X-MCD magnetometry of CMR perovskites La$_{0.67-y}$RE$_y$Ca$_{0.33}$MnO$_3$

M. Sikora[a,c,*], Cz. Kapusta[a], D. Zając[a,c], W. Tokarz[a,c], C.J. Oates[a], M. Borowiec[a],
D. Rybicki[a], E. Goering[b], P. Fischer[b], G. Schütz[b], J.M. De Teresa[c], M.R. Ibarra[c]

[a] Solid State Physics Department, Faculty of Physics and Nuclear Techniques, AGH-University of Science and Technology,
Av. Mickiewicza 30, Cracow 30-059, Poland
[b] Max-Planck-Institut für Festkörperforschung, Stuttgart 70569, Germany
[c] Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza – CSIC, Zaragoza 50009, Spain

Abstract

Field dependences of the magnetic circular dichroism at the Mn:K edge and RE:L$_2$, L$_3$ edges in colossal magnetoresistive perovskites La$_{0.67-y}$RE$_y$Ca$_{0.33}$MnO$_3$ ($y = 0$, Tb-doped $y = 0.1$, 0.22 and Nd-doped $y = 0.33$) are reported. Ferromagnetically ordered compounds show a similar dependence for the Mn and RE magnetic sublattices, in contrast to the cluster glass ($y = 0.22$) compound which revealed a weaker Mn–RE magnetic coupling. By comparison of X-MCD and VSM magnetometry an estimate of the relative amount of manganese atoms in the metallic ferromagnetic regions is obtained.
© 2003 Elsevier B.V. All rights reserved.

Magnetoresistive manganese oxides have been extensively studied during last decade especially because of their promising applications in magneto-electronic devices. The compounds studied belong to the (La, A)MnO$_3$ (A = alkaline earth) series. They exhibit a huge decrease in electrical resistivity, at applied magnetic fields, in the vicinity of magnetic ordering temperatures. This feature is known as "colossal magnetoresistance" (CMR) [1]. Doping of divalent Ca for trivalent La leads to a mixture of Mn^{3+} and Mn^{4+} states which interact via double exchange-like interaction [2] and promotes the ferromagnetic coupling of the adjacent Mn^{3+} and Mn^{4+} spins as well as "metallic" conductivity. The stoichiometry La$_{0.67}$Ca$_{0.33}$MnO$_3$ corresponds to the highest magnetic ordering temperature T_C of 270 K. Doping of Tb or Nd for La raises the

magnitude of the CMR effect and can dramatically change the magnetic structure. Compounds with large substitution of Tb ($y > 0.2$) exhibit a spin glass behaviour and at zero field are insulating in the whole temperature range [3]. Neodymium-doped compounds exhibit either ferromagnetic metallic state for light doping or charge-ordered state at high Nd concentration. For the compound with $y \approx 0.33$, macroscopic measurements indicate an "anomalous" ground state attributed to a competition of ferro- and antiferromagnetic interactions [4]. Recent X-MCD measurements [5] have revealed a derivative-like shape of the dichroic signal at Mn:K edges as well as at the La,Tb,Nd:L$_{2,3}$ edges. This behaviour has been attributed to the exchange splitting of the empty Mn 4p and La,RE 5d states. A dichroic signal with similar magnitude for all the samples is observed at the Mn:K edge and at the La:L$_{2,3}$ edges, whereas the magnitude of the RE:L$_{2,3}$ signals decreases with Tb doping. This behaviour is due to changes of magnitude of the RE–Mn and Mn–Mn

*Corresponding author. Tel.: +48-12-6172904; fax: +48-12-6341247.

E-mail address: marcins@uci.agh.edu.pl (M. Sikora).

interactions with doping. In order to elucidate a possible relation of this behaviour to terbium and neodymium magnetism, a systematic study of the element specific magnetisation by means of X-MCD has been undertaken.

Measurements have been carried out at the HASY-LAB (Hamburg) A1 beamline in a single beam mode with double Si(1 1 1) crystal monochromator under magnetic field as high as ± 2 T. The energy of the beam was fixed at the maximum of the dichroic signal. X-MCD measurements were carried out at 5 and 77 K on polycrystalline powder samples of $La_{0.67-y}RE_y$-$Ca_{0.33}MnO_3$ compounds with $y = 0$, Tb-doped $y = 0.1, 0.22$ and Nd-doped $y = 0.33$.

The X-MCD magnetometry curves of all the compounds, Fig. 1, at the Mn:K, $La:L_2$ edge as well as at the $Nd:L_2$ edge of $y = 0.33$ show magnetic saturation. It is
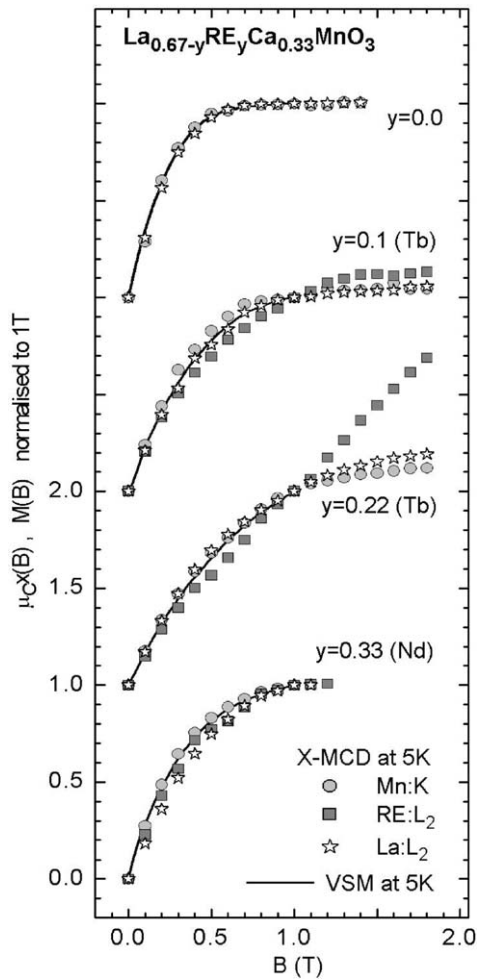
worth noting that the X-MCD magnetometry curves at Mn:K edges of all the compounds saturate similarly to the bulk magnetisation measured by vibrating sample magnetometry (VSM) on the same pieces of X-MCD samples. Similar behaviour is observed at the $La:L_2$ edge except for $y = 0.33$ where a saturation of the $La, Nd:L_2$ dichroic signal is observed at larger fields. However, the $Tb:L_2$ curve in Tb-doped compounds saturates at much higher fields, e.g. $B \approx 1.4$ T for $y = 0.1$, whereas for $y = 0.22$ it does not show any tendency to saturation, similarly to the bulk magnetisation of the compound. The effect is particularly pronounced at 5 K where the $Tb:L_2$ X-MCD magnetometry curve is linearly dependent on the magnetic field up to 1.8 T.

Since the magnitude of the Tb X-MCD signal is much larger than that of La we conclude that the magnetic moments of Tb are ordered at the temperatures of the measurements. A much different behaviour of the Tb X-MCD signal of $y = 0.22$ indicates that terbium magnetic moments exhibit a glassy state in which they are relatively weakly coupled to the manganese moments causing a lack of saturation of the bulk magnetisation, in contrast to other compounds.

As the field dependence of dichroic signal resembles that of the magnetisation of the element [6], the bulk magnetisation curve could be fitted by a linear combination of the Mn and RE X-MCD magnetometry curves. The results show that about 85–95% of the manganese atoms contribute to the ferromagnetic phase in all the compounds at $T = 5$ K. This agrees with recent NMR results which have also shown that the insulating $y = 0.22$ compound consists of clusters of ferromagnetically (DE) coupled Mn spins and all the compounds exhibit a similar temperature dependence of the mean Mn moment ($\langle S_z \rangle$) [7]. A contribution of terbium magnetic moment was determined at the saturation field of Mn magnetisation. The values obtained were 42(8)% and 10(4)% of the RE atomic moment, for $y = 0.1$ and 0.22, respectively, which indicate a canted Tb–Mn coupling or terbium moment significantly lower than its free ion value.

The amount of Mn atoms in ferromagnetic regions does not change significantly with temperatures up to $T = 77$ K, even for the $y = 0.22$ compound, which has the glassy temperature of 50 K [3]. The contribution from RE atoms in ferromagnetic regions decreases rapidly with increasing temperature except for the cluster-glass compound which shows opposite tendency, possibly related to a more isotropic Tb–Mn magnetic coupling and/or a lower terbium magnetic anisotropy above glassy temperature.

Fig. 1. X-MCD and VSM magnetometry results at 5 K. Curves are normalised to the value at $B = 1$ T for better comparison.

References

[1] S. Jin, et al., Science 264 (1994) 413.

[2] C. Zener, Phys. Rev. 82 (1951) 403.

[3] J. Blasco, et al., J. Phys.: Condens. Matter 8 (1996) 7427.

[4] M.R. Ibarra, et al., Phys. Rev. B 57 (1998) 7446.

[5] M. Sikora, et al., J. Alloys Comp. 328 (2001) 100.

[6] C. Giorgetti, et al., Phys. Rev. B 48 (1993) 12732.

[7] Cz. Kapusta, et al., J. Magn. Magn. Mater. 196–197 (1999) 446.