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Magnetic and transport properties of the solid solution system $La_{2-x}Sr_xMnRuO_6$ with double perovskite structure

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Abstract

The structure, magnetization and electrical resistance for the $La_{2-x}Sr_xMnRuO_6$ system with double-perovskite structure were investigated. The structural transition from an orthorhombic cell with a random arrangement of Mn and Ru to a cubic cell (rock salt sublattice) with an ordered arrangement occurs at near $x=1.0$. All samples $La_{2-x}Sr_xMnRuO_6$ ($0\leq x\leq 2.0$) show semiconducting behavior. The conductivity for the samples with $x\leq 0.3$ at higher temperature has a 2-dimensional variable-range-hopping (VRH) mechanism. But the temperature dependence of resistance for $La_{2-x}Sr_xMnRuO_6$ ($1.0\leq x\leq 2.0$) samples can be described using neither a VRH mechanism nor a thermal activation mechanism in a single energy gap. The samples with $x<1.0$ show ferromagnetism at lower temperatures. The $La_{2-x}Sr_xMnRuO_6$ ($1.0\leq x\leq 2.0$) samples show ferrimagnetism below 300 K. The molecular field constant radio N_{AB}/N_{AA} changes with the doping concentration of Sr for La.

Keywords: Double-perovskites; $La_{2-x}Sr_xMnRuO_6$; Ferrimagnetism

1. Introduction

Double perovskites [1–3] have the formula $A'A''B'B''O_6$, in which the primes indicate different cations. The perovskite structure can be described as a framework of corner-shared BO_6 octahedra that contains A cations in 12-coordinate sites. The study of double perovskites began in the early 1950s, and many of the double perovskites [4] were discovered and studied from the late 1950s to the mid 1970s. Perovskites have again gained attention for their ability to support superconductivity above 77 K in the late 1980s and in the 1990s. A central research theme for these studies has been the systematic change of the size, valence, and electronic configuration of the constituent ions in order to investigate the effect of these parameters on magnetic and electrical properties and crystal chemistry. The study on the electronic correlation in the perovskite compounds has especially obtained attention for different carrier concentration samples.

The B cations generally determine the physical properties of double perovskites, so the arrangement and position of the B ions is very important. It is known that [5,6] the differences in the valence and size between the B′ and B″ cations in double-perovkite type compounds $A'A''B'B''O_6$ are important factors for controlling the ordering of the B′ and B″ cations. And the electrical and magnetic properties of the compounds are strongly dependent on the valency pair (B′, B″).

On the other hand, recently, the further study on the structural, transport and magnetic properties for various Ru oxides and Mn oxides has been stimulated by the reports of superconductivity in Sr_2RuO_4 [7] and colossal magnetoresistance in the $La_{1-x}Sr_xMnO_3$ [8] system.

In this paper, the measurements on structure, magnetization and resistance were carried out for $La_{2-x}Sr_xMnRuO_6$ ($0\leq x\leq 2.0$) samples with double-perovskite structure. It was found that the valence of Mn changes from 2+ to 3+, 4+, the valence of Ru is always 4+, the structure of the $La_{2-x}Sr_xMnRuO_6$ ($0\leq x\leq 2.0$) system changes from a random sublattice to a rock salt sublattice with increasing of the Sr content. Systematical variations of the electronic and magnetic properties occur in this system.

2. Experimental methods

All samples $La_{2-x}Sr_xMnRuO_6$ ($0\leq x\leq 2.0$) were prepared by the standard solid state reaction method. La_2O_3, $SrCO_3$, MnO_2 and RuO_2 were mixed in stoichiometric

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amounts and ground in an agate mortar. The mixtures were heated at 900°C for 2 days in aluminum oxide crucibles in air at first, then ground again and reheated at 1200°C for 3 days in an oxygen atmosphere. The samples were determined to be single phase by X-ray diffraction (XRD). The magnetization from 4.2 to 300 K was measured using a SQUID magnetometer (Quantum Design), the magnetization from 300 to 700 K was measured using a Torsion Magnetic Balance. Resistance measurements were conducted using a standard d.c. four-probe technique.

3. Results and discussions

There are three B-cation sublattice types [4] known for double perovskites A′A″B′B″O$_6$: random, rock salt, and layered, the latter two are ordered arrangements. Fig. 1 shows the X-ray diffraction patterns for $La_{2-x}Sr_xMnRuO_6$ (x=0, 0.3, 1.0, 1.5, and 2.0) samples. All peaks in the XRD patterns for $La_{2-x}Sr_xMnRuO_6$ (x=0, 0.3) samples can be indexed by the orthorhombic cell (space group is *Pbnm*). The XRD results for $La_{2-x}Sr_xMnRuO_6$ (x=0.1, 0.15, 0.2, 0.3 and 0.5) samples are very similar to the La_2MnRuO_6 (x=0) sample. The tolerance factor t=0.855 for the compound La_2MnRuO_6 is less than unity. An orthorhombic cell is observed when the A–O bond length is less than two times the B–O bond length, that is, when the Goldschmidt [9] tolerance factor t is less than unity. The tolerance factor is defined:

$$t = \frac{\frac{r_{A'} + r_{A''}}{2} + r_O}{\sqrt{2}\left(\frac{r_{B'} + r_{B''}}{2} + r_O\right)}. \qquad (1)$$

In which $r_{A'}$, $r_{A''}$, $r_{B'}$, and $r_{B''}$ are the ionic radii of the ions. The orthorhombic cell results from rotation of the BO$_6$ octahedra about the axes $[011]_{cubic}$ and the $[100]_{cubic}$ [10]. The octahedra tilt to optimize eight of the originally equal 12 A–O bond distances. Compounds that have a random sublattice show no evidence of B-cation order.

All peaks in the XRD pattern of the $LaSrMnRuO_6$ (x = 1.0) sample can be indexed using a cubic cell with rock salt sublattice structure (space group is $Fm\bar{3}m$). But as the x value is over 1.0, the main peaks of cubic cell are split, as shown in Fig. 1. As we know, there have been no reports on the preparation and characterization of Sr_2MnRuO_6 compounds up to now. The exact structure of this compound is not known. We guess that Sr_2MnRuO_6 has a monoclinic cell with rock salt sublattice structure. The XRD results for other $La_{2-x}Sr_xMnRuO_6$ ($1.0 < x < 2.0$) samples are similar to that of Sr_2MnRuO_6. A monoclinic cell is observed when the tolerance factor (t = 0.96 for Sr_2MnRuO_6 compound) is somewhat less than unity and results from rotations of the BO$_6$ octahedra. Compounds with a rock salt sublattice show evidence of B-cation order. It is clear that a structural transition from an orthorhombic cell with a random sublattice to a cubic cell with an rock salt sublattice, which shows an ordered arrangement of Mn and Ru atoms, occurs at near x = 1.0.

The temperature dependence of the resistivity is shown in Fig. 2 for $La_{2-x}Sr_xMnRuO_6$ (x = 0, 0.1, 0.3, 1.4, and 2.0) samples. All samples $La_{2-x}Sr_xMnRuO_6$ ($0 \leq x \leq 2.0$) show a semiconductive behavior. Compared with the La_2MnRuO_6 sample, the resistivity of the Sr_2MnRuO_6 sample decreases three orders of magnitude at 300 K. In the lower temperature range, the resistivity of the sample with x = 1.4 is the smallest. This may be the optimum x value for the conductivity.

The conductivity is different for the samples with different x values. The samples with $0 \leq x \leq 0.3$ are insulators at lower temperatures and their conductivity at higher temperature is a 2-dimensional variable-range-hopping (VRH) mechanism. As shown in the inset of Fig. 3, it is found that the temperature dependence of the resistance of the $La_{1.7}Sr_{0.3}MnRuO_6$ sample can only be described using the formula $R = R_0 \exp(aT^{-1/3})$, where a and R_0 are constants, T is the temperature, which is typical for a 2-dimensional VRH mechanism. The temperature dependence of the resistance for the samples with x = 0, 0.1, 0.15 and 0.2 are similar to that of the x = 0.3 sample. These are consistent with Mn and Ru random arrangement in these compounds from the X-ray diffraction measurements, as shown as in Fig. 1. But the temperature dependence of resistance for the $La_{2-x}Sr_xMnRuO_6$ ($1.0 \leq x \leq 2.0$) samples can be explained neither by means of a VRH mechanism

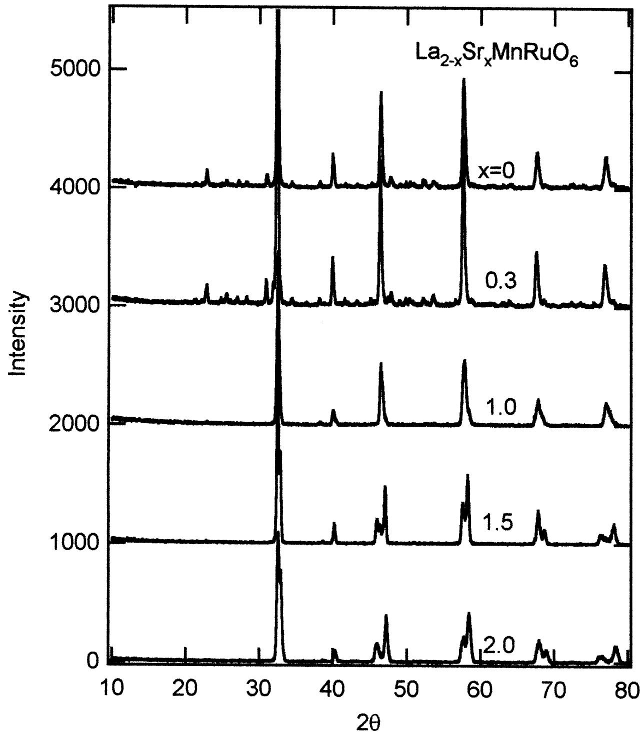

Fig. 1. X-ray diffraction patterns of $La_{2-x}Sr_xMnRuO_6$ (x = 0, 0.3, 1.0, 1.5, and 2.0) samples.

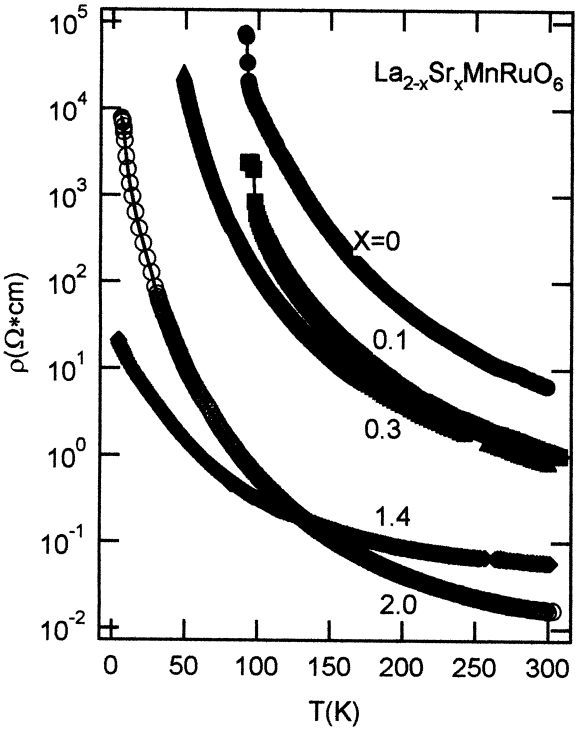

Fig. 2. The temperature dependence of the resistivity for $La_{2-x}Sr_xMnRuO_6$ ($x=0$, 0.1, 0.3, 1.4, and 2.0) samples.

nor by a thermal activation mechanism in a single energy gap.

Fig. 4 shows the temperature dependence of the magnetization for $La_{2-x}Sr_xMnRuO_6$ ($x=0$, 0.1, 1.0, 1.5, 1.6, 1.8 and 2.0) samples. The $La_{2-x}Sr_xMnRuO_6$ ($x=0$, and 0.1) samples show ferromagnetism at lower temperature, paramagnetism at higher temperature. The temperature dependence of the susceptibility at higher temperatures can be well described by the Curie–Weiss law. The inset of Fig. 5 shows the plot of $1/\chi$ vs. T for the La_2MnRuO_6 sample. The Curie temperature $T_C=116.71$ K, and the effective magneton value of $p_{eff}=4.88$ were obtained from the fitting results. Fig. 6 shows the $M(H)$ curve measured at 5 K for the same sample. There is a hysteresis below 1 T

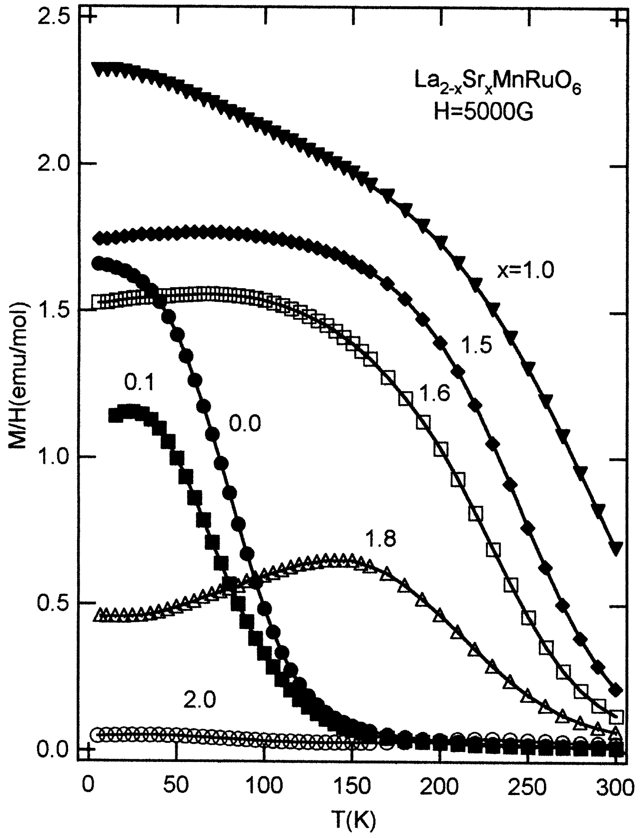

Fig. 4. The temperature dependence of the magnetization for $La_{2-x}Sr_xMnRuO_6$ ($x=0$, 0.1, 1.0, 1.5, 1.6, 1.8 and 2.0) samples.

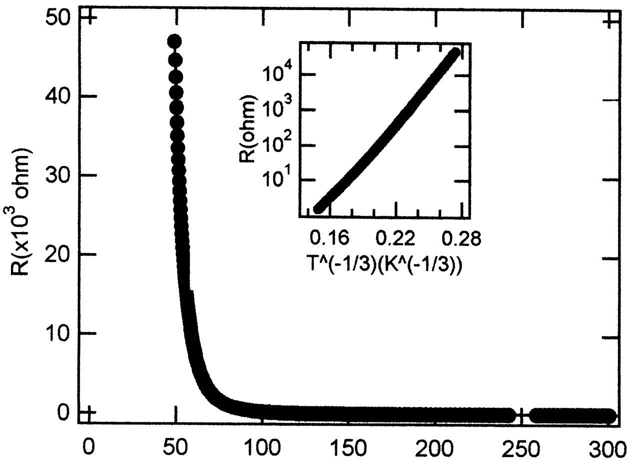

Fig. 3. The temperature dependence of the resistance for a sample $La_{1.7}Sr_{0.3}MnRuO_6$. The inset shows the relationship between $\log R$ and $T^{-1/3}$.

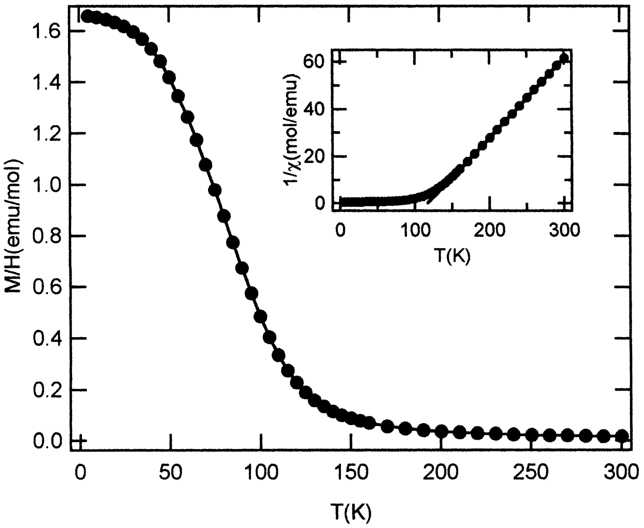

Fig. 5. The temperature dependence of the molar susceptibility, the inset: the temperature variation of the reciprocal susceptibility ($1/\chi$) for a sample of La_2MnRuO_6 sample.

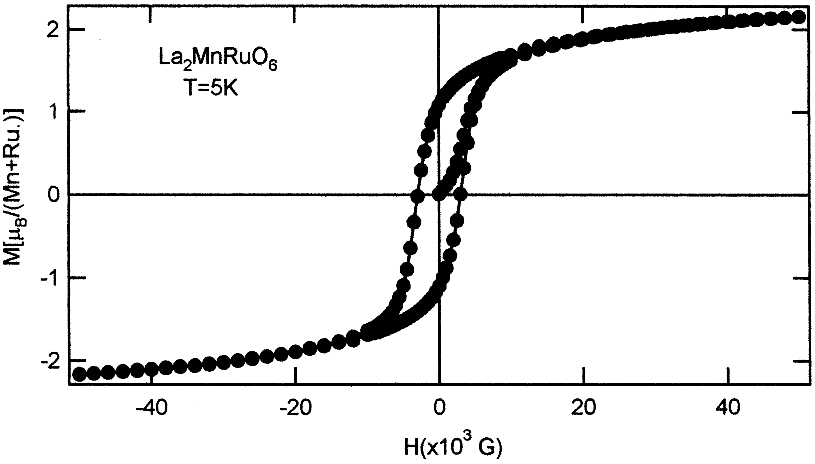

Fig. 6. The *M*(*H*) curve at 5 K for a sample of La$_2$MnRuO$_6$.

in the *M*(*H*) curve, which indicates that the sample is ferromagnetic. Although the magnetic field is up to 5 T, the *M*(*H*) curve does not show a saturation behavior. The magnetic moment estimated from the magnetization value at 5 T is about 2.15 μ_B. We suggest that the Mn^{2+}(μ_B), and Ru^{4+}(2 μ_B) ions have low spin states in this compound. The experimental value p_{eff} from the plot of $1/\chi$ vs. T is not consistent with that from the *M*(*H*) curve, which may originate from the complexity of the magnetic structure in this compound. It is known that LaMnO$_3$ is a canted antiferromagnet [11]. The arrangement in the *a*–*b* plane is ferromagnetic but successive planes are coupled antiferromagnetically. Cation-deficient lanthanum manganite (LaMn)$_{1-y}$O$_3$ is antiferromagnetic, orthorhombic and insulating when $y<0.03$, but compounds with $y>0.03$ are ferromagnetic. The magnetic structure in La$_2$MnRuO$_6$ may also be of a complex nature. The investigation of the magnetic structure of this system is in progress.

The behavior of the samples with $x=0.1$, 0.15, 0.2 and 0.3 is very similar to the $x=0$ sample. But the Curie temperature T_C increases with increasing value of x. It is well known that the explanation for the ferromagnetism in La$_{1-x}$Sr$_x$MnO$_3$ [12] is based on the 'double exchange', and the ferromagnetism in SrRuO$_3$ [13] is notionalized as an itinerant electron magnetism of the Ru 4d electrons, and both samples are metals. But La$_2$MnRuO$_6$ is an insulator and shows ferromagnetism at lower temperature. Up to now, the exchange interaction mechanism in these samples is unclear.

In Fig. 4, the temperature dependence of the magnetization for La$_{2-x}$Sr$_x$MnRuO$_6$ ($x=1.0$, 1.5, 1.8 and 2.0) samples is shown it is ferrimagnetic. For example, as shown in Fig. 7, the temperature dependence of the susceptibility for Sr$_2$MnRuO$_6$ ($x=2.0$) samples shows the typical behavior of ferrimagnetism. There is a compensation point near 150 K, at which the magnetization has a minimum value. And for the samples with different Sr content x, the *M*(*T*) curves have different shapes, which indicates [14] that the molecular field constant radio N_{AB}/N_{AA} changes with the doping concentration of Sr for La, where N_{AB} and N_{AA} are the molecular field constants for the nearest neighbor interaction and the next neighbor interaction, respectively. We suggest that the superexchange interaction between Mn^{4+} and Ru^{4+} via the intermediate O^{2-} ions may be the source of the strong ferrimagnetic coupling. The partial substitution of Sr^{2+} for La^{3+} has three effects. (1) With the increasing Sr content x, the carrier concentration will be increased, which is confirmed by the decrease of the resistivity. (2) As the radius of Sr^{2+} is larger than that of La^{3+}, the crystal structure is changed. (3) The valence of the Mn ion changes from 3+ to 4+ when the x value changes from 1.0 to 2.0 for La$_{2-x}$Sr$_x$MnRuO$_6$ compounds. So, with increasing Sr content, the superexchange interaction between Ru^{4+} and Mn^{3+}, and between Ru^{4+} and Mn^{4+} may be changed. It is necessary to know the details of magnetic

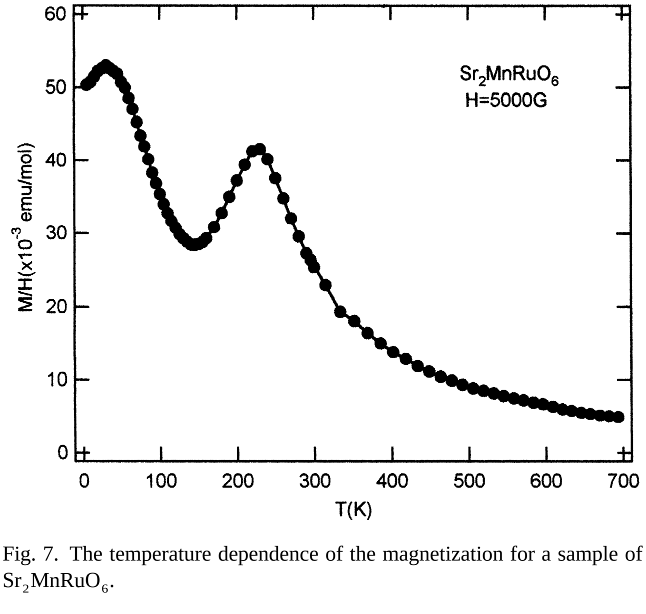

Fig. 7. The temperature dependence of the magnetization for a sample of Sr$_2$MnRuO$_6$.

structure in these compounds in order to understand the magnetic properties.

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