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計畫主持人：陳宏仁教授兼工程學群召集人
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中　華　民　國　97　年　10　月　28　日

行政院國家科學委員會專題研究計畫成果報告

(Ln,A)-(Mn,B)-O 及二元磁性複合物磁電傳輸與交換偏壓機制之探討

Study of electromagnetic transport and exchange bias mechanism in (Ln,A)-(Mn,B)-O and two phase magnetic composites

計畫編號：NSC 96-2112-M-164-003-
執行期限：96 年 8 月 1 日至 97 年 7 月 31 日
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1. Abstract

在計畫中我們持續對鈣鈦礦結構超巨磁阻 (CMR) 材料 $La_{0.7-x}Ln_xPb_{0.3}Mn_{1-x}Me_yO_3$ (Ln=Pr, Nd, Y, Sm, Dy and Gd, Me=Fe, Co, Ni)及超巨磁阻/金屬或絕緣氧化物複合物的物性、磁性與電傳輸特性作比較及研究。在二次元磁性複合物，我們將研究在這些近乎自旋極化異質結構複合物的晶粒內、晶粒間及晶界載子磁傳輸行為。我們持續系統性地研究 $La_{0.7-x}Ln_x\ Pb_{0.3}Mn_{1-x}Me_yO_3$ 磁性材料的各種特性。其中藉由作合物中鐠、釹、釩、釤和銪摻雜雜取代鑭位置，鐵、鈷如鎳摻雜取代鈷位置來研究取代效應所造成的晶格結構的變化對磁性與電性的影響。此外，將使用我們已具有的磁控濺鍍技術來成長高品質的鐵磁性(FM)/反鐵磁絨(AFM)雙層膜，並深入探討其短程耦合交換作用。而在結果中可發現不同組成的樣品其結構及磁電性皆有顯著的差異性。為了建立此系列材料能有一個完整的物磁電性的資料庫，計畫中我們將接續著對這些材料作整個完整系列的物磁電性系統化研究。我們預期這些結果將可提供有關於磁性材料製作與研究之準則，這些對電子工業及學術研究均甚重要

關鍵字：鈣鈦礦，超巨磁阻，晶格結構，磁性，電傳輸特性，鐵磁性，交換偏壓，複合物，晶界，傳輸機制。

In this project, a systematic investigation of the structural, magnetic and electrical properties in the perovskite colossal magnetoresistance (CMR) materials $La_{0.7-x}Ln_xPb_{0.3}Mn_{1-y}Me_yO_3$ (Ln=Pr, Nd, Y, Sm, Dy and Gd, Me=Fe, Co, Ni), CMR/(metal or insulator oxide) composites, have been studied. In the two-phase magnetic composites, we investigate the intragrain, intergrain, and ground boundary, carrier magnetotransport behaviors in these nearly spin polarization hetero-structureal composites. We have systematically studied the properties of the perovskite structure $La_{0.7-x}Ln_xPb_{0.3}Mn_{1-y}Me_yO_3$ materials. By substituting Pr, Nd, Y, Sm, D y, Gd for the La and Fe, Co, Ni for the Mn, the substitution effects on the crystallographic deformation, magnetotransport behavior and electrical properties in these compounds also have been studied. .From the measured and analytic result, we can obtain very good

results about physical, magnetic, and electrical properties. In this project, we shall have studied continually to series magnetic materials for established the more systematic database of physical, magnetic, and electrical properties. We shall anticipate that the results in the study can be provided as a criterion for fabrication and investigation of these type magnetic materials.

Keywords : perovskite, colossal magnetoresistance, lattice structure, magnetic, electrical transport properties, ferromagnetic, exchange bias, composite, grain boundary, transport mechanisms.

2. Introduction

The mixed-valence perovskite manganese oxides$Ln_{1-x}A_xMnO3$(where Ln=La, Nd, Pr, Y, etc., and A=Ca, Sr, Ba, Pb, etc.), have attracted considerable investigation because of colossal magnetoresistance (CMR) effects accompanied by the rich variety of electron transport properties [1-4]. The partial substitution of divalent ions for trivalent rare-earth ions, the resistivity exhibits the phenomenon of metal–insulator transition at a temperature $T=T_P$, these samples are a paramagnetic (PM) insulator above T_P and a ferromagnetic (FM) metal below T_P. The magnetotransport behaviour of CMR materials are usually modelled by the double exchange (DE) interaction, which considers the exchange of *e*g electrons between neighbouring Mn^{3+} and Mn^{4+} sites with strong on-site Hund's coupling. In the low temperature FM-metallic state, the conduction properties are affected by several factors, viz. impurity, lattice distortion, band structure, electron–electron, electron–magnon scattering, etc. Resistivity varies as a function of power law contributions, $\rho=\rho_0+\rho_2T^2+\rho_{5/2}T^{5/2}$, where the term ρ_2T^2 indicates the resistivity due to electron-electron scattering and $\rho_{5/2}T^{5/2}$ term represents the resistivity due to electronmagnon scattering process [1]. In the hightemperature PM insulating state, the *e*g electrons at Fermi surface are localized and the variable range hopping (VRH) conduction have been observed to obey an exponential temperature dependence $\rho(T)= \rho_n \exp[(T^*/T)^n]$, where n=1/4 and characteristic temperature $T^*=T_0$ is relative to the VRH in the absence of Coulomb interaction among electrons. The T_0 value depends on localization length ξ of the electron and density of state $N(E_F)$, $T_0=16/\xi k_B N(E_F)$ [1,6]. If hopping transport is taken electron-electron interaction into consideration, the VRH conduction with Coulomb effects obeys n=1/2 and $T^*=T_1$ can be estimated with the relationship $T_1=2.8e^2/(4\pi\varepsilon0\kappa kB\xi)$ [2,5]. To evaluate the transport properties of Y3+ ions substitution effect, we perform a systematic study of the La0.7-xYxPb0.3MnO3 (0.0 *x* 0.2) bulk materials. In particular, we focus on the electron scattering process at low temperature and the VRH conduction properties with or without Coulomb effects at high temperature.

3. Experimental

Polycrystalline bulk samples of compounds $La_{0.7-x}Y_xPb_{0.3}MnO_3$ ($0.0 \le x \le 0.2$) were prepared by the conventional

ceramic fabrication technique of solid-state reaction. Well-dried hyperfine powders, La_2O_3, Y_2O_3, $PbCO_3$, and $MnCO_3$, were mixed in a stoichiometric ratio and calcined in air at 800 ^oC for 24 hours with intermediate grindings three times and then pressed into disk-shape pellets. The disk samples were sintered in air at 1150 ^oC for 72 hours and then cooled down to room temperature at a cooling rate of 3 ^oC/min. The magnetization measurements between 5K and 350K were performed in a quantum designed superconducting quantum interference device MPMS-5S SQUID magnetometer. Resistivity was obtained from the standard four-point probe method. The temperature dependence of resistivity measurements were collected with or without a field of 10 kOe parallel to the direction of electrical current between 5 K and 350 K.

4. Results and Discussion

The X-ray diffraction data (not shown) confirm the structure and phase purity of the La0.7_xYxPb0.3MnO3 samples. The average grain sizes of the samples were 100.7 nm (x = 0.0), 75.3 nm (x = 0.1) and 64.7 nm (x = 0.2) obtained using the classical Scherrer's formula. The magnetic properties have been reported in our previous research [3].

The $\rho(T)$ curves with different Y contents are given as Fig. 1, which reveal a FM-metallic state to Pminsulating state transition as the temperature increases. The transition temperature T_P decreases as Y doping increases from 322 K for (x=0.0) to 152 K (x=0.2). The resistivity values also increases manifestly as Y-doped increases. The resistivity curve for x=0.1 shows two maxima values at two different temperatures, T_{P1} = 278 K for higher temperature peak and T_{P2} = 186 K for lower temperature peak, as shown in Fig. 1(b). The double-peaks resistivity curve has been observed in some other systems of CMR materials, e.g., $La_{0.9}Te_{0.1}MnO_3$ [4]. The difference in electrical conduction properties can be explained by the competition between DE mechanisms in the core of the grains and the tunneling magnetoresistance in the grain boundaries [4].

The experimental data of three samples in FM metallic region ($T<T_P$) were fitted with the equation $\rho=\rho_0+\rho_2T^2+\rho_{5/2}T^{5/2}$ to examine the electron scattering process. The best fitting parameters have been obtained and are given in Table 1. The ρ_0, ρ_2, and $\rho_{5/2}$ values are found to increase with increasing Y-content may be evidence for the increase of scattering processes due to the lattice distortion and spin disorder of the Y-doping.

In the PM insulating region ($T>T_P$), the experimental data of two samples (x=0.1 and x=0.2) were fitted with $\rho(T) = \rho_n \exp[(T^*/T)^n]$ in different temperature range as shown in Table 2. The $\rho(T)$ curves were fitted well by n=1/2 law at high temperatures (T>300 K, x=0.1) and with a localization length ξ estimated to be 3.2 nm using the relationship $\xi=2.8e^2/(4\pi\varepsilon_0\kappa k_BT_1)$. Since the localization length must exceed the Mn-Mn distance and e_g electrons hopping distance should be

several times greater, the reasonable ξ values can be evaluated to explain electron hopping between Mn-Mn sites with the presence of the Coulomb interactions in these CMR compounds. At intermediate temperature (211-261 K), the ρ(*T*) curve can be fitted using Mott's n=1/4 law with a T_0 value of 6.8×10^4 K (*x*=0.1) and 9.8×10^6 K (*x*=0.2), respectively. Using $\xi=16/T_0k_BN(E_F)$, the localization length was estimated to be ξ~0.65 nm for *x*=0.1 and ξ~0.12 nm for *x*=0.2, respectively [1,6]. The hopping distance is somewhat shorter than the expected, althougth as it is a several times longer than the Mn–Mn distance [6]. As the temperature increases, the small FM domains gradually form. The density of state $N(E_F)$ decrease due to a decrease in available hopping states. Consequently, the reasonable ξ values can been obtained from a deplted $N(E_F)$, and electron hopping between FM-domains may be explained by VRH conduction mechanisms in the absence of the Coulomb interactions.

5. Conclusions

We have successfully studied the transport properties of $La_{0.7-x}Y_xPb_{0.3}MnO_3$ polycrystalline manganites. The resistivity can be well fitted using power laws and VRH with or without Coulomb effects under different temperature ranges. The double-peak behavior can be explained by extrinsic magnetotransport induced by the grain boundary effects. This work was supported by the National Science Council of the Republic of China under Grant No. NSC 96-2112-M-164-003.

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Table 1
The best-fitting parameters of the equation, $\rho=\rho_0+\rho_2T^2+\rho_{5/2}T^{5/2}$, obtained from the experimental resistivity data in the FM-metallic region

Sample	ρ_0 (Ω cm)	ρ_2 (Ω cm/K^2)	$\rho_{5/2}$ (Ω cm/K$^{5/2}$)
$x=0.0$	0.026	1.35×10^{-6}	$\leqq10^{-9}$
$x=0.1$	0.45	4.92×10^{-6}	1.05×10^{-6}
$x=0.2$	3.43	90.00×10^{-6}	4.30×10^{-6}

Table 2
Fitted parameters in the equation, $\rho=\rho_n\exp[(T_0/T)^n]$, obtained from experimental resistivity data in the PM insulating region

Sample	n	Temp. range (K)	ρ_n(Ω cm)	T_0 (K)
$x=0.1$	$n=1/4$	211–246	0.012	6.8×10^4
	$n=1/2$	>300	6.9	14884
$x=0.2$	$n=1/4$	>216	2.626	9.8×10^6

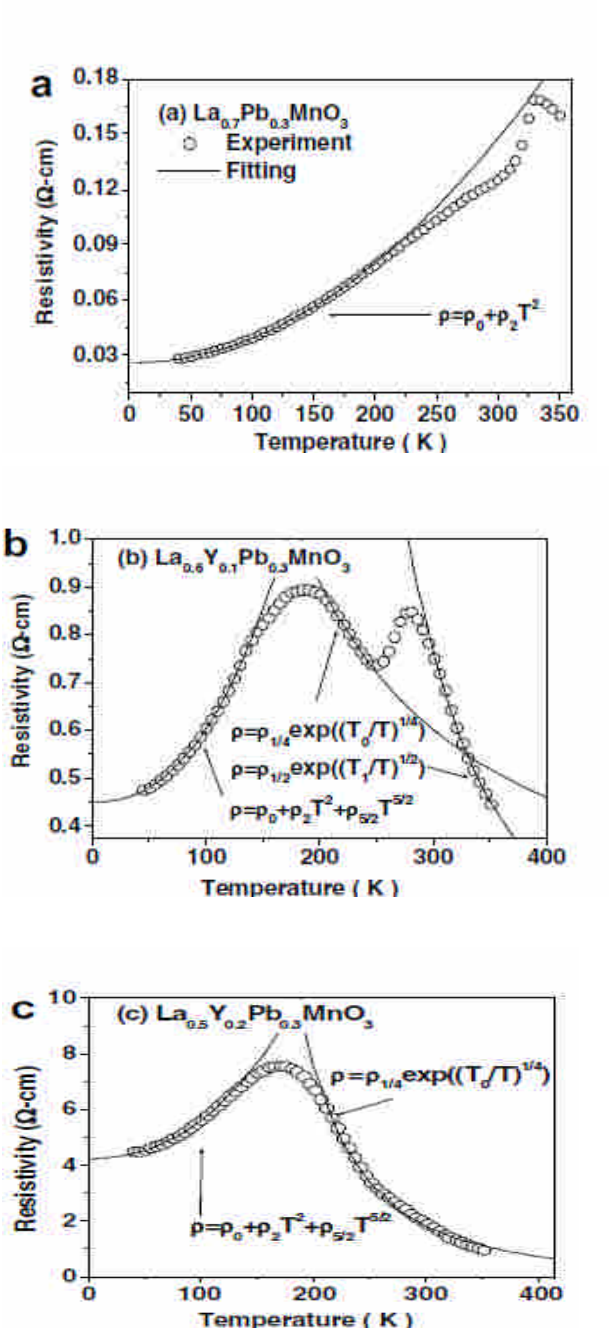

Fig. 1 The ρ(*T*) curves for (a) $La_{0.7}Pb_{0.3}MnO_3$, (b) $La_{0.6}Y_{0.1}Pb_{0.3}MnO_3$, (c) $La_{0.5}Y_{0.2}Pb_{0.3}MnO_3$; the solid line indicates the best fitting to equation $\rho=\rho_0+\rho_2T^2+\rho_{5/2}T^{5/2}$ and $\rho=\rho_n \exp[(T_0/T)^n]$

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