rare-earth oxides.<sup>8,15,17)</sup> In

$$\mathbf{M} = \mathbf{M}_{\text{Mn, Co}} + \frac{(1-y)C_{\text{Gd}}(\mathbf{H}_{\text{int}} + \mathbf{H}_{\text{ext}})}{T-\Theta} \quad (4)$$

this model, the temperature dependence of  $M_{FC}$  can be fitted using the following equation:

where  $M_{Mn, Co}$  is the saturated moment of the Mn and Co,  $C_{Gd}$  is the Curie constant for  $Gd^{3+}$ ,  $H_{int}$  is the internal field at Gd sites due to the canted Mn and Co moments,  $H_{ext}$  is the applied field, and  $\Theta$  is the Weiss temperature. The fitting parameters are listed in Table II. The fitting results for  $y=0.0$  and the La series are shown by a solid line in Fig. 3. We assume that the decrease in magnetization is caused by the interaction of the two magnetic sublattices “Gd” and “Mn and Co”, and that the Gd moment is paramagnetic. It is clear that the negative internal field induced by the Mn and Co sublattice affects the Gd sublattice, because at low temperatures the  $Gd^{3+}$  spin is oriented in a direction opposite to  $H_{ext}$  by  $H_{int}$ . With increasing concentration of R elements,  $M_{Mn, Co}$  increases in the La series, decreases in the Y and Lu series, and shows a more remarkable decrease in the Lu series.  $H_{int}$  shows a tendency to decrease with increasing concentration of R elements in all series.

The changes in  $M_{Mn, Co}$  indicate that the interaction between Mn and Co is enhanced by increasing  $V$  and suppressed by decreasing  $V$ . From Table II, we can deduce that the increase in  $H_{int}$  is caused by enhancement of the interaction between Mn and Co due to the increase in the maximum value of magnetization in the La series, and also that suppression of the spin reversal is caused by reduction of the Gd content due to substitution by non-magnetic elements.

#### 4. Conclusion

The unit-cell volume  $V$  for  $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$  increases or decreases depending on the average ion radius  $\langle r_A \rangle$ , which is dependent on the radius of the substituent R. The change in  $V$  due to the substitution by R indicates that this substitution induces a chemical pressure on the crystal structure. Both  $V$  and  $T_C$  vary linearly with  $\langle r_A \rangle$ , as shown in Fig. 4. When  $V$  increases, it leads to an increase in  $T_C$ , due to negative chemical pressure. For positive chemical pressure, decreasing  $V$  leads to a decrease in  $T_C$ .

On the other hand, the interaction between Mn and Co is enhanced by increasing  $V$  and

suppressed by decreasing  $V$ , and the enhancement of the interaction increases the maximum value of the magnetization. The substitution of Gd with non-magnetic rare-earth elements changes the unit-cell volume  $V$ , an increase in  $V$  raises the transition temperature  $T_C$ , and a decrease in  $V$  lowers  $T_C$ . It is considered that these chemical pressure effects and the spin reversal phenomenon occur simultaneously and produce the temperature dependence of  $M_{FC}$  shown in Fig. 3.

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## Figure Captions

Table I Lattice parameters for the solid solutions  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$  ( $R = \text{La}, \text{Y}$  and  $\text{Lu}$ ) as function of  $y=0.1, 0.3$  and  $0.5$ . The upper, middle, and lower values of each parameter correspond to the La, Y, and Lu series, respectively.

Table II Fitting parameters for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ .

Fig. 1. XRD patterns for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$  with  $y=0.1, 0.3$  and  $0.5$  with substitution by the non-magnetic elements La, Y and Lu. (a), (b), and (c) correspond to  $\text{Gd}_{1-y}\text{La}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ ,  $\text{Gd}_{1-y}\text{Y}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ , and  $\text{Gd}_{1-y}\text{Lu}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ , respectively,

Fig. 2. Average ion radius  $\langle r_A \rangle$  dependence of (a) lattice parameters  $a$ ,  $b/\sqrt{2}$ , and  $c$ . and (b) unit-cell volume  $V$ .

Fig. 3. Temperature dependence of  $M_{\text{FC}}$  for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ . Broken line shows  $T_C$  for  $\text{GdMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ . The solid lines in La series are fits using Eq. (4).

Fig. 4.  $V$  and  $T_C$  as a function of  $\langle r_A \rangle$ . Their linear dependence with the same slope suggests that there is a correlation between  $V$  and  $T_C$ . The dotted line denotes the ion radius of  $\text{Gd}^{3+}$ .

Figs. 5. Inverse magnetic susceptibility  $\chi_{\text{FC}}^{-1} = H/M_{\text{FC}}$  for (a) La series, (b) Y series, and (c) for Lu series.

Fig. 6.  $R$  concentration dependence of effective magnetic moment  $P_{\text{eff}}$  for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$  ( $R = \text{La}, \text{Y}$ , and  $\text{Lu}$ ).

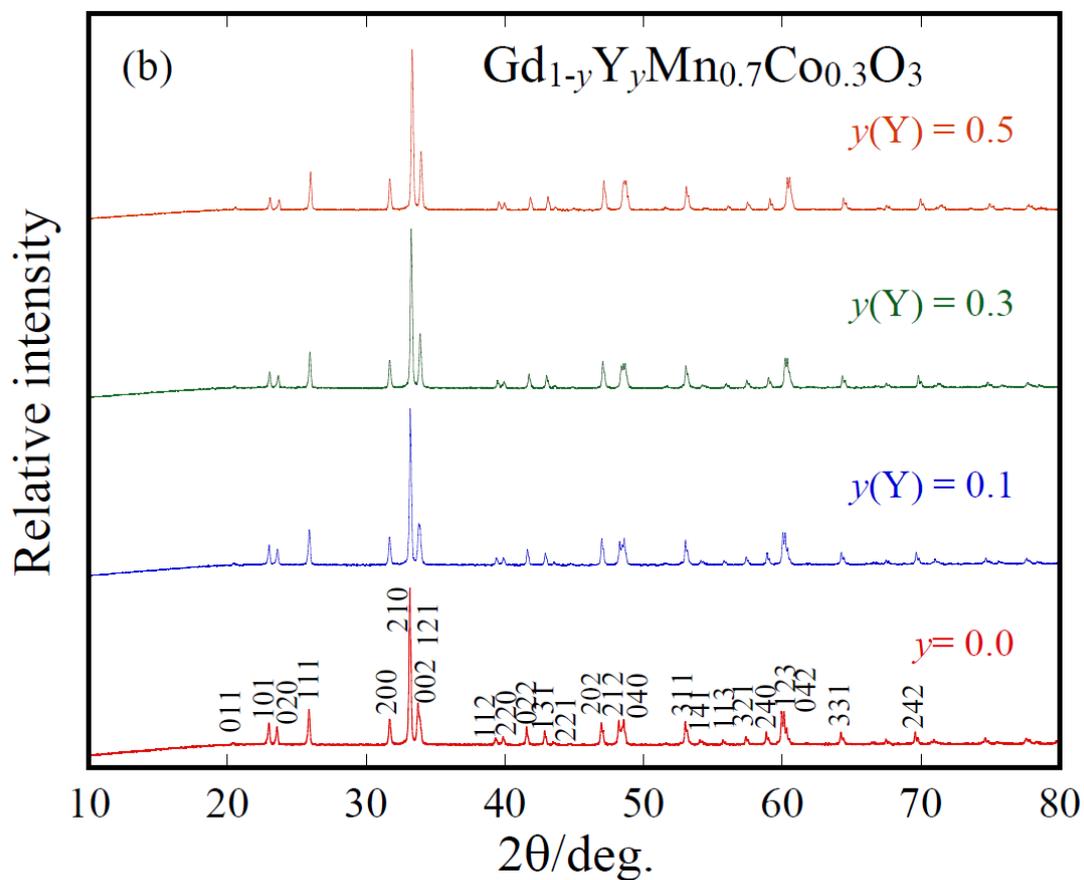
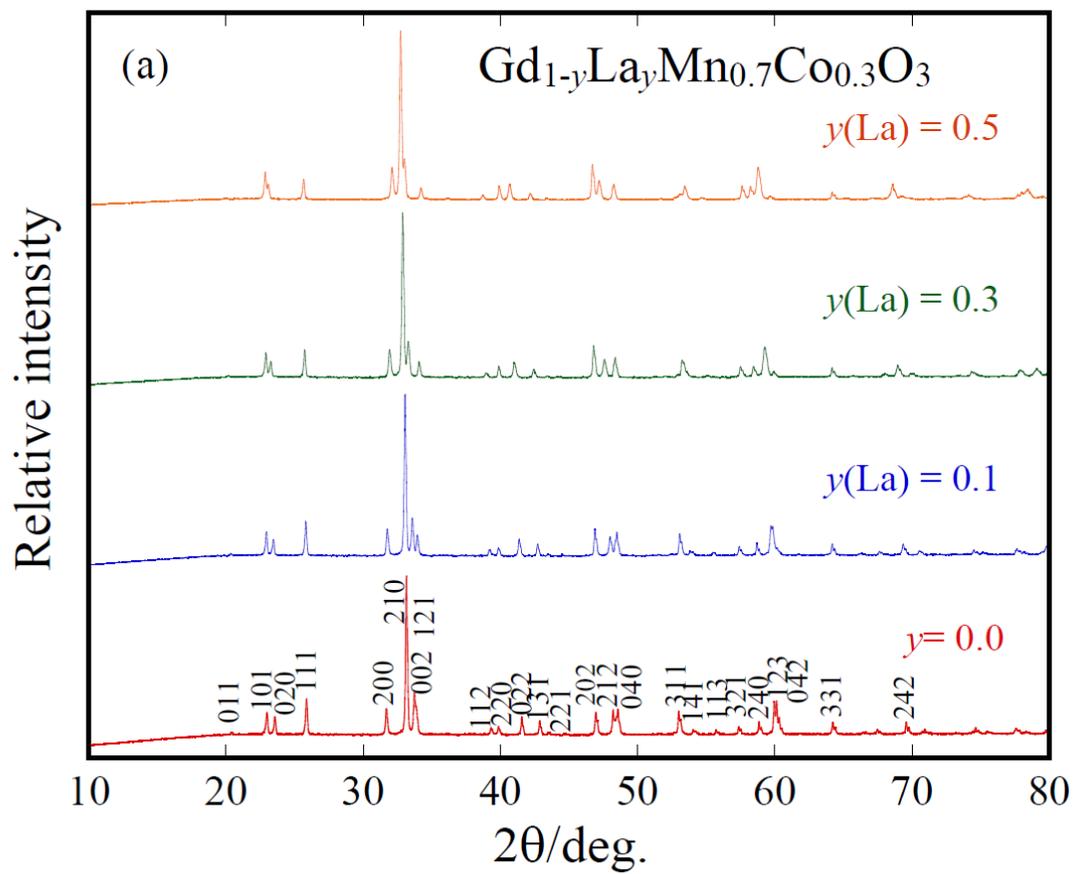
Table I

Lattice parameters of the solid solutions  $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$  (R= La, Y and Lu) as function of  $y=0.1, 0.3$  and  $0.5$ . The upper, middle, and lower values of each parameter correspond to the La, Y, and Lu series, respectively.

$y(\text{La})$ $y(\text{Y})$ $y(\text{Lu})$	<b>0.0</b>	<b>0.1</b>	<b>0.3</b>	<b>0.5</b>
$a/\text{\AA}$	5.6425	5.6301 5.6429 5.6411	5.6018 5.6419 5.6329	5.5724 5.6411 5.6263
$b/\text{\AA}$	7.5434	7.5775 7.5346 7.5311	7.6401 7.5175 7.5018	7.6991 7.5000 7.4757
$c/\text{\AA}$	5.3100	5.3331 5.3028 5.2969	5.3785 5.2889 5.2670	5.4243 5.2750 5.2414
$V/\text{\AA}^3$	226.01	227.52 225.46 225.03	230.19 224.32 222.56	232.71 223.17 220.45

Table II. Fitting parameters for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ .

Samples R concentration $y$		$M_{\text{Mn, Co}}/\text{emu g}^{-1}$	$H_{\text{int}}/\text{kOe}$	$\Theta/\text{K}$
La series	0.5	17	-1.2	-9.4
	0.3	8.3	-5.4	-19
	0.1	6.3	-5.6	-12
$\text{GdMn}_{0.7}\text{Co}_{0.3}\text{O}_3$	0.0	6.1	-7.4	-16
Y series	0.1	5.0	-5.9	-14
	0.3	3.8	-3.9	-9.9
	0.5	3.4	-4.0	-15
Lu series	0.1	4.3	-6.0	-15
	0.3	2.1	-3.6	-22
	0.5	0.38	-0.7	-36



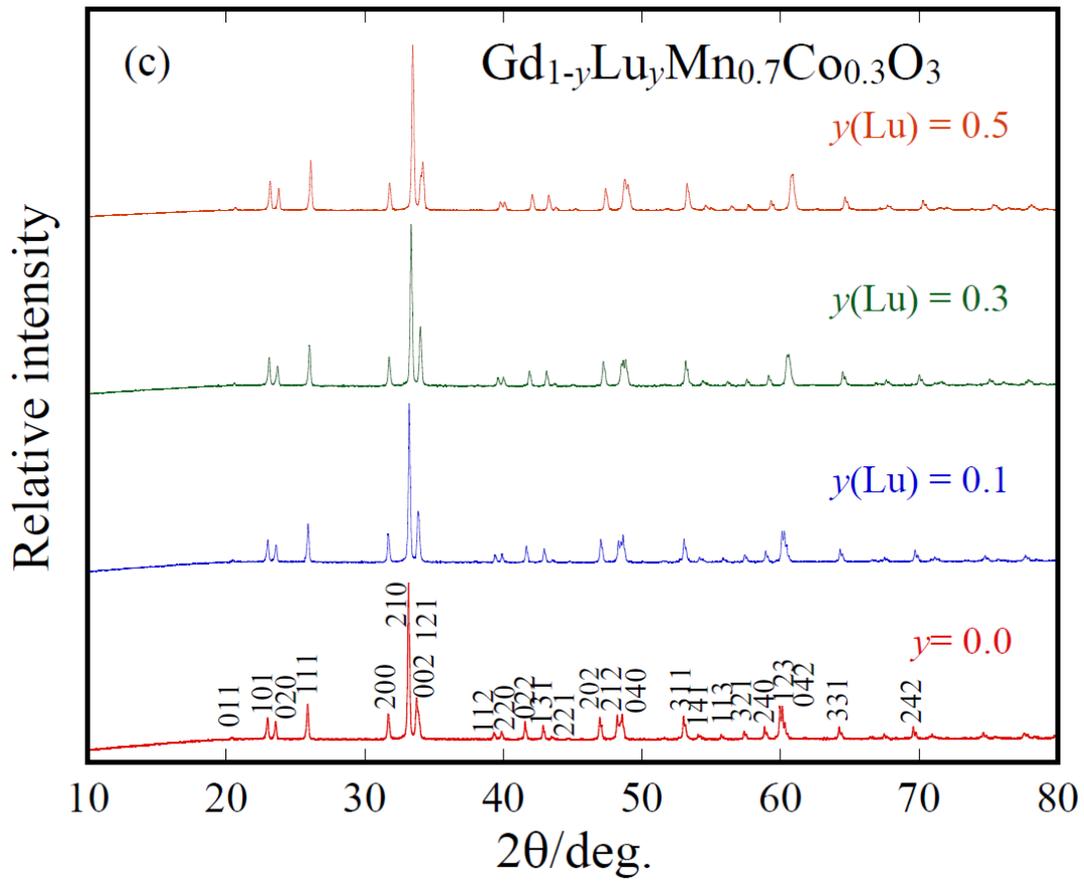


Fig. 1. XRD patterns for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$  with  $y=0.1, 0.3$  and  $0.5$  with substitution by the non-magnetic elements La, Y and Lu. (a), (b), and (c) correspond to  $\text{Gd}_{1-y}\text{La}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ ,  $\text{Gd}_{1-y}\text{Y}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ , and  $\text{Gd}_{1-y}\text{Lu}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ , respectively,

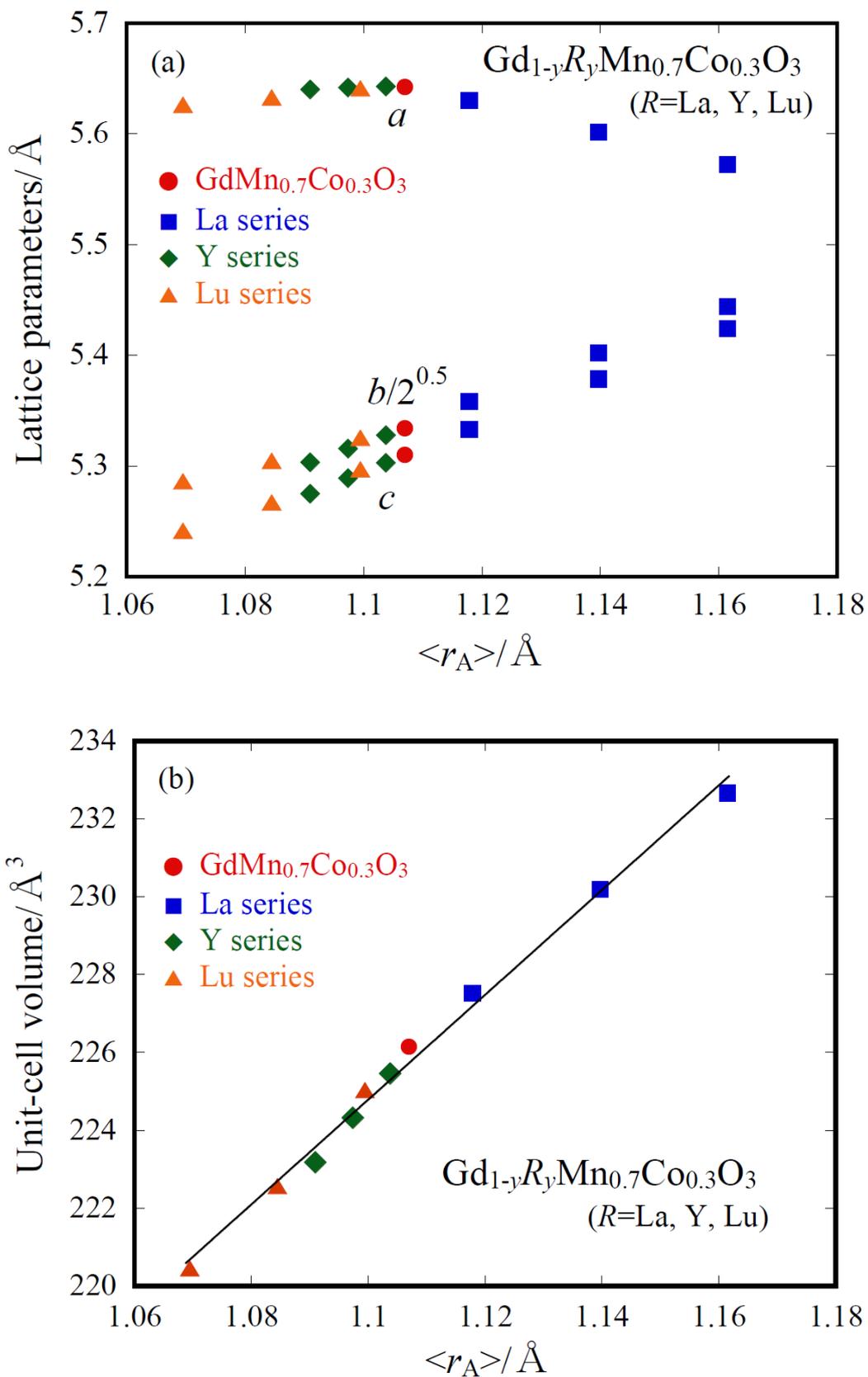


Fig. 2. Average ion radius  $\langle r_A \rangle$  dependence of (a) lattice parameters  $a$ ,  $b/\sqrt{2}$ , and  $c$ , and (b) unit-cell volume  $V$ .

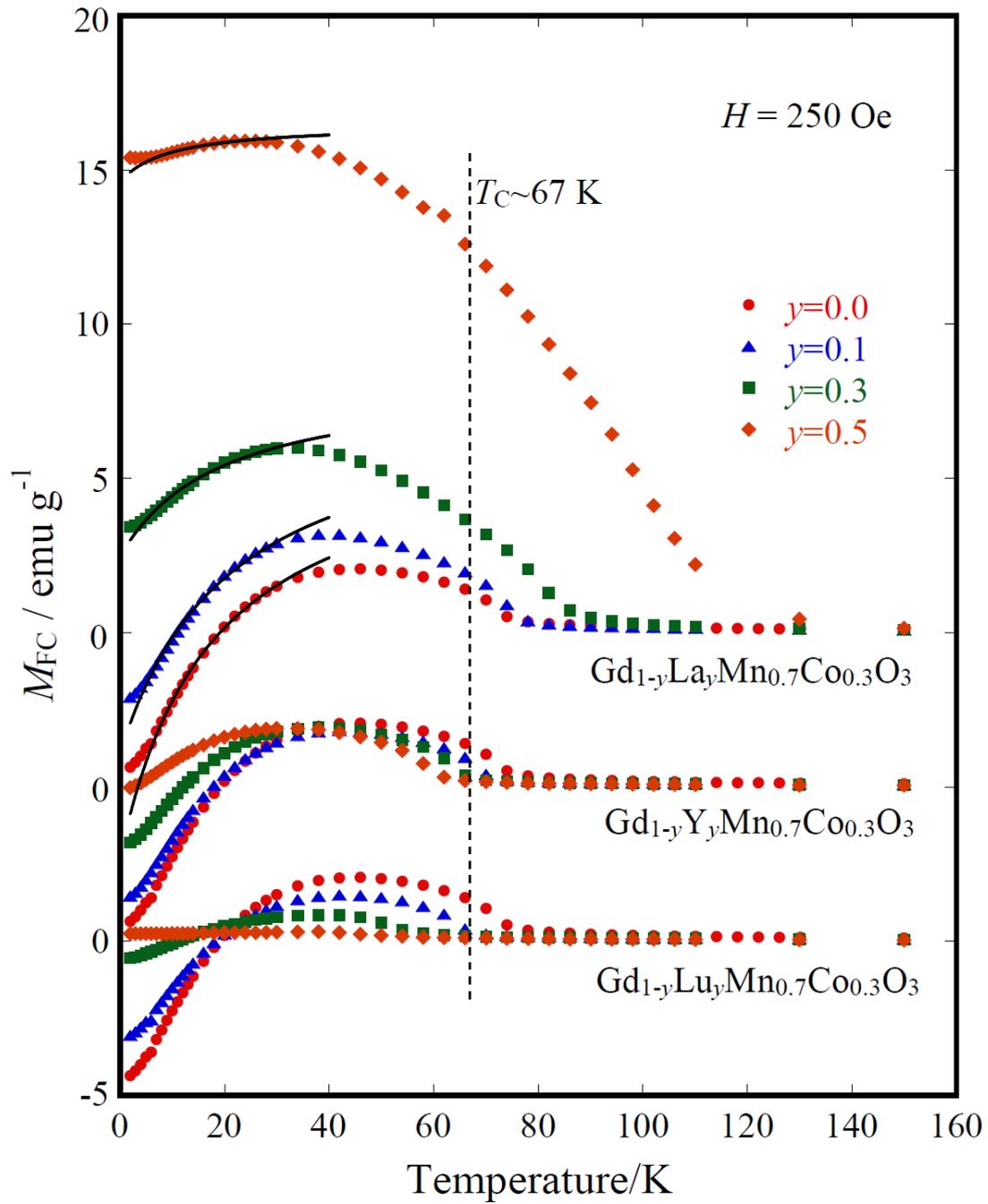


Fig. 3. Temperature dependence of  $M_{FC}$  for  $\text{Gd}_{1-y}\text{R}_y\text{Mn}_{0.7}\text{Co}_{0.3}\text{O}_3$ . Broken line shows  $T_C$  for  $\text{GdMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ . The solid lines in La series are fits using Eq. (4).

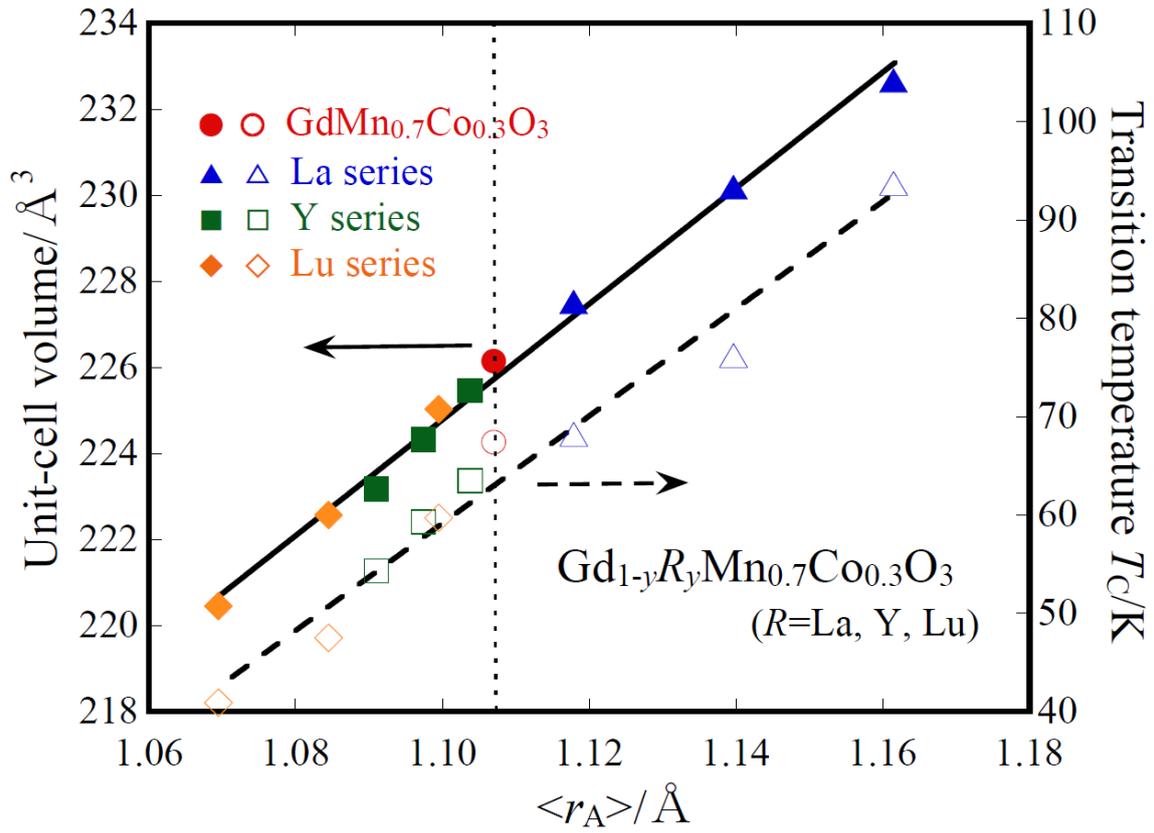
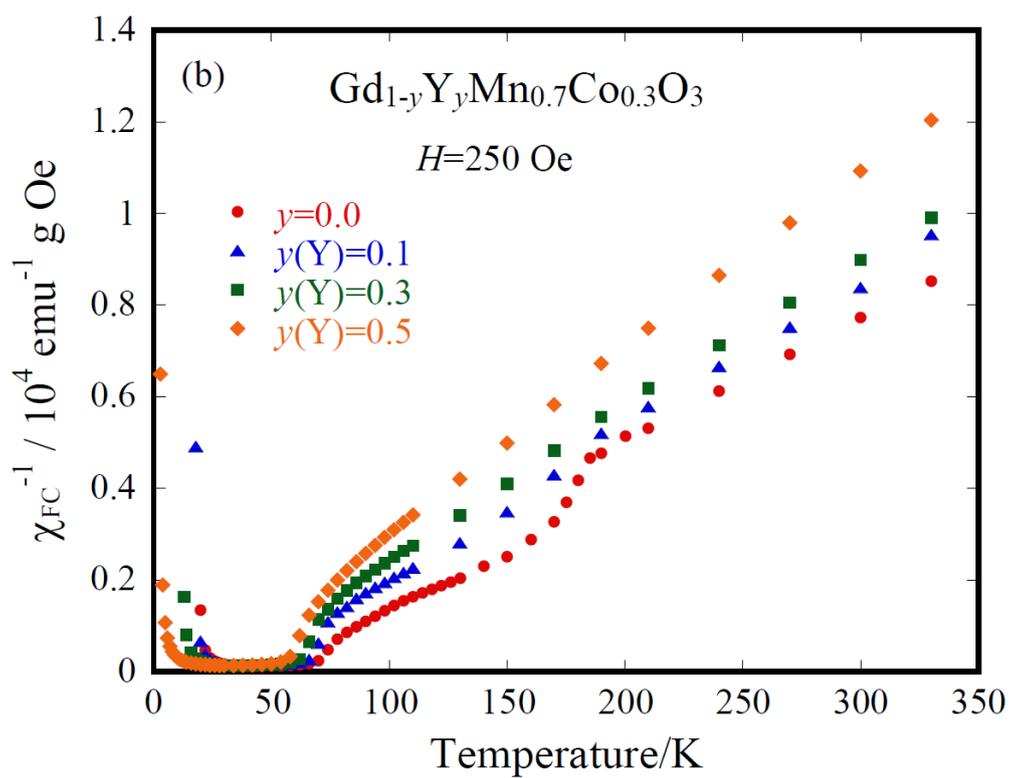
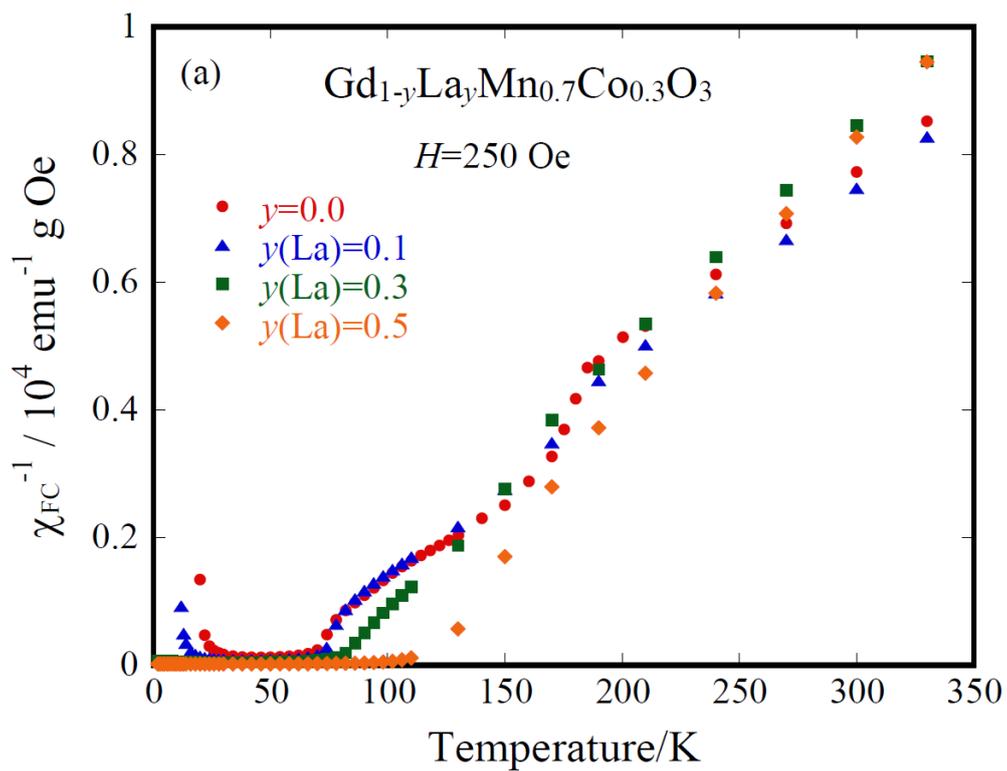
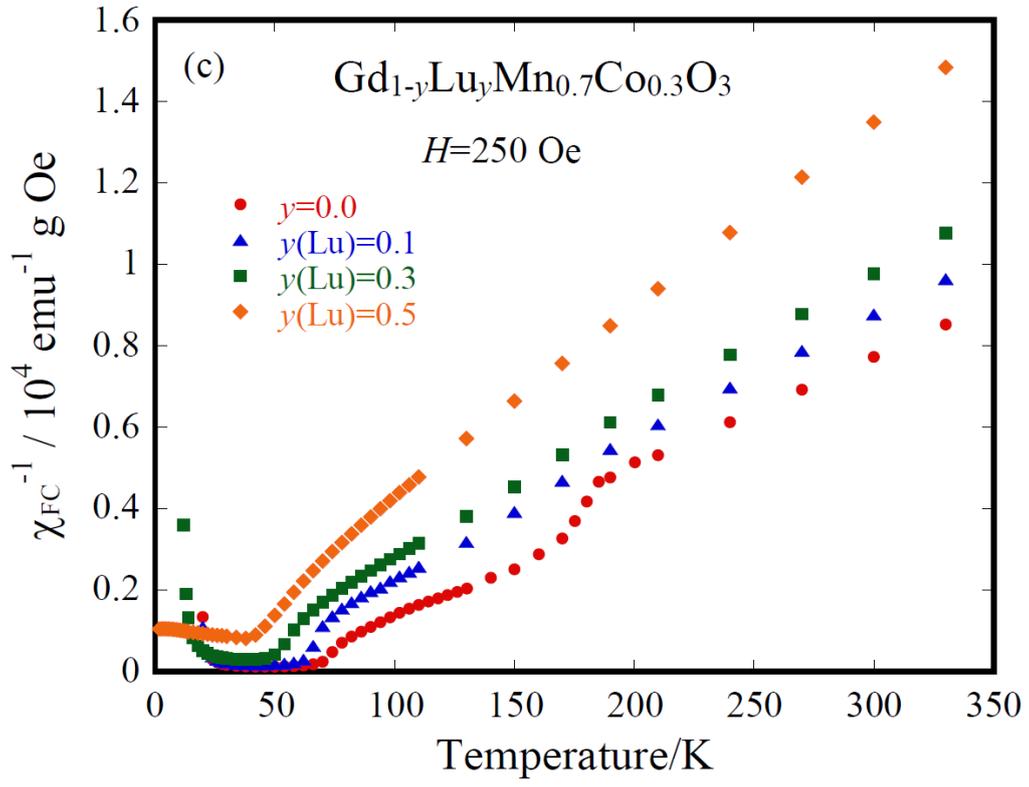


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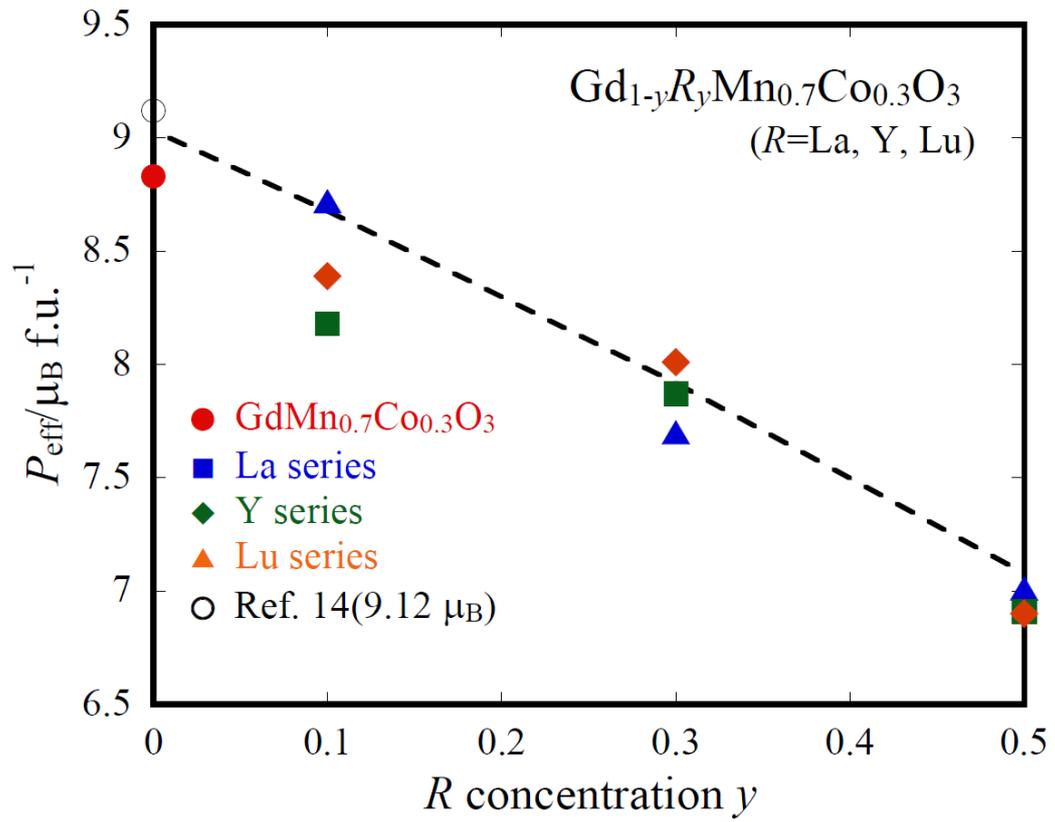


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