论文题目：钙钛矿结构氧化物中的超大磁电阻效应及相关物性

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摘　要

以钙钛矿结构氧化物为代表的巨磁电阻材料，由于它们所表现出来的超大磁电阻效应(Colossal Magnetoresistance)在提高磁存储密度及磁敏感探测元件上具有十分广阔的应用前景，因而受到人们的广泛关注。同时，这类材料还表现出诸如磁场或光诱导的绝缘体-金属转变，电荷有序、轨道有序、以及相分离等十分丰富的物理内容，涉及到凝聚态物理的许多基本问题，一旦解决了这些问题的微观物理机制，必将对凝聚态物理的发展和完善起到巨大的推动作用。

在本论文中，作者通过理论和实验研究，对巨磁电阻氧化物的物理性质和新型磁电阻材料作了一些研究和探索。相关的研究结果已在国际科技期刊上发表 10 篇，其中 Appl. Phys. Lett. 2 篇，Phys. Rev. B 4 篇，J. Phys.: Condens. Matter 1 篇，J. Magn. Magn. Mater. 3 篇。

本论文分为上下两篇，共七章。上篇为基础篇，包括第一、二章；下篇为研究篇，包括第三—七章。

第一章综述了磁电阻效应研究的历史、发展与现状。介绍了各种磁电阻材料的物理化学性质，如磁性多层膜、磁性纳米材料、钙钛矿结构氧化物、焦绿石结构和尖晶石结构化合物等。通过本章的介绍，我们将对磁电阻效应以及磁电子学都有一个概括的了解。

第二章介绍了超大磁电阻材料锰氧化物丰富的物理性质。包括晶体结构、电子结构、磁性质、输运性质、电磁相图、有序相，以及其他奇特的物理现象。通过本章，我们将了解到掺杂锰氧化物的基本物理性质，并对诸如双交换作用、Jahn-Teller 效应、电荷有序等物理概念有所认识，为进入该研究领域作好了准备。

第三章研究了 A 位和 B 位元素替代对锰氧化物的性质和磁电阻效应的影响。其中，第一节研究了 Gd 替代 La 位所产生的影响，目的是为了研究 A 位平均离子半径及额外的稀土磁性对锰氧化物磁性和磁电阻的影响。通过用 Gd 对 $La_{0.7}Sr_{0.3}MnO_3$ 中的 La 进行部分替代，我们发现金属-绝缘体转变以及磁电阻效应都被显著地增强了，对$(La_{0.3}Gd_{0.4})Sr_{0.3}MnO_3$ 和 $(La_{0.4}Gd_{0.3})Sr_{0.3}MnO_3$，在 6 T 下，其最大磁电阻比率分别为 8300%和 930%；即使在 1 T 下，其最大磁电阻比率也高达 520%和 150%。第二节研究了 Mn 位被 Ga 替代的影响。重点讨论了顺磁态小极化子的本质和非最近邻跳跃的输运行为。第三节研究了 $La_{0.67}Ca_{0.33}MnO_3$ 和 $La_{0.67}Sr_{0.33}MnO$ 体系中的 Cr 掺杂效应。实验结果显示了特殊的双峰 CMR 行为，而且 CMR 效应的温区被极大地拓宽，从低温直到室温以上，说明 Mn 位的 Cr 掺杂可以是调节 CMR 效应的有效方法。这些研究结果对认清巨磁电阻机制以及探索新型磁电阻材料都提供了重要的信息。

第四章研究了钙钛矿结构钴氧化物的磁电阻效应以及 Fe 掺杂对 La0.67Sr0.33CoO3 的影响。首先介绍了钴氧化物的基本物理性质以及其独特的自旋态转变现象。然后研究了一个典型钴氧化物磁电阻材料 La0.67Sr0.33CoO3 中的 Fe 掺杂效应，通过与锰氧化物中的 F 掺杂效应相比较，发现两者的磁电阻机制可能不同，并提出了磁场导致的自旋态转变来解释钴氧化物中的磁电阻效应。

第五章对直接 Mn 位掺杂体系（即 LaMn1-xCuxO3 和 LaMn1-xCrxO3）的磁性、电输运、磁电阻、红外声子谱、电子自旋共振谱等物理性质进行了深入地研究。实验结果证明可以通过直接在锰位掺入+2 价离子（如 Cu）来获得双交换铁磁性和大的磁电阻；同时，对 LaMn1-xCrxO3 的研究表明 Mn3+-O-Cr3+可能是一种类似于 Mn3+-O-Mn4+的双交换作用，并比较了两种双交换作用的异同。

第六章研究了混价锰氧化物种的输运机制。第一节介绍了铁磁金属态的输运行为和可能的输运机制；第二节对关于顺磁半导体态的输运机制的各种观点做了总结；第三节在前人理论的基础上，考虑到同时存在强的电-声相互作用以及强烈的无序，提出一种新的极化子输运机制—小极化子的变程跳跃。

第七章研究了巨磁电阻锰氧化物的磁热效应，以探索应用于磁致冷技术的新型磁制冷剂。其中第一节介绍了磁热效应的原理以及磁制冷的研究历史与背景；第二节讨论了磁热理论和磁熵计算；第三节介绍了巨磁电阻锰氧化物中的大的磁热效应，并研究了几个典型材料的磁熵变化。

关键词： 超大磁电阻效应、极化子、双交换作用、变程跳跃、磁热效应

Abstract

Since the discovery of colossal magnetoresistance effect (CMR) in perovskite manganites, it has sparked considerable renewed interests in these long-known materials with an eye towards both an understanding of the CMR and related properties and potential applications in magnetic information store and low-field magnetic sensors. Beside the CMR effect, these materials also exhibit intriguing physical properties such as insulator-metal and/or structure transition induced by applied magnetic-field or photo radiation, charge ordering, orbital ordering, and phase separation etc. The full understanding of these properties will definitely stimulate the progress of condensed matter physics.

In this thesis, the author devoted his effort to the study of the fundamental physics in CMR oxides as well as the exploring of novel materials, by both experimental and theoretical methods.

The whole thesis consists of seven chapters.

1. A brief overview of magnetoresistance effect

This chapter aims at a brief overview of the history, progress, and current status of all kinds of magnetoresistance materials, such as magnetic multilayers, nano-materials, perovskite oxides, pyrochlore manganites, spinel compounds, magnetite, chromium dioxide, and so on. By these illustration, we may acquire a basic sight on magnetoresistance effect as well as magnetoelectronic.

2. An introduction to the physical properties of perovskite manganites.

This chapter deals with the influent physics properties and some spectacular phenomenon observed in perovskite manganites, including the structural, magnetic, electronic transport, phase diagram, charge/orbital ordering, and insulator-metal transition induced by applied magnetic field or photo radiation etc. Some special physics concepts,such as double exchange, Jahn-Teller effect, electron-phonon coupling, are interpreted. This part is helping to build up a background for the research on colossal magnetoresistance.

3. The effects of A-site/B-site element substitution in perovskite manganites.

In this chapter, the effects of A-site or B-site doping by foreign elements were studied by preparing several series of samples, $(La_{0.7-x}Gd_x)Sr_{0.3}MnO_3$, $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$, $La_{0.67}Ca_{0.33}Mn_{1-x}Cr_xO_3$, and $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$. (1) It was found the Curie temperature T_c and magnetization decrease with increasing Gd content, but the insulator-metal transition associated with ferromagnetic ordering transition is greatly enhanced. More important, this enhanced insulator-metal transition is very sensitive to applied magnetic field, which leads to an enhanced CMR effect, for example, the maximum MR ratio of $(La_{0.3}Gd_{0.4})Sr_{0.3}MnO_3$ is as high as 8´103 in 6 T and above 5´102 even in 1 T. Besides, the enhanced insulator-metal transition gives rise to a large temperature coefficient of resistance (TCR), which is beneficial for bolometric

application. (2) A large variation of the resistivity coefficient and the polaron activation energy with Ga doping was found. The variation of implies the change of both polaron concentration and average hopping distance with Ga doping. Considering the possibility of on-site coulomb repulsion and polaron-polaron interactions, we suggest a combination of polaron nearest–neighbor hopping and non-nearest-neighbor hopping dominating the transport process in La1-yCayMnO3. Combining with the data of thermopower, we found a large increase of polaron binding energy with nonmagnetic Ga doping, which strongly suggests the additional magnetic nature of the lattice polaron in La0.67Ca0.33 MnO3. (3) Extraordinary transport and colossal magnetoresistance behaviors, characterized by double peaks, were observed in Cr-doped samples. The temperature range of CMR response in some samples is greatly broadened, from the lowest temperature to above-room temperature. These results suggest that Cr substitution can be a potent way in tuning CMR response.

4. The CMR in cobalt oxides and the effects of Fe doping in La1-xSrxCoO3.

Perovskite cobalt oxides have many similar properties such as mixed valence and CMR effect, with perovskite manganites. However, a peculiar feature in cobalt oxides is the thermally induced spin-state transition. In this chapter, we first introduced the basic aspects, especially the magnetic phase diagram, of cobalt oxides. Then we studied the effects of Fe doping in a typical cobalt oxide LaSrCoO. It was found Fe doping weakened the CMR peak near Tc but enhanced the low-temperature MR. By comparing with manganites, we found apparent difference between two systems. The origin of CMR in is proposed to result from the spin-state transition induced by applied magnetic field.

5. The study of LaMn1-xCuxO3 and LaMn1-xCrxO3.

The magnetic, electrical transport, and magnetoresistance properties of direct Mn-site doped systems, LaMn1-xCuxO3 and LaMn1-xCrxO3, were studied by measurments of resistivity, magnetization, electron spin resonance, raman spectroscopy etc. Ferromagnetism and large magnetoresistance were observed in LaMn1-xCuxO3, which is believed to be consistent with Mn3+-O-Mn4+ double exchange mechanism. These results suggest that double exchange and giant magnetoresistance can be obtained by direct Mn-site doping. It was found that the doping of Cr in LaMnO3 introduces ferromagnetism and cluster glass behaviors. Moreover, a close correlation between magnetic state and transport behavior as well as a large magnetoresistance were observed when x ~ 0.3. These results suggest that a ferromagnetic exchange interaction similar to double exchange could occur between Mn and Cr.

6. The transport mechanism in mixed-valence manganites.

The transport mechanism in mixed valence manganites is attractive but still controversial. In the paramagnetic phase, the carriers are trapped in localized states as small polarons due to the incorporation of three different localization features: (i) strong electron-phonon interaction, (ii) the variations in the Coulomb potential due to the presence of R3+ and A2+ ions in the lattice, (iii) the magnetic localization due to spin disorder on the interatomic scale. When the thermal energy is not enough for small polaron to hop between nearest-neighbour sites, the transport of small polaron could be accomplished by two steps: first, the small polaron is thermally activated into an intermidate state in which the carrier is weakly localized; then it feels the potential fluctuation due to localization feature (2) \& (3) and transport by variable-range hopping. We term this kind of transport mechanism as variable-range hopping of small polaron, and derive the expression of resistivity from this model.

7. The magnetocaloric effect of CMR magnanites.

The magnetocaric effect can be used in magnetic refrigeration technology. In this chapter, we first reviewed the history and current status of magnetic refrigeration research. Then we discussed magnetocaloric theory and the caculation of magnetic entropy change. Finally, we studied the magnetocaloric effect of several doped manganites. These result suggests that perovskite manganites are suitable candidates as working substance in magnetic refrigeration technology.

Key Words: colossal magnetoresistance, small polaron, double exchange, variable-range hopping, magnetocaloric effect 回主页