Enhanced low field magnetoresistance in Mn substituted nanocrystalline

La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$M$_{0.1}$O$_3$

LETTER TO THE EDITOR

Enhanced low field magnetoresistance in Mn substituted nanocrystalline $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$

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Abstract
Nanocrystalline $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ (M = Cr, Mn, Fe, Ni, Cu) powder samples were prepared by a sol–gel method. In the samples Mn atoms were partially substituted by a transition metal M. Pure perovskite phase nanocrystalline grains ($\sim$60 nm in diameter) were confirmed for all the samples through XRD and SEM observations. Magnetization and magnetoresistance of selected samples were investigated over a temperature range of 5 to 350 K, under a magnetic field of up to 5 T. Strong low field sensitive magnetoresistance was detected in Fe and Ni substituted samples. Spin polarized tunnelling and substitution modified non-balance magnetization processes are believed to be the origin of the enhanced low field sensitivity.

1. Introduction

Considerable interest has been aroused by the colossal magnetoresistance (CMR) effect discovered in doped rare-earth oxides, such as $Ln_{1-x}A_xMnO_3$ (A is a divalent ion) [1–4]. This effect is commonly detected in the vicinity of the insulator–metal transition temperature (T_{MI}) and can be qualitatively modeled as a field induced shift of the transition [5]. The first model of the magnetotransport in CMR materials was based on the double-exchange concept [6, 7]. In recent reports Jahn-Teller distortions were taken into account [8, 9]. Many CMR research projects have focused on seeking room temperature magnetoresistance (MR) materials for applications in magnetic sensors, switches and recording devices. This involves adjusting T_{MI}, optimizing MR ($R_{H=0}/R_H$) and enhancing the field sensitivity (dMR/dH).

In 1996, Hwang *et al* [10] discovered that the existence of grain boundaries and interfaces in the manganite polycrystalline material favours the so-called low-field magnetoresistance

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(LFMR). This is commonly suggested to be an effect of spin-polarized inter-grain tunnelling. In essence, the tunnel process takes place across interfaces or grains separated by an energy barrier that contains a magnetic term related to the magnetic disorder at each part of the barrier. Controlling the properties of interfaces and grain boundaries is important for enhancement of LFMR. In thin films and nanocrystalline powders, direct grain boundary controlling methods, such as microstructure modification, have been successfully put into practice [10–16]. Additional barrier effects can also be introduced into the system by atom substitution. This can introduce in-grain barrier layers, such as magnetic domain walls and weak-link junctions, as well as modify the grain boundaries indirectly. By modifying the total carrier number, total magnetic moment, mean cation size and band structure, substitution of the mixed valence Mn atoms can modify the magnetotransport properties significantly. For example, the intrinsic MR and the maximum resistance temperature T_p depend greatly on the insulator–metal transition; substituting strong magnetic atoms into the sample can increase the MR and T_p through modification of the transition [17–19]. On the other hand, since the correspondence length of the ferromagnetic order is generally much longer than the lattice parameter of manganites, the spin polarized tunnelling effect is not very sensitive to substitution if the sample is fully magnetized. Therefore the LFMR effect is not sensitive to substitution under a high magnetic field. However, in low field cases, when the lattice is not yet fully magnetized, an additional magnetized particle in the sample can be a very important source of polarized spin and/or a basis for further magnetization. This, in consequence, will enhance considerably the tunnelling effect and low field sensitivity of the sample.

In this paper we report our investigations on modification of the spin polarized tunnelling effect *via* substitution of Mn by Cu, Cr, Fe and Ni atoms in nanocrystalline powder samples. The magnetotransport properties were measured systematically in a temperature range of 5 to 350 K, under a magnetic field of up to 5 T. The results demonstrate a dramatic enhancement of the MR low field sensitivity in the magnetic atom (such as Fe and Ni) substituted samples.

2. Experiments

$La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ (M = Cr, Mn, Fe, Ni, Cu) nanocrystalline powder samples were fabricated by a sol–gel method. Stoichiometric nitrates and acetates dissolved in an aqueous solution were used as the starting chemicals. Citric acid was used as the chelating reagent. For the substituted samples, the molar ratio of the substituting atom and Mn was kept at 1/9 in the solution. After adding a suitable amount of citric acid to the solution and stirring, a transparent uniform gel was obtained which was then evaporated in a porcelain crucible at about 110 °C to yield a xerogel mixture. The as-prepared xerogel was ground and calcined at 500 °C for 1 h followed by 1000 °C for another 2 h under stagnant air. For electric and magnetic measurements, the compounds were fine ground again and compressed under a pressure of ~1.25 Gpa to pellets 6 mm in diameter which were then heated to 400 °C for 1 h to remove the remaining organic solvents.

X-ray diffraction (XRD) patterns obtained from the D/max-2000 rotating powder diffractometer (Rigaku) using Cu K_α radiation demonstrated clean single phase and pure perovskite structures for all the samples. Room temperature lattice constants calculated from XRD results evinced no obvious changes for different substituted samples, within experimental error limits. This indicates that the substitution atoms, which have nearly the same ion sizes as Mn^{3+}, directly replaced Mn ions in the final compound, therefore the lattice variation effects caused by substitution can be neglected. The chemical composition of the samples was examined by an inductively coupled plasma atomic emission spectrometer (ICP, Leeman Lab. Inc.). The results confirmed the nominal composition for all samples within error limits.

The Mn^{4+} content was measured by iodometric titration, and was found to correspond to the valance of the substitution atoms. This again confirms the successful substitution of Mn in our sample preparation. The grain size of all samples was probed by scanning electron microscopy and confirmed to be ~60 nm in diameter.

3. Results and discussion

A standard four-probe technique was used for magnetoresistance measurements on a MagLab System 2000 (Oxford, UK) extracting sample magnetometer, which was also used to measure the magnetization of the samples. Figure 1 demonstrates the strong substitution effects on the temperature dependence of magnetization in samples with different substitution atoms. As shown, the highest ferromagnetic transition temperature T_C (defined as the point where dM/dT is a maximum) appears in the non-substituted sample. The Fe and Ni substituted samples have sharper transitions compared with Cu and Cr substituted ones, while the Cu substituted sample demonstrates the lowest T_C. This indicates that in Fe and Ni substituted samples ferromagnetic correlations can be formed much faster than in Cu and Cr substituted ones.
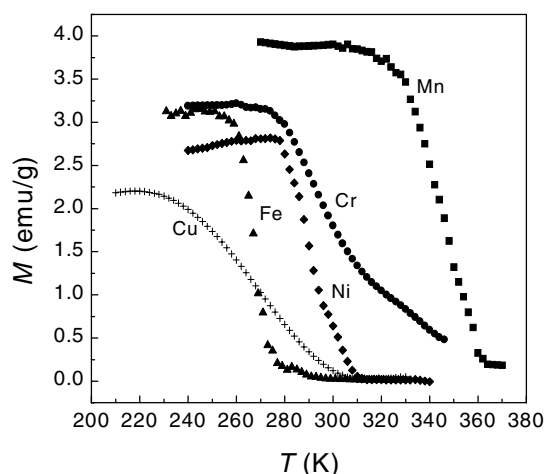

Figure 1. Temperature dependence of the magnetization under an applied field of 0.01 T for $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ (M = Cr, Mn, Fe, Ni, Cu) samples.

The temperature dependence of the zero field resistance of samples with different substitution atoms is illustrated in figure 2. The resistance peak temperature T_p has a dependence on the substitution similar to that of T_C. As shown in the figure, all substituted samples have a lower T_p than the non-substituted one, but a much larger resistance. The extra resistance is believed to originate from the substitution atom induced extra barrier effects during the spin polarized tunnelling process. As shown in figure 1, complete magnetization of the substituted sample requires a lower temperature because the formation of the ferromagnetic order between the substitution atom and Mn is either difficult or impossible. Therefore the substitution atoms can introduce extra non-magnetic particles into the sample, similar to the non-magnetic grain boundaries as discussed in the introduction. This will consequently lead to extra tunnelling resistance. The lower T_p and wider MI transition range for the substituted samples also indicate that it is difficult for the ferromagnetic order to be formed in these samples.
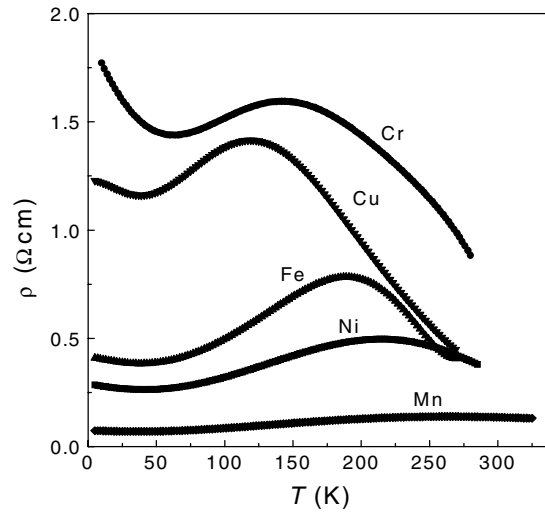
Figure 2. Temperature dependence of the zero field resistance in $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ samples.

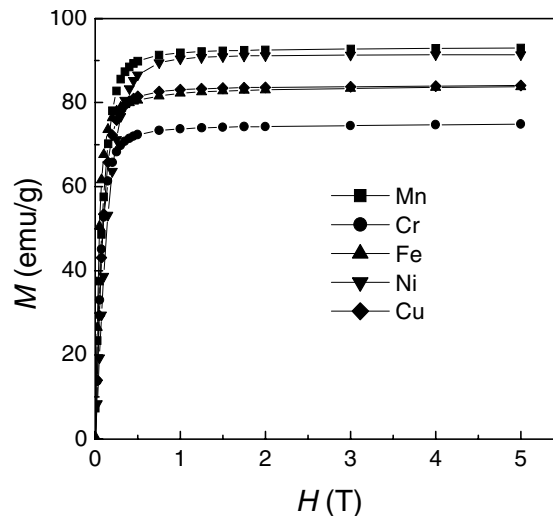**Figure 3.** Field dependence of the magnetization in $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ samples at 5 K.

The M–H curve shown in figure 3 reveals the contribution of the substitution atoms to the total magnetization. It can be seen that all Mn substituted samples show less total magnetization moment in the fully magnetized state compared with the non-substituted ones. The final magnetization numbers calculated from the figure are 3.77 μ_B for the non-substituted sample, and 3.71, 3.40, 3.42 and 2.99 μ_B for the Ni, Fe, Cu and Cr substituted samples, respectively. In the Cr substituted sample, Cr^{3+} ions were suggested to be dominant instead of Cr^{2+}, as reported by Sun *et al* [20]. Our calculation results demonstrate the modification of the ferromagnetic order in the fully magnetized state by the different electronic and magnetic structures of the substitution atoms.

However, at the beginning of the magnetization, the substitution atom plays another important role. The MR dependence on the magnetic field up to 5 T at 5 K is illustrated
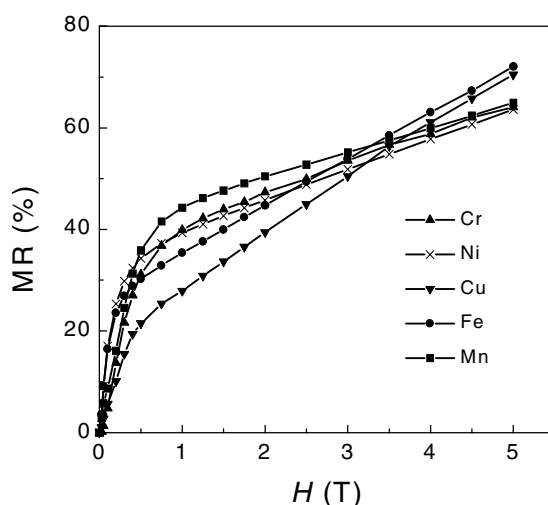
Figure 4. Field dependence of the magnetoresistance in $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ samples at 5 K.

in figure 4. As shown in the figure, under a relatively high field, while the ferromagnetic correlation is almost fully formed in the sample, the substitution atom would weaken the ferromagnetic order and reduce the MR. Therefore the non-substituted sample has the highest MR in the range from 0.5 T to 3 T. Under an even higher field, after the ferromagnetic correlation is fully formed, the contribution of the substitution atom to MR depends only on its correlation with the Mn atom. As revealed in the magnetization and neutron-diffraction measurements [19, 20], Cr and Ni atoms can form ferromagnetic correlation with the Mn atom while the Cu and Fe cannot. Thus, at high field ($\sim$5 T), the MR of Cr and Ni substituted samples is nearly the same as the non-substituted one, while that of Cu and Fe substituted ones is larger because substitution atoms can create extra MR, as detected in many film and polycrystalline samples [17–19]. The most interesting part of the field and substitution dependence of MR is at low fields ($<$ 1 T). For clarity, this is re-illustrated in figure 5 by plotting the dMR/dH curves. As shown, the Fe and Ni substituted samples are much more sensitive than the other three at low fields. One possible explanation for this is that the strong magnetic substitution ions can be magnetized even faster than Mn, and has become the centre for further magnetization. According to the spin-polarized tunnelling model, more spin polarized charge carriers favour lower resistance, hence the resistance of the samples with the strong magnetic substitution atoms drops faster than the others at the beginning of the magnetization process. As the field increases, the substitution atoms resist further magnetization because it is difficult for them to form ferromagnetic correlation with Mn atoms. Therefore, as shown in the figure, for a field over 0.15 T the MR sensitivity of Fe and Ni substituted samples quickly drops to the level of the Cu substituted one. For the Cr substituted sample, the MR sensitivity is similar to the non-substituted sample during the whole magnetization process. This can be explained by the fact that Cr^{3+} and Mn^{4+} ions have the same electronic structures. Finally, all the samples show similar MR field sensitivity under an even higher field ($\sim$1 T), because the ferromagnetic order is already formed and all the samples are insensitive to substitution in such a field range.

Mn substitution dependent magnetotransport properties in both charge localized (Mn^{3+}/Mn^{4+} $<$ 1) and delocalized (Mn^{3+}/Mn^{4+} $>$ 1) manganites have been frequently reported [17–22]. According to the literature, substitution atoms can modify the electronic and magnetic transport properties of the manganites by changing the Mn^{3+}/Mn^{4+} ratio and
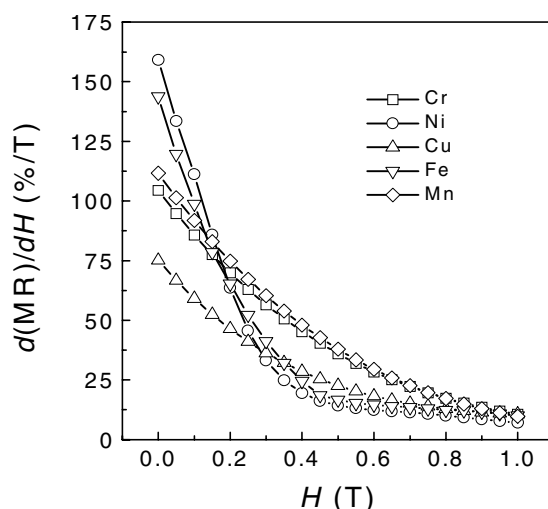
Figure 5. Enhanced low field sensitivity by Mn substitution illustrated by dMR/dH curves.

opening a narrow band very close to the conduction band of Mn [17]. This can decrease the ferromagnetic Curie temperature T_C and increase MR. Moreover, the substitution atoms can also build in-grain barriers while the ferromagnetic order is formed in the lattices. This, in view of the spin-polarized tunnelling, will introduce extra MR, similar to the influence of inter-grain barriers in thin films and polycrystals. Based on this idea, we have prepared Mn site substituted $La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3$ (M = Cr, Mn, Fe, Ni, Cu) samples and studied the effects of substitution on the magnetotransport properties. Our experimental results demonstrate an enhancement of the low field MR sensitivity at the beginning of the magnetization process in the magnetic atom (such as Fe and Ni) substituted samples. The non-balanced substitution dependent magnetization process is considered to be the origin of this low field sensitive MR.

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