Phase diagram of Sm$_{1-x}$Sr$_x$MnO$_3$ perovskite manganites

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Abstract. We present the electronic, structural and magnetic phase diagram of the colossal magnetoresistive Sm$_{1-x}$Sr$_x$MnO$_3$ (0.16 $\leq x \leq$ 0.67) perovskite manganites, constructed on the basis of their regular investigations by high-resolution neutron powder diffraction, temperature magnetic and transport measurements. It is shown, that a real pattern of the physical phenomena in Sm-Sr manganites is considerably more various and is interesting than it was followed from macromeasurements. The tendency of researched system to formation of the phase-separated states on crystallographic as well as, in the even greater extent, on magnetic level is demonstrated. It is shown that there is a clear correlation between fine specific features and temperature evolution of crystal structures and the corresponding types of low-temperature magnetic ordering.

1. Introduction

In this work, we present the electronic, magnetic and structural phase diagram of perovskite manganites Sm$_{1-x}$Sr$_x$MnO$_3$ (0.16 $\leq x \leq$ 0.67) constructed using the results of our long-term systematic studies of this system by high-resolution neutron powder diffraction and magnetic and transport measurements reported previously [1–7] as well as new unreported data. There have been almost no neutron diffraction studies of the crystal and magnetic structures of manganites containing samarium because of the very high neutron-absorption cross section of natural samarium. One of the purposes of this work is to show that the interpretation of physical processes in complex strongly correlated manganite systems based only on the results of macroscopic measurements (without using adequate structural data) can be insufficiently deep.

We used here the phase diagrams of samarium–strontium manganites obtained from magnetic and transport macroscopic measurements on ceramic [8] and single-crystal [9, 10] samples as initial data. The previous measurements of the temperature and field dependences of the electrical resistivity and magnetization of ceramic samples of the Sm–Sr system [8] have shown that CMR is manifested only in the range of hole doping 0.3 $\leq x \leq$ 0.52 and reaches a maximum at $x = 0.44$. Recently, these data have been confirmed by similar studies on single crystals [9]. In [10], the phase diagram of the Sm–Sr compounds was studied in detail near a doping level of 50% by small steps of 0.01 in strontium concentration. It was shown that a 1% change in $x$ near $x = 0.5$ substantially modifies the ground state. Three different phases were identified depending on $x$: a ferromagnetic (F) metal ($0.3 \leq x \leq 0.48$), an orbitally ordered (OO) or charge-ordered (CO) insulator ($x = 0.49$ and 0.50), and an antiferromagnetic (AF) nonmetal at $0.51 \leq x \leq 0.6$. The CO/OO insulator exists only at $x = 0.49$ and 0.50, and the coexistence of two phases (F metal + CO/OO insulator) is observed only at $x = 0.49$. Furthermore, it is found from the measurement of an X-ray diffuse scattering that for $x = 0.48$ and 0.51 a short-range CO/OO exists (disappears) above (below) $T_C$ and $T_N$, respectively. Because of this, in Sm$_{1-x}$Sr$_x$MnO$_3$ single crystals, the competition between the F, CO/OO, and AF states becomes dominant near $x = 0.5$, and tricritical peculiarities are observed in the $x$-dependent electronic phase diagram. For this reason, the point $x = 0.5$ and $T \approx 120$ K in the diagram is considered a multicritical point near which the three phases compete with each other [10].

2. Experiment

Samples for neutron diffraction studies were synthesized using the $^{152}$Sm and $^{154}$Sm isotopes in order to suppress very strong neutron absorption by the $^{150}$Sm isotope in natural samarium. We studied manganite samples prepared and characterized in the CRISMAT Laboratory of Caen University (France) by using a conventional synthesis process in air. The characterization of the samples in terms of the stoichiometry, single-phase state, and homogeneity of the compositions in individual crystallites
was performed using electron microscopy, energy-dispersive spectroscopic analysis, Raman spectroscopy, X-ray and neutron diffraction, iodometric titration, and electron paramagnetic resonance.

Neutron diffraction measurements were performed on a high-resolution neutron powder diffractometer G4.2 (ORPHEE reactor, LLB, Saclay, France). The neutron diffraction patterns were measured in a superposition mode with monochromatic neutrons of wavelength $\lambda = 2.34 \, \text{Å}$ in the angle ranges $3^\circ \leq 2\theta \leq 174^\circ$ at temperatures from 1.5 K up to room temperature in a cryogenic furnace.

Determination of the types of the crystal and magnetic structures and their parameters from the experimental neutron diffraction patterns was performed using the FULLPROF and FULLPROF Suite program packages.

### 3. Experimental results and discussion

The neutron diffraction data indicate that materials of the Sm$\_x$Sr$_3$MnO$_4$ series with a strontium concentration $0.16 \leq x \leq 0.55$ crystallize at room temperature in orthorhombic space group $Pbnm$ [1-6]. However, the relation between the unit cell parameters is varied with $x$. Up to $x=0.4$, the $Pbnm$ lattice belongs to the so-called O-structure phase for which $b > a > c / \sqrt{2}$ [1]. In concentration range from $x=0.45$ up to 0.55, the $Pbnm$ lattice exhibits of the $O'$ type structure ($a > b > c / \sqrt{2}$) [2-6]. For $x=0.63$, the crystal structure of the samples is described by the tetragonal space group $I4/mcm$ [7].

At a helium temperature $T = 1.5 \, \text{K}$, the crystal structure of the most studied manganites is the same as that at room temperature. However, there are exclusions. For example, at $T \sim 180 \, \text{K}$, Sm$_{0.6}$Sr$_{0.4}$MnO$_3$ undergoes a structural phase transition from the room-temperature $O$ state to the $O'$ state [5]. In the compound with $x=0.5$, a structural phase transition is detected at $T = 135 \, \text{K}$ from the room-temperature $Pbnm$ phase to a mixture of two phases, namely, the orthorhombic $Pbnm$ and monoclinic $P2_1/cm$ phases. The latter crystal system, unlike the orthorhombic one, provides two different positions for of Mn ions and, thus, allows charge ordering of the Mn$^{\text{III}}$ and Mn$^{\text{IV}}$ ions. Note that the actual monoclinic structure of Sm$_{0.5}$Sr$_{0.5}$MnO$_3$ coincides metrically with $Pbnm$ (the monoclinicity angle is $90.03(3)^\circ$). In a result, the crystal structure of the manganite Sm$_{0.5}$Sr$_{0.5}$MnO$_3$ at low temperatures can be considered as a mixture of two $Pbnm$ phases which are coherent with respect to the atomic sites in the unit cell but exhibit different lattice parameters. While the temperature changes from 135 to 75 K, the content of the room-temperature phase decreases gradually that is accordingly accompanied by the increasing the content of the other phase. Below $T = 75 \, \text{K}$, the manganese ions are completely ordered magnetically and the distribution between the phases is stabilized to be 36:64% [5].

As for the spin ordering of the manganese ions at low temperatures, the neutron diffraction studies show that the manganites with concentrations $0.16 \leq x \leq 0.45$ have a phase-separated metallic ground state with coexistence of the F phase and some amount of the AF phase of the $A$-type ($A$-AF) with predominance of the ferromagnetism. In the $A$-AF structure, the magnetic moments of the Mn ions in planes are ordered ferromagnetically and the neighboring planes are ordered antiferromagnetically; i.e., the ferromagnetic ordering is two-dimensional. We pay attention to a special case, that for for the Sm$_{0.75}$Sr$_{0.25}$MnO$_3$ compound there is almost no antiferromagnetic contribution. The ground state of the compounds with $x=0.45$ and 0.48 is a homogeneous metallic ferromagnet [2-4]. The character of anomalies of the physical properties, including CMR, in the vicinity of $T_C \sim 120 \, \text{K}$ confirms that the phase transition becomes a clearly defined first-order transition. The existence of a homogeneous F state at temperatures below $T_C$ is also unusual since the paramagnetic state of the same samples is magnetically inhomogeneous and exhibits a complex temperature dependence according to measurements of small-angle neutron scattering, muon spin relaxation ($\mu$SR), and nonlinear magnetic response [2, 3]. The composition with $x=0.5$ again demonstrates the phase-separated ground state with the coexistence of the F and $A$-AF phases in which, however, antiferromagnetism dominates. The F and $A$-AF phases of this compound correspond accordingly to the room- and low-temperature crystal phases described above. The metallic behavior of the electrical resistivity is observed only below 50 K and is related to the F phase. The $A$-AF phase is an insulator [5]. The ground state of the manganite with $x=0.55$ is a single-phase $A$-AF insulator at low temperatures [6, 7]. The compounds with $x=0.63$ [7] and 0.67 have the $I4/mcm$ tetragonal crystal structure over the temperature range from 1.5 to 288 K and exhibit a single-phase magnetic ground state with an AF ordering of the C type (C-AF) and an insulator behavior. The C-AF structure is formed by the chains of the ferromagnetically arranged Mn...
ions with antiferromagnetic ordering between neighboring chains, and the ferromagnetic ordering is, in fact, one-dimensional.

Thus, the magnetic phase diagram is found to be fairly unusual for manganites. In this diagram, homogeneous ferromagnetic states exist in very narrow ranges of strontium concentrations near $x=0.25$ and 0.45 surrounded by wide regions of phase-separated states.

The most important deformation characteristics of the main building block of manganites, namely, MnO$_6$ octahedron, are the Mn–O bond lengths in it. The neutron diffraction data show that, in the compositions $0.16 \leq x \leq 0.50$, Mn–O$_21$ > Mn–O$_1$ > Mn–O$_22$; i.e., the length of the apical bond is between the equatorial bond lengths. In the Sm$_{0.5}$Sr$_{0.5}$MnO$_3$ compound, which is two-phase at low temperatures, the deformations of the manganese–oxygen octahedron are different for each phase. In the crystal phase corresponding to the F ordering, the above relation is satisfied. In the low-temperature A–AF phase, the relation between the bond lengths is Mn–O$_21$ > Mn–O$_22$ > Mn–O$_1$. The apical bond length remains the shortest one as strontium concentration increases further.

Our neutron diffraction measurements permit conclusions regarding the type of orbital ordering of the Mn $e_g$ electrons in the AF phases based on the precision determination of the Mn–O bond lengths in the distorted MnO$_6$ octahedron. The appearance of orbital ordering $d_{z^2,r^2}$ is accompanied by anisotropic uniaxial compression of the oxygen octahedra along the direction perpendicular to the plane in which $e_g$ orbitals are located. On the contrary, the appearance of $d_{x^2-r^2}$ orbital ordering is accompanied by anisotropic uniaxial elongation of the oxygen octahedra along the direction in which the $e_g$ orbitals are oriented. As for the orbital ordering in the Sm$_{1-x}$Sr$_x$MnO$_3$ system, the bond lengths calculated from the neutron diffraction data allow one to conclude that, as $x$ increases, the ordering of the Mn $e_g$-electron orbit is changed from the $(3y^2-r^2)(3z^2-r^2)$ for low-doped compounds to $(x^2-y^2)$ type and then to the $(3z^2-r^2)$ type in the AF phases. This transition is not continuous; it exhibits discontinuities when the delocalized F state is formed.

It is important that the relation between the bond lengths in the MnO$_6$ octahedron does not correlate with the $Pbmn$ type of the crystal lattice (O or O') but is associated with the type of magnetic ordering of the Mn ions. For the F phases, the relations Mn–O$_21$ > Mn–O$_1$ > Mn–O$_22$ are always satisfied. For the A–AF ordering, there are two versions of such relations. In the case of hole doping of the samarium manganites with strontium ($x<0.5$), the relations between the bond lengths are similar to those in their F phases and, at $x>0.5$, the Mn–O$_1$ apical bond length becomes the shortest. In this case, an AF insulating state is established. At $x>0.5$, the Neel temperature is significantly higher than the Neel and Curie temperatures at $x<0.5$; thus, the AF structure is energetically more preferable here as compared to a possible F structure. The antiferromagnetism overcomes in the competition between F and AF states, and there is no CMR effect at concentrations $x>0.5$.

Figure 1 shows the summary phase diagram of the perovskite manganites Sm$_{1-x}$Sr$_x$MnO$_3$ ($0.16 \leq x \leq 0.67$). It is constructed using the diagram from [8] with addition of the above results on the crystal and magnetic structures obtained from the neutron diffraction data. The diagram from [8] is taken as the initial diagram since all critical temperatures ($T_C$ and $T_N$), in it practically coincide with those measured on our samples. In addition, we indicate the concentration ranges with different types of crystal structure $Pbmn$ (O and O'), $I4/mcm$ (over the entire temperature range), and a $Pbnm + P2_1/m$ mixture (only at low temperatures). It is shown where there are homogeneous magnetic ground states (F, A–AF, and C–AF).

It is also shown that, in fairly wide concentration ranges, phase-separated magnetic systems with a mixture of ferromagnetism and A-type antiferromagnetism are formed. In this case, depending on the composition, the dominant type of magnetic order is either F- (when the F phase dominates) or A- AF (when the AF phase dominates). The diagram also schematically shows the types of orbital ordering in the AF phases, depending on the strontium concentration.

Finally, correlations were elucidated between the crystal structure, spin ordering of the manganese ions, and the physical properties of the samarium–strontium series of manganites obtained from temperature magnetic and transport measurements.

The main result of this work, in our opinion, is that the actual pattern of the physical phenomena occurring in samarium–strontium manganites is significantly richer than it follows from macroscopic measurements. We have shown that there is a tendency for the system under study to form ordered phase-separated states on a crystalline level and, even to a greater extent, on a magnetic level. Our new results do not contradict the earlier results but complement them. We have revealed correlations
between the crystal structure, spin ordering of the Mn ions, and physical properties of the samarium–strontium manganites using the temperature magnetic and transport measurements.

Figure. 1. Magnetic and structural phase diagram of the Sm$_{1-x}$Sr$_x$MnO$_3$ system. Close circles and triangles correspond accordingly to the values of $T_C$ and $T_N$ from [8]. The arrows at the top indicate the region of existence of CMR and phase separation (PS) [8]. The horizontal inscriptions indicate the types of the ground state as derived from macroscopic measurements in [8] (FMI stands for FM insulator; FMM, for FM metal; and AFMI, for AFM insulator). The vertical inscriptions correspond to the neutron diffraction data: F is homogeneous ferromagnet; $A$-AF is $A$-type homogeneous antiferromagnet; C-AF is C-type homogeneous antiferromagnet; and $F+\cdot A$-AF, $A$-AF+F are phase-separated magnetic systems with a mixture of ferromagnetism and antiferromagnetism in which the F and AF phases dominate, respectively. The dashed areas correspond to homogeneous magnetic states: F (horizontal hatching), $A$-AF (vertical hatching), and C-AF (diagonal hatching). Areas, corresponding to different types of crystal structure $Pbnm$ (O and O') and $I4/mcm$ (at all temperatures) and a mixture $Pbnm + P2_1/m$ (only at low temperatures), are also indicated by arrows. The supposed types of orbital ordering in AF phases ($3z^2-r^2$) and ($x^2-y^2$) are shown schematically.

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