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强关联锰氧化物体系中有序相的竞争与量子相变行为研究

● 作者：曹桂新
● 专业：无线电物理
● 导师：张金仓　沈学础

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图书在版编目(CIP)数据

2006年上海大学博士学位论文.第2辑/博士学位论文编辑部编.—上海:上海大学出版社,2010.6

ISBN 978-7-81118-513-3

Ⅰ.2... Ⅱ.博... Ⅲ.博士—学位论文—汇编—上海市—2006 Ⅳ.G643.8

中国版本图书馆CIP数据核字(2009)第162510号

2006年上海大学博士学位论文

——第2辑

上海大学出版社出版发行

(上海市上大路99号 邮政编码200444)

(http://www.shangdapress.com 发行热线66135110)

出版人:姚铁军

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南京展望文化发展有限公司排版

上海华业装潢印刷厂印刷 各地新华书店经销

开本 890×1240 1/32 印张 278 字数 7 760千

2010年6月第1版 2010年6月第1次印刷

印数:1—400

ISBN 978-7-81118-513-3/G·514 定价:880.00元(44册)

Shanghai University Doctoral Dissertation (2006)

Study of the Competition of Ordering Phase and Quantum Transition in Strongly Correlated Manganites

Candidate: Cao Guixin
Major: Radio Physics
Supervisor: Zhang Jincang
Shen Xuechu

Shanghai University Press
· Shanghai ·

上 海 大 学

本论文经答辩委员会全体委员审查，确认符合上海大学博士学位论文质量要求.

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答辩委员会对论文的评语

曹桂新同学的博士学位论文“强关联锰氧化物体系中有序相的竞争与量子相变行为研究”选题为当今物理、材料和信息科学领域十分有趣而又重要的前沿课题，在自旋电子学材料和量子信息领域有着潜在的应用背景，具有重要的基础研究价值和实际意义。论文的主要结果如下：

(1) 研究了 $Pr_{5/8}Ca_{3/8}MnO_3$ 单晶的输运与低温反常磁化阶跃行为，提出了自旋重定向的概念和物理图像以及由于自旋-轨道相互作用可能存在自旋量子转变的思想，拓展了量子相变的研究范围。为锰氧化物 CMR 机理研究中占主导地位的相分离理论提供了直接的实验证据。

(2) 研究了 $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ 体系的低温反常输运与多重阶跃式磁化行为，给出了自旋/电荷/轨道耦合与低温电阻最小之间的关联，发现了存在于该体系的磁控量子转变特征。其结果为进一步完善基于相分离逾渗模型和介观相分离的唯象理论，为 CMR 磁电子学材料在场效应量子器件，磁控量子开关等方面的潜在应用提供了相应的基础研究资料。

(3) 研究了 $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ 体系亚微米尺度和半掺杂 $(La, Pr)_{0.5}Ca_{0.5}MnO_3$ 体系纳米尺度的相分离特征，观察到磁竞争失措和淬火无序对电荷有序反铁磁相和轨道长程序的抑制作用，证明磁场诱导产生的自旋/轨道量子转变和载流子的退局域化乃是输运/磁化阶跃式产生的原因。

曹桂新同学的博士论文立论正确，数据丰富可信，分析合理，有创新。在答辩过程中，曹桂新同学能正确回答问题，概念明确，思路清晰，反映了该生对所研究的领域有清楚的了解，具有扎实的理论基础知识和较强的分析问题解决问题的能力，具备了独立进行科学研究的能力。

答辩委员会表决结果

经答辩委员会讨论，一致认为该论文是一篇优秀的博士学位论文。经无记名投票表决，全票通过曹桂新同学的博士学位论文答辩，建议授予理学博士学位。并推荐参加全国优秀博士论文评选。

答辩委员会主任：**龚昌德**

2006 年 6 月 16 日

摘　要

强关联钙钛矿锰氧化物体系存在诸多奇异而有趣的物理现象和丰富而又复杂的物理内涵,成为近年来物理学和信息材料物理领域十分活跃而又引人注目的前沿研究领域。特别是该类材料中所表现出的电荷/自旋/轨道和晶格自由度之间存在的相互作用和竞争现象,和由此而诱发产生的绝缘-金属转变、有序化和相分离等一系列新奇物理现象,向现代物理学和信息科学的传统概念提出了挑战,从而给物理学家、材料科学家和信息科学家提出了新的研究课题,诸多与此相关的一些新现象的解释和新概念的提出,将导致以强关联物理学、自旋物理学和自旋电子学等为代表的基础学科和未来信息技术的革命,使得强关联钙钛矿锰氧化物体系的研究成为21世纪科学技术特别是凝聚态物理强关联电子系统的主要研究热点之一。本论文工作以具有典型低温相分离特征的Pr掺杂锰氧化物$La_{5/8-x}Pr_xCa_{3/8}MnO_3$体系和半掺杂的$(La,Pr)_{0.5}Ca_{0.5}MnO_3$体系为具体研究对象,在制备高质量单晶和多晶样品的基础上,采用磁场诱导技术,研究了低温相分离特征与step型输运异常现象的关联、电荷/自旋/轨道有序结构、磁场诱导产生的自旋重定向/载流子退局域化与可能的自旋/轨道量子转变的本质,以及与电荷有序和轨道有序等多种序参量之间的关联等等,本论文共分为六章,主要内容如下:

第一章综述了近年来强关联钙钛矿锰氧化物物理与自旋

电子学领域的研究进展，重点就强关联钙钛矿锰氧化物的相分离问题、CMR 机理研究和自旋/轨道之间的强耦合作用导致存在于低温下的一些奇异物理现象，并就本文工作的研究目的和出发点进行了概括性描述。

第二章主要介绍了实验样品的制备、样品质量表征以及物性测量手段和基本原理，主要包括电磁输运性质和比热性质测量等。

第三章研究了利用光学浮区法制备的 $Pr_{5/8}Ca_{3/8}MnO_3$ 单晶的结构、输运和磁特性。发现在几个特斯拉的较低外磁场诱导下，体系在 60 K 以下出现的 step 型电荷有序反铁磁-铁磁转变(COAFM - FM)，存在于～4.2 K 以下异常陡峭的磁化 step 变化行为，在场冷模式下发现了存在于 $Pr_{5/8}Ca_{3/8}MnO_3$ 单晶中 $T = 2$ K 下的双重磁化 step 跳跃现象。并使 Mn^{3+} 离子 e_g 电子的轨道占据态随磁场发生改变，e_g 电子的轨道有序态的变化导致 $M-H$ 曲线上磁化 step 的产生以及与历史有关的磁化效应。在关于这种多重磁化跳跃物理机制的理解上，结合理论分析，提出了自旋重定向的概念和物理图像，以此为出发点，对这种转变跃迁随温度的变化给予了自恰的解释，与相应的实验结果得到了很好的符合。这一研究结果在一定程度上突破了此前诸多研究者基于两相共存的马氏体相变机制解释这类低温下 step 跳跃行为的局限，对当今锰氧化物强关联物理中占主导地位的相分离机制和理论结果提供了直接的实验证据。

第四章研究了 $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ 体系输运和磁特性随 Pr 含量 x 的变化，在实验上发现了低温下异常的单重和三重不可逆电阻率陡峭下降同时伴随着单重和三重磁化强度 step

跃变的出现，给出了体系在低温区域的磁相图，发现异常的输运行为和相分离体系中的长程(l－r) COAFM相存在着密切的关联。研究了相分离体系中step型输运异常与低温电阻最小现象之间的紧密关联特征。结果表明，在低场下具有相分离体系中FM团簇很容易沿外场方向排列，当增大外磁场时诱导量子化的轨道相变行为出现，此时轨道的极化状态被改变同时伴随着载流子退局域化和自旋重定向行为。为澄清磁化、输运特性和电阻最小现象之间的关联，以及该类体系异常step型转变的物理机制，我们提出了相分离体系中共存团簇的微观竞争机制和物理图像，提出这种step型的输运异常源于磁场诱导的单重或三重的量子轨道转变，从而证明了低温下分别存在着电荷-轨道和自旋-轨道自由度的耦合相互作用。该研究结果为电荷-轨道-自旋耦合以及对该类复杂相分离体系的深入认识和理解提供了较为详尽可靠的基础实验证据。

第五章研究了半掺杂$(La, Pr)_{0.5}Ca_{0.5}MnO_3$体系的磁特性，发现了存在于该体系低温下的再入型自旋玻璃(RSG)转变行为。发现随温度降低在该体系中相继出现PM－FM－AFM－RSG多重的转变行为，且在低温区存在有团簇SG和FM团簇的共存，表明了体系的基态存在多种复杂而丰富的磁相互作用之间的竞争现象，证明半掺杂$(La, Pr)_{0.5}Ca_{0.5}MnO_3$为一种典型的纳米尺度相分离体系。由于体系中存在的FM双交换和AFM超交换相互作用的竞争失措和磁矩长程关联特征的破坏，致使磁场诱导下难以产生step型的输运特性，证明纳米尺度相分离与亚微米尺度相分离的本质区别表现在共存团簇之间的长程关联性，前者表现为自旋关联的交换作用产生的短程

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取向无规，从而抵制了外磁场的影响使得体系难以达到自旋的有序排列和磁饱和；而后者主要表现为共存相之间的长程相互竞争和相互作用，对体系的输运特性有着巨大的影响，而且这两类共存团簇之间可能存在的大量不同长程关联相，是造成大量 Barkhausen-like 小的磁化 step 现象出现的主要原因。

最后，在第六章中对本论文工作给予了总结和展望，指出可以利用 A 位高度有序的 $RBaMn_2O_6$（R 为 La、Y、Pr、Sm 等）体系在很高温度即表现出典型的 COAFM 和 FM 两相共存的特征，拓展 step 型输运行为研究的范围。将磁场诱导产生输运 step 与自旋/轨道/电荷及温度影响自旋/轨道波动的机制的研究向室温过渡，期待能够给出相分离体系各有序相之间的竞争机制与动力学微观图像以及该过程中自旋/轨道结构的具体存在状态。

关键词 磁化/输运 step 型跃变，自旋重定向，载流子退局域化，轨道量子相变

Abstract

The study of the manganites, widely known belonging to strongly correlated electron systems, that exist many novel and interesting physical phenomena and complex physical mechanism is among the active and attractive areas of research within the area of physics and information material physics. Significantly, the strong coupling and competition among the spin, charge, orbital, and lattice degrees of freedom in these systems can induce a wide variety of newly novel phenomena such as insulator-metal transition, orderings and phase separation etc. All these challenge the traditional understanding of physics and information science and will provide newly subject for the physicist, material scientist and information scientist. A lot of related new physical phenomena and concepts have been brought forward, which will arouse a revolution of some basic subjects (such as strongly correlated systems, spinelectronics physics) and the information technology in the future. This probably makes strongly correlated manganites the one of the hotspots in the field of condensed matter physics in the 21st century. In this dissertation, based on the preparation of high quality single crystal and polycrystalline samples, the typical phase-separated $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ and half doped $(La, Pr)_{0.5}Ca_{0.5}MnO_3$ systems were investigated

in magnetic fields. The correlation between low temperature phase separation and novel step-like transport, and the correlation among ordering parameters such as charge ordering and orbital ordering etc. were studied Meanwhile, the charge/spin/orbital ordering structure, the mechanism of magnetic induced spin reorientation/carrier delocalization, and the possible quantum spin/orbital transition were studied in these systems. The content of the dissertation are divided into six chapters and main results are summarized as follows.

The first chapter describes the content status and progress of the studies concerning the strongly correlated manganites and correlative spin electronic physics, stressing on the phase separation in the manganites, the mechanism of the colossal magnetoresistance effect, and a wide variety of newly novel phenomena at low temperatures due to the strong coupling of spin-orbital and charge-orbital. Meanwhile, the aims and motivations of the present work were synoptically given.

The second chapter gives the preparation of samples, the structural characterization of the sample, as well as the measurement technology and basic principles. Main measurements include electrical and magnetic properties and the heat capacity measurement.

The third chapter displays the structural, magnetic and transport properties of $Pr_{5/8}Ca_{3/8}MnO_3$ single crystal, which was successfully grown by the optical floating-zone method. One step-like charge ordered antiferromagnetic-ferromagnetic

(COAFM - FM) transition was observed at the temperatures below 60 K and the applied magnetic field of a few tesla. Such a step in the $M - H$ curve became ultrasharp at the temperatures below 4.2 K. Two-sharp-step transition appeared in the different field-cooled (FC) conditions at a given low temperature (2.0 K). These results indicated that magnetic field can induce changing of orbital occupancy of the e_g electron in Mn^{3+} with the magnetic filed. And then this orbital occupancy of e_g electron causes the occurrence of the $M - H$ step and the history-dependent magnetization effect. According to the model of spin and orbital coupling, the steps should be the result of spin reorientation under the magnetic fields. Meanwhile, the physical picture was provided. Based on these, the change of step-like transition with temperature was explained completely. These results break through to some extent the circumscribing of martensitic model based on phase coexistence and they contribute to directly support the phase separation scenario that is one of the leading theories to explain the physics of manganites.

The fourth chapter is mainly about the study of transport and magnetic characteristic of phase-separated (PS) $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ ($x = 0.0 - 0.625$) manganites. Novel single and triplex irreversible resistivity sharp drop accompanying with the single and triplex magnetization step were observed at low temperatures. The resulting phase diagram indicates the correlation of novel transport jump and the l - r COAFM phase in the PS region. The correlation between step-like transport jump and resistivity minimum were observed at low temperature. The results prove that low fields induce the alignment of spins for the FM clusters in the PS manganites. And the strong field probably induces quantum orbital transfer, in which the orbital polarization is changed and accompanied with carrier delocalization and spin reorientation. In order to clarify the correlating mechanism of step-like transport jump and resistivity minimum, we propose the competing mechanism of coexisting clusters and microscopic physical picture in the PS manganites. This proves a possible existence of single and triplex quantum orbital transfer and shows the importance of the strong interaction of charge-orbital and/or spin-orbital at low temperature. Present study may provide abundant experimental information for understanding the coupling of charge-orbital-spin in the complicated phase-separated systems.

The fifths chapter study the magnetic properties of half doped $(La,Pr)_{0.5}Ca_{0.5}MnO_3$ manganites. The reentrant spin glass behavior was observed at low temperatures. The distinctive feature is that the RSG state undergoes sequential multiple magnetic transitions of paramagnetic (PM) - ferromagnetic (FM) - antiferromagnetic (AFM) - reentrant spin glass (RSG) transitions. Meanwhile, the present experimental data establishes the coexistence of FM clusters and spin glass clusters, which indicates the complex competing interactions and is a typical microscopic phase-separated system. Due to the frustration caused by the competition between FM (double exchange) and AFM (super-exchange) interactions and the destruction of long range correlation, there didn't appear any step-like transport for the system in magnetic fields. Probably, the difference of nanoscopic and submicrometer scale phase separation is with or without the long range correlation. The former is related to the disorder of short range spin orientation due to exchange interaction, which can resist applied magnetic fields and make it hard to be complete spin ordering. Whereas, the latter reflects the long range competing and interaction showing an important effect on the transport properties of systems. There possibly exist a variety of collective effects of phases between the two types of phase separation, producing a series of Barkhausen-like small magnetization steps.

In the sixth chapter, a summarization of the present work was given, altogether with the expectations of the further work. Due to the typical phase separation characteristic appearing at higher temperature in A-site-ordered $RBaMn_2O_6$ (R is La、Y、Pr、Sm) systems, one can look into the study of transport step behavior and can study the magnetic field induced transport step characteristic and the coupling fluctuation of spin/orbital in a wide temperature range, even to temperature. These results will be expected to provide the competing mechanism among all these orderings, the dynamical picture, and the concrete spin/orbital structure in the process.

Key words Magnetization/transport step-like transition, spin reorientation, carrier delocalization, orbital quantum transition

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