Vol. 34 (2003) ACTA PHYSICA POLONICA B No 2

# MAGNETIC PROPERTIES OF $\mathbf{GdMnO_3}$ AND $\mathbf{Gd_{0.67}Ca_{0.33}MnO_3}$ COMPOUNDS*

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*(Received July 10, 2002)*

The AC and DC susceptibilities, $^{57}$Fe and $^{155}$Gd Mössbauer and XRD studies of $GdMnO_3$ and $Gd_{0.67}Ca_{0.33}MnO_3$ manganites are presented. It was found that Mn moments order antiferromagnetically at 40 K for $GdMnO_3$ and at 60–70 K for $Gd_{0.67}Ca_{0.33}MnO_3$ (although with ferromagnetic component). The Gd moments order antiferromagnetically at 20 K for $GdMnO_3$ and at 25 K for $Gd_{0.67}Ca_{0.33}MnO_3$ but in this case some polarisation of Gd moments by Mn sublattice exists up to 60–70 K.

PACS numbers: 75.30–m, 75.30.Cr, 75.50.Gg, 75.50–y

The perovskite-type manganites $A^{3+}_{1-x}B^{2+}_{x}MnO_3$ (A=rare earth and B=alkaline earth) exhibit very interesting structural, magnetic, and transport properties including the colossal magnetoresistance (CMR) effect [1]. The pure $AMnO_3$ is an insulator with the strongest $Mn^{3+}-O-Mn^{3+}$ antiferromagnetic superexchange interactions but the substitution of $B^{2+}$ for $A^{3+}$ introduces holes into $e_g$ orbitals of Mn what gives rise to $Mn^{3+} - O - Mn^{4+}$ ferromagnetic double-exchange (DE) interaction. On the other hand, by tuning the size mismatch of $A^{3+}$ and $B^{2+}$, one can modify exchange interactions by changing Mn–O–Mn angle and Mn–O bond length. Two more types of magnetic interactions, $Mn^{3+} - A^{3+}$ and $A^{3+} - A^{3+}$ exist in manganites with magnetic A what makes their magnetic properties complex.

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* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

Therefore, the optimally doped $Gd_{0.67}Ca_{0.33}MnO_3$ is showing complex ferrimagnetic behaviour with transition temperature between 50 and 80 K [2, 3]. There is practically no information available about expected complex magnetic properties of pure $GdMnO_3$ [4]. In the present study we have carried out X-ray diffraction, microscopic $^{57}$Fe and $^{155}$Gd Mössbauer effect and macroscopic magnetisation and AC susceptibility measurements in order to clarify the magnetic properties of these manganites.

Polycrystalline $(Gd_{1-x}Ca_x)(Mn_{1-y}{}^{57}Fe_y)O_{3+\delta}$ samples with expected $\delta = 0.10$ for $x = 0$ and $\delta = 0$ for $x = 0.33$, and $y = 0$, 0.001 were prepared by the standard solid-state reaction technique. Temperature dependent X-ray diffraction (XRD) measurements in the temperature range 4–300 K were performed on a Siemens D5000 diffractometer. The magnetic data were collected with a SQUID magnetometer and with a convectional AC susceptometer (frequency 188.9 Hz and 0.5 Oe magnetic field) from 4.2 to 300 K. The $^{57}$Fe and $^{155}$Gd Mössbauer effect measurements were performed in the transmission geometry.

XRD measurements showed that $GdMnO_3$ and $Gd_{0.67}Ca_{0.33}MnO_3$ crystallise in the $GdFeO_3$-type structure and at 300 K can be characterised by the unit cell parameters: $a = 5.316(1)$ Å, $b = 5.845(1)$ Å, $c = 7.436(1)$ Å and $a = 5.337(1)$ Å, $b = 5.547(1)$ Å, $c = 7.511(1)$ Å, respectively. The temperature variations of $a$ and $b$ for $GdMnO_3$ exhibit clear anomalies approximately at 40 K while for $Gd_{0.67}Ca_{0.33}MnO_3$ some anomalies of parameters $b$ and $c$ *vs.* $T$ are seen at about 60 K. No anomalies were found in thermal evolution of the unit cell volume for both samples. No significant difference in lattice parameters was found for the corresponding samples doped with $^{57}$Fe.

Temperature dependence of AC magnetic susceptibility $\chi_{AC}$ of $GdMnO_3$ shows small anomaly at about 55 K and a strong increase in magnitude for temperatures lower than 25 K (see Fig. 1b) but the $\chi_{AC}$ curve of $Gd_{0.67}Ca_{0.33}MnO_3$ peaks at 60 K. The $\chi_{AC}$ measurements were also performed on 1 % $^{57}$Fe-doped samples. The only effect of $^{57}$Fe doping was to rise the position of the maximum in the $\chi_{AC}$ to about 65 K for $Gd_{0.67}Ca_{0.33}Mn_{0.99}{}^{57}Fe_{0.01}O_3$.

The thermal evolutions of magnetic moment $m$ of the zero-field-cooled (ZFC) $GdMnO_3$ and $Gd_{0.67}Ca_{0.33}MnO_3$ samples measured in order of increasing temperature under an applied magnetic field of 10 Oe are shown in Fig. 1a. One should note that $m(T)$ of $Gd_{0.67}Ca_{0.33}MnO_3$ shows maximum at about 55 K and that no anomaly is seen at about 40 K in $m(T)$ of $GdMnO_3$. Fig. 1a shows also the $m(T)$ of $Gd_{0.67}Ca_{0.33}MnO_3$ sample measured in order of decreasing temperature at $H = 100$ Oe. Comparing this dependence with the corresponding ZFC $m(T)$ curve one should interpret the broad minimum at about 25 K as the compensation point of a ferrimagnetic order of Gd and Mn sublattices.

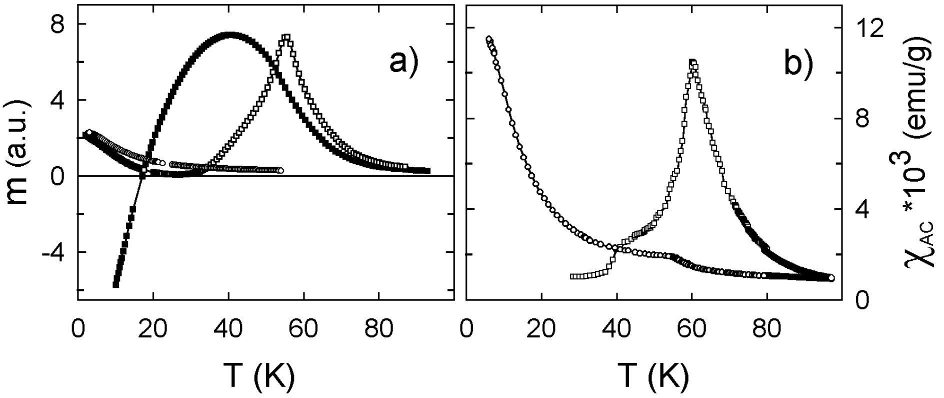

Fig. 1. (a) Temperature dependence of ZFC magnetic moment $m$ for $Gd_{1-x}Ca_xMnO_3$ (○: $x = 0$; □: $x = 0.33$, measured under 10 Oe) and $m$ for $x = 0.33$ (■, measured under 100 Oe). (b) $\chi_{AC}$ *vs* $T$ for $Gd_{1-x}Ca_xMnO_3$ (○: $x = 0$; □: $x = 0.33$).

Fig. 2 shows the main results of the paper: the temperature variation of the $^{155}$Gd mean hyperfine field $B_{hf}$ obtained from the fits of $GdMnO_3$ and $Gd_{0.67}Ca_{0.33}MnO_3$ Mössbauer spectra. In the fitting procedure the linewidths of the given spectrum were kept fixed on the value at 80 K. One can note clearly different temperature variation of $B_{hf}$ for both compounds. In addition, the temperature dependence of $B_{hf}$ of $Gd_{0.67}Ca_{0.33}MnO_3$ shows different character below and above 25 K.

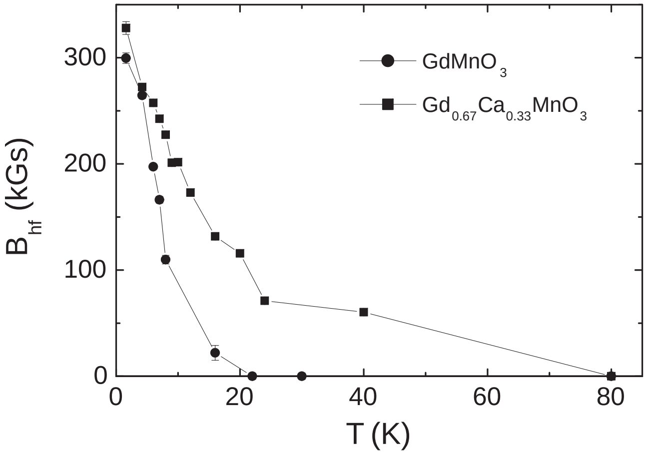

Fig. 2. Temperature dependence of the $^{155}$Gd mean hyperfine field $B_{hf}$ for $Gd_{1-x}Ca_xMnO_3$ (●: $x = 0$; ■: $x = 0.33$).

The substitution of $^{57}$Fe for Mn allows to monitor the magnetic behaviour of the manganese sublattice. The $^{57}$Fe Mössbauer effect measurements of $\mathrm{Gd(Mn_{0.99}{}^{57}Fe_{0.01})O_3}$ showed that it is in paramagnetic state from 300 K down to 40 K and that $\mathrm{Gd_{0.67}Ca_{0.33}Mn_{0.99}{}^{57}Fe_{0.01}O_3}$, is in paramagnetic state down to 70 K. Below these temperatures a magnetic order begins to develop in both samples what was reflected in progressive splitting of Mössbauer spectra with lowering temperature.

Combining our XRD, magnetic and $^{57}$Fe Mössbauer results of $^{57}$Fe-doped and undoped $\mathrm{Gd_{0.67}Ca_{0.33}MnO_3}$ samples together with literature data [2,3] one can infer that Mn sublattice orders antiferromagnetically with small ferromagnetic component at $T_\mathrm{N}$ of about 60–70 K in this compound. The $^{155}$Gd Mössbauer results show that small transferred $B_\mathrm{hf}$ field from Mn sublattice, and due to this some polarisation of Gd moments starts at $T_\mathrm{N}$, but sharp increase of $B_\mathrm{hf}$ and an ordering of Gd moments takes place below 25 K. The ferromagnetic component of basically antiferromagnetically ordered Gd moments cancels small ferromagnetic component from Mn sublattice at 25 K (compensation point). The $^{155}$Gd and $^{57}$Fe Mössbauer measurement of $\mathrm{Gd(Mn_{1-y}{}^{57}Fe_{y})O_3}$, where $y = 0$, 0.01, showed clearly that Mn and Gd magnetic moments order at about 40 K and 20 K, respectively. The neutron diffraction measurements of $\mathrm{TbMnO_3}$ (the adjacent compound in the series of rare earth manganites) showed that this compound develops an incommensurate sine-wave ordering of Mn moments at 40 K and a short range sine-wave ordering of Tb moments at 7 K [5]. It seems natural to expect that also this type of complex sine-wave magnetic structures appear in $\mathrm{GdMnO_3}$ at about 40 K and 20 K.

This research was supported by the Polish State Committee for Scientific Research (KBN) grant No. 2 P03B 042 18 and by the Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy.

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