The effect of artificial boundary grain on the magneto- and electro-transport properties of \((1 - x)\La_0.7\Ca_0.3\MnO_3 + x\A (\A = \Al_2\O_3 \text{ and Ag})\) nanocomposite

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Abstract
The magneto- and electro-transport properties of two series of nanocrystalline \((1 - x)\La_0.7\Ca_0.3\MnO_3 + x\A (\A = \Al_2\O_3 \text{ and Ag})\) composites have been systematically and thoroughly studied. The observed electronic transport behavior over the whole temperature range (5–300 K), especially the change in metal–insulator transition temperature with increasing \Al_2\O_3 \text{ and Ag content while the ferromagnetic–paramagnetic transition remained unaffected, was explained by applying a two-component phenomenological model. We have attributed the unusual low-temperature resistivity upturn of composites to a change in charging energy. Most interestingly, magneto-transport measurements showed that the low-field magnetoresistance (LFMR), as well as the high-field magnetoresistance (HFMR), displayed a Curie–Weiss-like law behavior. Basing on the spin-polarized transport of conduction electrons at the grain boundaries, we have analyzed our experimental data and found that the temperature dependence of low- and high-field magnetoresistance is controlled predominantly by the nature of the temperature response of surface magnetization of particles. The competition between grain-boundary pinning strength \(k\), magnetic field and thermal energy \(k_B T\) created the temperature sensitive behavior of magnetoresistance as well as that of surface spin susceptibility \(\chi_b\).

Keywords: manganite composites, low-field magnetoresistance, polarized tunneling

Classification numbers: 5.02, 5.11

1. Introduction

The discovery of the colossal magnetoresistance (CMR) effect in doped manganites \(\R_{1-x}\A_x\MnO_3\) (\R is rare earth, A is Ca, Sr or Ba) has generated renewed interest in the study of these materials. So far, two CMR effects have been found in these manganites: intrinsic CMR and extrinsic CMR. The intrinsic CMR is caused by the double exchange (DE) mechanism. According to Zener [1] the DE mechanism is useful to explain the CMR phenomena observed near the Curie temperature \(T_C\) at a relatively high magnetic field (up to several kOe). The extrinsic CMR, which is related to the grain boundaries (both natural as well as artificial), can be explained by spin polarized tunneling [2] or spin-dependent scattering [3]. In the case of the polycrystals, the grain surface plays a major role. On the surface of the particles,
the crystal structure will be changed. Firstly, the octahedral symmetry of Mn ions is broken due to the appearance of the incomplete coordination or the strong Jahn–Teller distortion. The splitting of the $e_g$ orbitals is different and, if one orbital moves away from the Fermi level, the double exchange interaction is canceled and the direct super exchange between the core $t_{2g}$ spins is promoted. As the kinetic energy of the carriers is reduced, the Coulomb repulsion pushes the charge to the outermost layer, thereby generating a barrier to electron transfer between grains [4]. The change in the magnetic interactions does alter the spin stiffness at the surface. In addition, surface dislocations and the presence of extra phases in contact at the grain boundary change locally the anisotropy energy, thereby providing pinning centers for the surface spin. The general result is the creation of an insulating layer at the interface of the grains [5] with a high degree of spin disorder. Nowadays, research is focusing on how to obtain a large value of the magnetoresistance (MR) at a low field and room temperature in order to satisfy practical applications. Many attempts have been made to enhance the low-field magnetoresistance (LFMR) effect of manganites by a mixture of the CMR materials with secondary phases, including insulators [6–9], magnetic materials [10–12] and metals [13–16]. Most of these studies mainly focus on the influence of artificial grain boundaries on electro-magnetic behavior and enhancing LFMR in composites. However, the effect of surface magnetization ($M_S$) on the LFMR and the unusually low temperature resistivity minimum have not been studied widely.

In this article, we intend to review our recent research on the magnetic and electrical properties of $(1 - x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Al}_2\text{O}_3$ (LCMO/$\text{Al}_2\text{O}_3$) and $(1 - x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Ag}$. LCMO/Ag composites [7, 13, 15, 17–19]. This review consists of two parts. The first part deals with some salient features, e.g. structure, electro-magnetic properties, especially the change in metal–insulator transition temperature with increasing $\text{Al}_2\text{O}_3$ and Ag content while the ferromagnetic–paramagnetic transition remained unaffected. We have attributed the unusual low-temperature resistivity upturn of composites to a change in charging energy. The second part is devoted to an overview of experimental results on CMR and related magneto-transport characteristics at low magnetic fields for LCMO-based composites with artificial grain boundaries, such as $\text{Al}_2\text{O}_3$ and Ag. Further, analyzing the data in the following of the theoretical perspective as proposed by Lee et al [20], we found that the temperature dependence of MR is governed predominantly by the nature of the temperature response on the surface magnetization ($M_S$) of manganite composite particles.

2. Experimental

The $(1 - x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Al}_2\text{O}_3$ (LCMO/$\text{Al}_2\text{O}_3$) $(x = 0, 0.01, 0.02, 0.03, 0.04$ and $0.05)$ composites were prepared in three steps. Firstly, the LCMO powder was synthesized by a conventional solid state reaction method combined with a high-energy milling method. Secondly, the LCMO and $\text{Al}_2\text{O}_3$ powders were ground by a high-energy milling machine for 2 h. Finally, the appropriate amounts of LCMO nano powder and $\text{Al}_2\text{O}_3$ nano powder were mixed and a homogenous powder was pressed into pellets and sintered at 900 °C for 3 h. Meanwhile, the $(1 - x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Ag}$ (LCMO/Ag) with $x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$ samples were prepared in two steps. Step 1: the LCMO powder was prepared by the sol–gel process. Step 2: appropriate amounts of LCMO and $\text{Ag}_2\text{O}$ powders were mixed according to the desired molar ratio. The mixtures were then ground and pressed into pellets. The pellets were finally sintered at 900 °C in air for 2 h, and then slowly furnace-cooled to room temperature. The crystalline structure of the samples was determined using a Siemens D-5000 x-ray diffractometer. Magnetic properties were characterized by a vibrating sample magnetometer (VSM) in the temperature range 100–300 K and at a field of up to 100 Oe. The resistivity and the magnetoresistance ($R–H$) of all of the composites were examined by a PPMS (Physical Property Measurement Systems) machine in the magnetic field from 0 to 10 kOe and the temperature range from 5 to 300 K.

3. Results and discussion

X-ray diffraction pattern analyses showed that the reflection peaks of LCMO remained unshifted by adding the artificial boundary materials. The peaks corresponding to $\text{Al}_2\text{O}_3$ and Ag are also observable, and their intensity increases with increasing alumina and silver percentages, respectively. This is an indication that no reaction between the two compounds occurred. The grain size increased up to around 70 nm in the final sintering process. On the other hand, the Curie temperature $T_C$ appeared to remain unchanged at around 260 K and about 250 K for LCMO/Ag and LCMO/$\text{Al}_2\text{O}_3$, respectively. The observed constancy of $T_C$ also indicates that the stoichiometry of the LCMO phase within the strains remains essentially unaffected as $\text{Al}_2\text{O}_3$ and Ag is not accommodated within the perovskite structure and it occupies only at the grain boundaries of LCMO granules. The saturation magnetization values at 5 K of LCMO/$\text{Al}_2\text{O}_3$ and LCMO/Ag are obtained from the corresponding high-field magnetization curves by fitting these experimental data to the ‘saturation approach law’ [5],

$$M(H) = M_s[1 - a/H - b/H^2] + \chi d H,$$

where $a$ and $b$ are suitable constants. The results can be seen in figure 1, and it is clear that the linear decrease in $M_S$ is due only to the alumina and silver percentage present in the sample. The addition of $\text{Al}_2\text{O}_3$ or Ag does not change the magnetic transition of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ but leads to a decrease in $M_S$ due to the magnetic dilution. $M_S$ decreases with increasing $x$ as would be expected due to the decrease in content fraction of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ phase and increase in non-ferromagnetic materials. It is seen that the decrease in $M_S$ with increasing $x$ for the LCMO/$\text{Al}_2\text{O}_3$ system is larger than that for the LCMO/Ag system. The reason is that the volume percentage of $\text{Al}_2\text{O}_3$ is larger than that of Ag with the same $x$ (mole content).

Figure 2 shows the temperature dependence of resistivity ($\rho$) measured in the temperature region from 5 to 300 K for the two composites. As seen in figure 2, there are contrasting results of electric properties in the two series of the
nanocrystalline \((1-x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{Al}_2\text{O}_3\) systems. In the case of \(\text{LCMO/Al}_2\text{O}_3\), the resistivity of all of the composites increases and their metal–insulator transition temperature \(T_{\text{MI}}\) shifts down to a lower temperature with increasing \(\text{Al}_2\text{O}_3\) content (figure 2(a)). Conversely, the presence of \(\text{Ag}\) in \(\text{LCMO}\) matrices results in a decrease in resistivity and an increase in the metal–insulator transition temperature (figure 2(b)). However, at temperatures below 50 K, a minimum of resistivity has been observed for both of the sample series.

The strong depression of \(T_{\text{MI}}\) could be caused by the induced lattice disorder and also by the increase in the non-magnetic \(\text{Al}_2\text{O}_3\) phase or \(\text{Ag}\) phase fractions segregated at the grain surface boundaries. This improves the atomic disordered structure and magnetic state on the grain surfaces and decreases or increases the connectivity between the grains. In order to clearly explain the electrical transport, a modified model proposed by de Andres et al [21], Rubinsten [22] and Das et al [23] is accepted and the most adopted one. They proposed the concept of a conduction channel mechanism based upon the nature of connectivity between grains. Moreover, due to the disordered nature of the grain boundaries, grain boundary resistivity is higher than the resistivity inside the grains. In the pure \(\text{LCMO}\) samples, the electrical transport is realized through a direct contact between the \(\text{LCMO}\) grains, the electrical channel homogeneous between the intergrains of \(\text{LCMO}\). As the introduction of an \(\text{Al}_2\text{O}_3\) insulator or \(\text{Ag}\) metal, there are two kinds of conduction channel coexisting in parallel in the \(\text{LCMO/Al}_2\text{O}_3\) and \(\text{LCMO/Ag}\) composites. One is related to the \(\text{LCMO}\) grains, which determines the transport properties of the system. The second is related to \(\text{Al}_2\text{O}_3\) or \(\text{Ag}\) grains, mostly distributed at the grain boundaries of \(\text{LCMO}\).

In the case of the \(\text{LCMO/Al}_2\text{O}_3\) composites, the \(\text{Al}_2\text{O}_3\), mostly located at the grain boundaries, acts as a barrier. Since the resistivity of \(\text{Al}_2\text{O}_3\) is greater than that of \(\text{LCMO}\), the second channel can be regarded as an energy barrier that inhibits the direct conduction between the \(\text{LCMO}\) grains. Therefore, with the increase in \(\text{Al}_2\text{O}_3\) grains at the grain boundaries, the effective electrical channel of the composites can be reduced, leading to an increase in resistivity. Otherwise, the location of high conductivity metal \(\text{Ag}\) among the grains opens a new channel for electron transport, which in turn results in decreased resistivity of the \(\text{LCMO/Ag}\) samples. On the other hand, the increase in oxygen content released from \(\text{Ag}_2\text{O}\) in the sintering process not only improves the magnetic inhomogeneity of the samples and decreases the microstructure deficiency but also enhances the concentration and hopping mobility of carriers through a little change in the \(\text{Mn}^{3+}/\text{Mn}^{4+}\) ratio [24].

As discussed, all of the samples show an unusually low temperature resistivity minimum at some temperature \(T_{\text{min}}\) below 50 K (see figure 2). This is another extrinsic effect that is not present in single crystals but is common in

**Figure 1.** Saturation magnetization at 5 K for samples of (a) \(\text{LCMO/Al}_2\text{O}_3\) and (b) \(\text{LCMO/Ag}\). The line is a linear fit to the data [17].

**Figure 2.** Resistivity versus temperature, \(\rho(T)\), for nanocomposite samples (a) \(\text{LCMO/Al}_2\text{O}_3\) [18] and (b) \(\text{LCMO/Ag}\) [13, 15].
Figure 3. Reduced resistivity versus $T^{-1/2}$ for samples with a grain boundary of $\text{Al}_2\text{O}_3$ (a) and Ag (b) [7]. Lines are fits to the data. The slope of the fits is proportional to the electrostatic energy barrier between grains.

Figure 4. Variation in the fitting factor $A$ (or $E_C$) for low $T$ resistivity: (a) with various $\text{Al}_2\text{O}_3$ content and (b) various Ag content.

nano-polycrystalline ceramic samples and can be tentatively related to an electrostatic blockade of carriers between grains.

In order to describe this sharper rise in resistivity observed for all of the samples at low temperature, we have adopted the theoretical results as proposed by Sheng et al [25], according to which

$$\rho(T) \propto \exp\left(\frac{A}{T}\right)^{1/2}. \tag{2}$$

This functional form can be recognized in the fits of figure 3 [7]. The slope of those lines ($A$) is somehow proportional to the electrostatic blocking energy ($E_C$). As we can see in figure 4(a), the proportional constant increases with $\text{Al}_2\text{O}_3$ content. This indicates an increasing influence of the barrier between particles with increasing $\text{Al}_2\text{O}_3$ content. Otherwise, as shown in figure 4(b), the decrease in $E_C$ in the case of LCMO/Ag proved that the barrier between particles decreases with increasing Ag content.

Figure 5 presents the MR ratios as a function of applied field for LCMO/$\text{Al}_2\text{O}_3$ and LCMO/Ag at a fixed temperature of $T = 5\,\text{K}$ and $T = T_C$ measured in the magnetic field range of 0–30 kOe. The behavior of the MR is interesting. At low temperature ($T = 5\,\text{K}$), the MR value increases by nearly 5% by adding 20% of Ag to the pure LCMO (see figure 5(a)). At this point, we must adduce percolation as the most likely underlying effect in order to explain the magneto-transport results presented previously. The percolation threshold value obtained is 20% for our composites. Nevertheless, the MR at 260 K gains largest value for $x = 0.5$, suggesting that increasing Ag content improves the MR around $T_C$. Meanwhile, at low temperature ($T = 5\,\text{K}$), the MR value increases by nearly 15% by adding 5% of $\text{Al}_2\text{O}_3$ to the pure LCMO (see figure 5(a)). Nevertheless, the MR at 250 K is largest for $x = 0$. The decrease in MR at $T_C$ can be explained by taking into account the dilution of the ferromagnetic phase and the DE mechanism around the paramagnetic to ferromagnetic phase transition temperature as a consequence of increasing $\text{Al}_2\text{O}_3$ content.

In order to further evaluate the property of the MR behavior observed in this Ag and $\text{Al}_2\text{O}_3$-added composite, we survey the magnetic field dependence of MR for all samples by using a phenomenological model, which takes into account the spin polarized tunneling at the grain boundaries [26]. According to this model, one gets the expression for MR as follows:

$$\text{MR} = -A' \int_0^H f(k)dk - JH - KH^3. \tag{3}$$

Within the approximation of the model, in zero fields, the domain walls are pinned at the grain boundaries pinning centers with pinning strengths $k$. At the grain boundaries,
Figure 5. MR ratios as a function of applied field for composites (a) LCMO/Al$_2$O$_3$ at 5 K, 250 K [7], and (b) LCMO/Ag at 5 K, 260 K [15].

the distribution of pinning strengths (defined as the minimum necessary field to overcome a particular pinning barrier) $f(k)$ is given as

$$f(k) = A \exp(-Bk^2) + CK^2 \exp(-Dk^2)$$

(4)

where all of the adjustable fitting parameters, $A$, $B$, $C$, $D$, $J$, $K$ with $A'$ absorbed in $A$ and $C$ are determined from a nonlinear least square fitting to calculate MR$_{spt}$, which was defined as

$$\text{MR}_{spt} = \int_0^H f(k) dk.$$  

(5)

Differentiating equation (3) with respect to $H$ and putting into equation (4), we get

$$\frac{d(\text{MR})}{dH} = A \exp(-BH^2) + CH^2 \exp(-DH^2) - J - 3kH^2.$$  

(6)

In order to find the best-fit parameters at several temperatures, the experimental MR versus $H$ curves were fitted to equation (4). The differentiated curves are fitted by equation (6) at $T = 5$ K for LCMO/Al$_2$O$_3$ and LCMO/Ag composite samples (not shown here). Next, these parameters were put in equation (3). Figure 6 shows the theoretical curves from equation (3), which are quite matched to the experimental curves at several temperatures below $T_C$. We observe that the total magnetoresistance is a monotonic function of temperature with a slow decrease at low temperature. The intrinsic contribution (MR$_{\text{int}}$), however, follows the expected double exchange behavior with a steady increase in temperature. On the other hand, MR$_{spt}$ decreases steadily with rising temperature.

Figure 7 shows the best fit of MR$_{spt}(T)$ to the expression $a + b/(c + T)$. The fitted curves match well the extracted values of MR$_{spt}$ from the model. However, our values of $b$ and $c$ for the best fit are much higher compared to those observed by Hwang et al [2], although the $T_C$ value of our system is much smaller. This may be attributed to the structure of the composite. Al$_2$O$_3$ or Ag distributing at the grain boundaries can alter the size of the ferromagnetic, introducing artificial boundaries or defects, or diluting the ferromagnetic grains with a non-magnetic insulator. These procedures will significantly influence the tunnel of conduction electrons and hence an enhancement of MR would be expected.

Figure 8 shows the temperature variation of the total experimental MR$(T)$ at $H = 10$ kOe. Most interestingly, the temperature dependence of MR is also described quite well by an expression of the type $a + b/(c + T)$. In the case of polycrystalline materials, grain boundaries provide defect sites where the anisotropy energy of the surface spin is the lowest. At the disordered surface of polycrystalline grains, strong pinning of surface spins is expected. In the case of LCMO with the Al$_2$O$_3$ or Ag grain boundaries, these defects occur with high possibility at the grain surface. This is attributed to the magnetic dilution. When applying a magnetic field, the surface spins would be freezed as a consequence of the interactions between the grain boundary pinning center $(k)$ and the magnetic field. However, when the temperature increases up to a remarkable value, the
Figure 6. Experimental MR versus H curve (dot) at various temperatures in the magnetic field range of 0–10 kOe for samples (a) LCMO/Al₂O₃ [7] and (b) LCMO/Ag [15], and the fitted curve (line) using equation (3).

Figure 7. The best fit of MRspt at $H = 10$ kOe to the function $a + b/(c + T)$ for (a) LCMO/Al₂O₃ [19] and (b) LCMO/Ag [15].

thermal energy is high enough to break the pinning of surface spin. As a result, MR is varied with temperature following the relation $a + b/(c + T)$, similar to the case of MRspt.

Further, in order to clearly elucidate the temperature dependence behavior of LFMR and HFMR, we used the theoretical perspective proposed by Lee et al [20]. Under the consideration of the present model, the slope of the magnetoconductivity (MC) versus $H$ curve (correct form) at high field, i.e., $H > 5$ kOe, can be taken to be a measurement of the boundary spin susceptibility $\chi_b$ according to the equation

$$MC \sim \frac{\sigma}{\sigma_0} \approx 1 + \frac{1}{3} M^2 + 2\chi_b HM.$$  

Here, $\sigma$ is the conductivity in the presence of magnetic field $H$, $\sigma_0$ is the zero-field conductivity, $M$ is the normalized magnetization of the bulk spin, and $\chi_b$ is the spin susceptibility of the boundary spins. Figure 9 shows the high-field MC = $\sigma/\sigma_0$ in $H = 10$ kOe, as a function of temperature and magnetic field for the six samples of LCMO/Al₂O₃ ($x = 0.01, 0.03$ and $0.05$) and LCMO/Ag ($x = 0.1, 0.3$ and $0.5$). Figure 10 shows the high-field ($H = 10$ kOe) MC slope ($S$), i.e. surface spin susceptibility ($\chi_b$), as a function of temperature for the six samples. Very interestingly, we found that the temperature dependence of $S$ follows an almost similar nature to the temperature dependence of MRspt and MR of the respective samples, namely being described quite well by an expression of
Figure 8. Magnetoresistance at $H = 10$ kOe versus temperature for composites (a) LCMO/Al$_2$O$_3$ [19] and (b) LCMO/Ag [15], and the corresponding fitted curves (line) by a function $a + b/(c + T)$.

Figure 9. Normalized conductivity as function of magnetic field at several temperatures for samples (a) LCMO/Al$_2$O$_3$ [19] and (b) LCMO/Ag [15].

the type $a + b/(c + T)$. This highly correlated temperature dependence behavior of MR$_{\text{tot}}$, MR and $\chi_b$ indirectly supports our understanding of the role of $M_S$. It is believed to be the controlling factor for temperature dependence behavior of MR$_{\text{tot}}$ and MR in manganite composites. It is worth noting that Dey and Nath [27] and Mandal et al [28] have recently also found that the temperature dependence of MR is decided predominantly by the nature of the temperature response of surface magnetization of these nanosized magnetic particles, as proposed by Lee et al [20] in La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ba$_{0.3}$MnO$_3$.

4. Conclusion

In this work, we have investigated the effect of artificial boundary grain on the magneto-transport and magnetic properties of $(1 - x)$La$_{0.7}$Ca$_{0.3}$MnO$_3 + x$A ($A = $ Al$_2$O$_3$, Ag). In spite of increasing Al$_2$O$_3$ or Ag content, the ferromagnetic–paramagnetic transition temperature is still preserved. It is found that the presence of Ag in La$_{0.7}$Ca$_{0.3}$MnO$_3$ matrices results in a decrease in resistivity and an increase in the metal–insulator transition temperature. Conversely, the increase in resistivity and a lowering of the metal–insulator transition temperature are observed with
the addition of Al$_2$O$_3$ in La$_{0.7}$Ca$_{0.3}$MnO$_3$ grain matrices. It is suggested that the introduction of Al$_2$O$_3$ or Ag into the niche of grain boundaries forms an artificial conducting network and blocks or improves the carriers to transport (which affects carrier transport). We have attributed the unusually low-temperature resistivity upturn of composites to a change in charging energy. It has been found that LFMR increases as the Al$_2$O$_3$ or Ag content increases (in the case of Ag doping, the maximum of LFMR was observed at the threshold value $x = 0.2$). This enhanced LFMR is due to increased spin polarized tunneling behavior at lower temperatures. We have analyzed our experimental MR data following a phenomenological model to separate out the MR arising from spin polarized transport in our nanosized $(1-x)$La$_{0.7}$Ca$_{0.3}$MnO$_3$ $+ x$A (A = Al$_2$O$_3$, Ag) composite samples. We also clearly show the major role played by the surface effects in an applied field. It is found that the temperature dependence of the LFMR and HFMR displays a Curie–Weiss law like behavior, i.e. $MR(T) = a + b/(c + T)$. This temperature dependence of MR is observed to be controlled predominantly by the nature of the temperature response of surface magnetization ($M_S$). It also requires deeper investigations of the Al$_2$O$_3$ (or Ag) manganite interaction, including the way in which Al$_2$O$_3$ or Ag disturbs the spin state at the grain boundaries of manganite.

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**References**

[1] Zener C 1951 Phys. Rev. 82 403
[2] Hwang H Y, Cheong S W, Ong N P and Batlogg B 1996 Phys. Rev. Lett. 77 2041
[3] Gupta A and Sun J S 1999 J. Magn. Magn. Mater. 200 24
[4] Sandu V, Popa S, Ivan I, Plapcianu C, Sandu E, Hurdac N and Nor I 2009 Proc. SPIE 7493 74934F-1
[5] Balcells L, Fontcuberta J, Martínez B and Obradors X 1998 J. Phys.: Condens. Matter. 10 1883
[6] Gaur A and Varma G D 2008 J. Alloys Compd. 453 423
[7] Phong P T, Khiem N V, Dai N V, Manh D H, Hong L V and Phuc N X 2009 Mater. Lett. 63 353
[8] Kumar J, Singh R K, Singh H K, Siwach P K, Ramadhar Singh and Srivastava O N 2008 J. Alloys Compd. 455 289
[9] Miao J H, Yuan S L, Yuan L, Ren G M, Xiao X, Yu G Q, Wang Y Q and Yin S Y 2008 Mater. Res. Bull. 43 631
[10] Eshraghi M, Salamati H and Kameli P 2007 J. Alloys Compd. 437 22
[11] Hong C S, Kim W S and Hur N H 2002 Solid State Commun. 121 657
[12] Gaur A and Varma G D 2006 Solid State Commun. 139 310
[13] Khiem N V, Phong P T, Dai N V, Manh D H, Hong L V and Phuc N X 2009 Mater. Lett. 63 899
[14] Awana V P S, Tripathi R, Balamurugan S, Kishan H and Takayama-Muromachi E 2006 Solid State Commun. 140 410
[15] Phong P T, Khiem N V, Dai N V, Manh D H, Hong L V and Phuc N X 2009 J. Alloys Compd. 484 12
[16] Xiong C, Hu H, Xiong Y, Zhang Z, Pi H, Wu X, Li L, Wei F and Zheng C 2009 J. Alloys Compd. 479 357
[17] Phong P T, Dai N V, Manh D H, Khiem N V, Hong L V and Phuc N X 2009 J. Alloys Compd. 485 L39
[18] Phong P T, Khiem N V, Dai N V, Manh D H, Hong L V and Phuc N X 2009 J. Magn. Magn. Mater. 321 3330
[19] Thanh T D, Phong P T, Dai N V, Manh D H, Khiem N V, Hong L V and Phuc N X 2011 J. Magn. Magn. Mater. 323 179
[20] Lee S, Hwang H Y, Shraiman B I, Ratcliff W D II and Cheong S-W 1999 Phys. Rev. Lett. 82 4508
[21] de Andres, Garcia-Hernandez M and Martinez J L 1999 Phys. Rev. B 60 7328

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**Figure 10.** The best fit of the high-field MC slope ($S$) at 10 kOe to a function $a + b/(c + T)$ for the samples (a) LCMO/Al$_2$O$_3$ [19] and (b) LCMO/Ag [15].
[22] Rubinstein J M 2000 J. Appl. Phys. 87 5019
[23] Das D, Srivastava, Bahadur D, Nigam A K and Malik S K 2004 J. Phys.: Condens. Matter 16 4089
[24] Li J, Huang Q, Li Z W, You L P, Xu S Y and Ong C K 2001 J. Appl. Phys. 89 7428
[25] Sheng P, Abeles B and Arie Y 1973 Phys. Rev. B 31 44
[26] Raychaudhuri P, Sheshadri K, Taneja P, Bandyopadhyay S, Ayyub P, Nigam A K and Pinto R 1998 J. Appl. Phys. 84 2048
[27] Dey P and Nath T K 2006 Phys. Rev. B 73 214425
[28] Mandal S K, Nath T K and Rao V V 2008 J. Phys.: Condens. Matter 20 385203