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Anomalous magnetic behavior for Mn-site doped $La_{0.7}Ca_{0.3}MnO_3$: internal magnetic interactions and extrinsic inhomogeneity

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ABSTRACT

Magnetic properties of Mn-site doped $La_{0.7}Ca_{0.3}Mn_{0.94}TM_{0.06}O_{3+\Delta}$ (TM=Cu, Zn) were experimentally and theoretically studied. The low-temperature magnetization and magnetic phase transition temperature T_C of the samples combining with simulations of 2D doped Ising model suggest that Cu^{2+} ions have an antiferromagnetic interaction with their nearest neighboring Mn ions. Interestingly, an anomalous magnetic behavior, a "step-like" magnetic phase transition, is observed. The existence and magnitude of this step vary with different doping ions and oxygen ratio, which is experimentally suggested to be relevant to the interaction between magnetic ions and oxygen content. A superposition between two independent magnetic systems with different values of an exchange integral J well explains the anomalous magnetic phase transition, which suggests that this step-like behavior results from extrinsic inhomogeneity and negligible coupling between grains in polycrystalline.

1. Introduction

Colossal magneto-resistance (CMR) effect [1], mostly occurring in perovskite manganites along with paramagnetic (PM) to ferromagnetic (FM) phase transition [2], has been paid intensive attention in past decades due to its potential applications in spintronic devices [3]. The magnetic phase transition has been considered as the main focus to the origin of CMR effect.

In perovskite CMR materials, several possible magnetic phase states (FM, Antiferromagnetic (AFM) phase [4], spin-glass (SG) state [5,6], and Griffiths phase [7], etc.) exist and the competition among those ordered states plays a key role in the nature of CMR and related physical properties. Traditional phase transition from FM to PM occurring at Curie temperature is recognized either as the first [8] or second [9] order phase transition. SG-like behavior is generally induced in FM or AFM systems with large disorder [7,8]. Griffiths phase as a model of percolation occurs nonlinear behavior above the Curier temperature in the magnetization curve as a function of temperature (*M*–*T* curve) [10].

Interestingly, there is a "step-like" magnetic phase transition in magnetization curve as a function of temperature, which mostly occurs in cobaltites. Zhao et al. [11] reported that a "step-like" magnetization appears in the *M*–*T* curve at a certain temperature T^*, which is different from the value of Griffiths phase characteristic temperature T_G in $La_{0.98}Pb_{0.02}Mn_{0.74}Co_{0.25}O_3$ single crystal. Kundu et al. [12] studied nonequilibrium magnetic properties of single-crystalline $La_{0.7}Ca_{0.3}CoO_3$, which revealed the nonequilibrium phase (similar to that observed in reentrant ferromagnets) occurring below 170 K and a reentrant SG-like phase emerges below 100 K. A reentrant magnetization behavior with decreasing temperature was observed in $Pr_{2-x}Sr_xCoO_4$ as well [13]. Tang et al. [14] observed the similar magnetic behavior in $La_{0.88}Sr_{0.12}CoO_3$ with a peak around 50 K and a wide shoulder around 170 K. And this wide shoulder is attributed to the intercluster interactions and the sharp peak at 50 K is assigned to a collective freezing of magnetic moments. Recently, the specific magnetic phase transition was observed in multiferroics. Vijayanand et al. [15] studied anomalous magnetic characteristics at low temperature in nanocrystalline $BiFeO_3$ sample after applying a field and degaussing, which is possibly ascribed to domain structure instead of SG-like behavior. So far, there are few related reports on the step-like magnetic phase transition in doped perovskite manganites, and the mechanism for the existence of this specific "step-like" magnetic phase transition has not been totally understood.

For the doped perovskite manganites ($La_{0.7}Ca_{0.3}Mn_{1-x}TM_xO_3$,

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TM=transition metal ions), the possible interaction between distinct magnetic ions is also of physical importance in the study on these magnetic systems. Jonker [16] reported that spin interaction between Mn ions and their nearest neighboring doped Cr^{3+} ions shows FM double exchange (DE) interaction by the participation of electrons in O 2*p* orbits due to the comparable electronic configuration Cr^{3+} ($t_{2g}{}^3e_g{}^0$) with Mn^{4+} ($t_{2g}{}^3e_g{}^0$). Martin et al. [17] pointed out that Cr^{3+} in $Pr_{0.5}A_{0.5}Mn_{1-x}M_xO_3$ (A=Sr, Ca; M=Cr, Al) could promote the appearance of FM metallic state. However, Mahendiran et al. [18] proposed the AFM alignment between Cr^{3+} and Mn^{3+} to explain the magnetic behavior of $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$. Therefore, the magnetic interaction between these distinct magnetic ions is full of controversy and needs to be further studied.

Moreover, it is inferred that the magnetic interaction between two different magnetic ions in perovskite magnanites is likely comparable with the possible interaction in cobaltites due to the formation of high/intermediate/low spin states of cobalt ions. If a different electronic state induced by doping different ion in Mn-site, a possible step-like magnetic phase transition is thus prone to occur. In this paper, the Cu/Zn ions doped $La_{0.7}Ca_{0.3}MnO_3$ samples were taken to study the possible interaction between doped magnetic ion (Cu^{2+}, $t_{2g}{}^6e_g{}^3$) /non-magnetic ion (Zn^{2+}, $3d^{10}$) and its neighboring Mn ions experimentally and theoretically. A step-like magnetic phase transition behavior was observed in Cu doped $La_{0.7}Ca_{0.3}MnO_3$ compound. The magnetic properties of samples indicate an existence of AFM exchange interaction between Mn ions and Cu ions, which is identical to the simulations of doped 2-D Ising model. More importantly, according to this simulation, two or more independent magnetic systems with different values of an exchange integral (J) is indicated to the origin of the anomalous magnetic phase transition, reflecting an intrinsic magnetic interaction with an external inhomogeneity in samples.

2. Experiments and simulations

The $La_{0.7}Ca_{0.3}Mn_{0.94}Cu^{2+}_{0.06}O_3$ (labeled as LCu^{2+}-0) compound is synthesized by solid-state reaction method [19]. The high-purity composition La_2O_3, $CaCO_3$, MnO_2, CuO with stoichiometric ratio were mixed and grounded for 2 h. The mixture powders were sintered at 1050 °C and 1150 °C, respectively. Then the powders were pelletized and sintered again at 1250 °C. The same type precursor was done another time, labeled as LCu^{2+}-1, to clarify the repeatability for an anomalous magnetic result. At the same time, the samples $La_{0.7}Ca_{0.3}Mn_{0.94}Cu^{1+}_{0.06}O_3$ (labled as LCu^{1+}-1) employing Cu_2O as one of the raw materials, and $La_{0.7}Ca_{0.3}Mn_{0.94}Zn_{0.06}O_3$ (labeled as LZn^{2+}-1), both doped by nonmagnetic ions were also prepared for comparison. Moreover, $La_{0.7}Ca_{0.3}Mn_{0.94}Cu^{2+}_{0.06}O_{3+\Delta}$ (LCu^{2+}-2), $La_{0.7}Ca_{0.3}Mn_{0.94}Cu^{2+}_{0.06}O_{3+\Delta}$ (LCu^{1+}-2) and $La_{0.7}Ca_{0.3}Mn_{0.94}Zn_{0.06}O_{3+\Delta}$ (LZn^{2}_{+}-2) were also synthesized in a sufficient oxygen atmosphere when sintering at the last two times at temperature 1150 °C and 1250 °C.

X-ray diffraction (XRD) pattern for LCu^{2+}-0 was measured at National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China (USTC) [19] and XRD patterns for other samples were measured at room temperature by X-ray diffractometer with Cu $K\alpha$ radiation. The magnetization as a function of temperature for samples was measured by Quantum Design Physical Property Measurement Systems (PPMS-9) with an external magnetic field H=100 Oe.

A magnetic phase transition behavior was studied by 2-D orthogonal Ising model. For perovskite manganites, the magnetic ions, Mn^{3+} and Mn^{4+}, locating at the body center of perovskite cell, make up a cubic structure. In order to simplify the simulation process, just considering the exchange interaction between transitional metal ions, the ions at the center of perovskite cell with periodic arrangement were abstracted into a cubic grid with spins. To simulate the magnetic systems doped with different ions, the Hamiltonian in this model is written as $H=-J\sum_{i,j}S_i{\cdot}S_j-gh\mu_B\sum_i S_i$, where $J>0$, or $J<0$ represents FM or AFM exchange integral, respectively; h is an external magnetic field. In this 2-D orthogonal doping Ising model simulation, a 50×50 cubic grid net is set up. For the undoped case, we define a normalized initial spin values S, that is S=1 or −1. A smaller value of S=0.3 or −0.3 is taken to simulate partially doped sample by magnetic ion (Cu^{2+}, $3d^9$) and S=0 is the case of no magnetic ion (Zn^{2+}, $3d^{10}$) doped. Monte-Carlo method and Metropolis algorithm is applied to simulate and determine the evolutionary process of this canonical ensemble.

3. Results and discussions

The quality of all prepared samples is characterized by XRD patterns at room temperature (as shown in Fig. 1). The samples are in single phase of orthorhombic *Pbnm* crystal structure, comparing to the reference data from literatures [19,20]. The *M–T* curve for these samples without oxygen annealing are shown in Fig. 2. A traditional FM to PM phase transition occurs for all samples. From Fig. 2(a), it can be seen that there is not only a phase transition at Curie temperature T_C=157.3 K but also an anomalous magnetic shoulder at T=97.5 K for sample LCu^{2+}-0, clearly shown in the inset of Fig. 2(a). The samples LCu^{2+}-1, LCu^{1+}-1, and LZn^{2+}-1 show the normal magnetic phase transition at T_C=165.0, 158.5, and 126.1 K, respectively. And the Curie temperature for LCu^{2+}-1 is higher than those of LCu^{1+}-1[1] or LZn^{2+}-1, while the magnetization at low temperature is lower, shown in Fig. 2(b).

For LCu^{2+}-1 with the same preparing condition as LCu^{2+}-0, the anomalous magnetic shoulder does not occur, which may be due to the non-uniformity of samples or formation of defects. In order to improve the uniformity or reduce the number of oxygen defects, the samples LCu^{2+}-2, LCu^{1+}-2, and LZn^{2+}-2 were synthesized at sufficient oxygen atmosphere. From the *M–T* curve of these samples (Fig. 3), it is interestingly seen that a step-like magnetic phase transition occur for Cu ions doped samples (i.e. LCu^{2+}-2, LCu^{1+}-2) and a normal phase transition for LZn^{2+}-2. In addition, compared the step-like magnetic behavior of LCu^{2+}-2 and LCu^{1+}-2 to that of LCu^{2+}-0, the shoulder appears at the onset of FM phase transition.

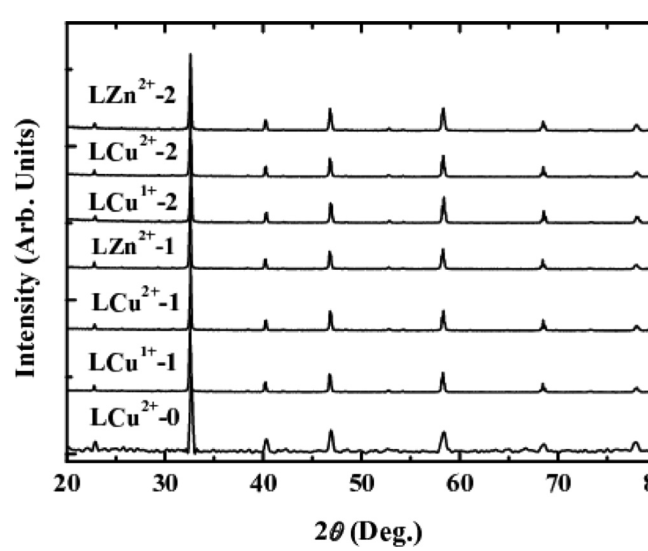

Fig. 1. X-ray diffraction patterns of polycrystalline samples LCu^{2+}-0, LCu^{1+}-1, LCu^{2+}-1, LZn^{2+}-1, LCu^{1+}-2, LCu^{2+}-2, and LZn^{2+}-2.