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Effect of the Jahn–Teller Distortion on Double Exchange Interaction in $La_{0.8}K_{0.2}MnO_3$ Nanoparticles

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Electric resistance and effect of hydrostatic pressure on magnetic properties has been studied on the $La_{0.8}K_{0.2}MnO_3$ nanoparticles. Magnetic phase transition is affected by pressure only slightly, the Curie temperature T_C decreases with the rate of –1.02 K/GPa, on samples with orthorhombic structure where the Jahn–Teller distortion of lattice is large. On the other hand, T_C increases with the rate of 20.1 K/GPa on samples with rhombohedral structure, where the Jahn–Teller distortion of lattice is absent. Insulator type of electrical resistance is characteristic feature of sample with large Jahn–Teller distortion of lattice and insulator–metal transition was observed on samples where the Jahn–Teller distortion is negligible. Our results are in line with theoretical calculation predicting that double exchange interaction is suppressed by the Jahn–Teller distortion.

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1. Introduction

The mixed-valence manganese oxides of the general formula $La_{1-x}A_xMnO_3$ (A is a divalent ion like Ca, Sr, Ba, and Pb) are a subject of interest due to a desire to understand and exploit the large negative magnetoresistance and magnetocaloric effects [1]. Recently, the same type of manganites doped with univalent metals, such as Ag, K, and Na become of great interest, because their physical properties are very sensitive to a magnetic field at room temperature. Group of $La_{1-x}K_xMnO_3$ manganites provides a series of new oxides to study magnetocaloric effect [2, 3] and insulator-to-metal transition [4] at room temperature.

Newly [5] we have studied magnetic properties of $La_{0.8}K_{0.2}MnO_3$ on nanoparticles, which were prepared by glycine–nitrate method. Crystal structure and particles size were modified by heat treatment. We have found that the crystal structure changes from orthorhombic (space group *Pnma*) to rhombohedral (space group *R-3c*) after annealing at 600 °C/2 h. MnO_6 — the building blocks of crystal structures are distorted and tilted. We attributed the distortion of the lattice mainly to the Jahn–Teller (JT) distortion, the JT distortion is gradually removed from the sample and completely vanishes in the rhombohedral crystal structure. Scanning electron microscopy (SEM) method revealed that the average size of particle varied with annealing from about 30 nm to 135 nm. The Curie temperature T_C and the saturated magnetization μ_s increased with annealing and T_C was nearly doubled in the sample with the rhombohedral crystal structure [5]. The exchange bias effect was observed on samples with particles size smaller than 60 nm [5].

In this work we study the effect of Jahn–Teller (JT) distortion on double exchange interaction in this system. It was shown theoretically that the JT coupling drastically reduces the Anderson–Hasegawa double exchange (DE) [6] and our present work together with the previous results [5] probes the extent of this theoretical result on the $La_{0.8}K_{0.2}MnO_3$ system of nanoparticles experimentally.

2. Experimental details

The preparation of nanoparticles followed the glycine–nitrate method, where glycine was used as a fuel and nitrates as oxidants [7] and the size of particles was modified by the annealing. The detailed description of annealing procedure, X-ray and SEM analysis is present in [5]. An additional characterisation of prepared sample was performed by transmission electron microscopy (TEM) using a scanning transmission electron microscope JEOL JEM 2100F UHR. Microscope operates with accelerating voltage 80 kV to 200 kV and also enables structure observations at atomic level (HRTEM). Colloids, mixture of the sample and acetone, were prepared for TEM investigation and subsequently a droplet of the colloid was placed on a grid covered by carbon. These particles were covered by carbon layer in next step. Magnetization measurements were performed by a SQUID (MPMS XL−5) in the temperature range from 1.8 K to 380 K and in mag-

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netic field up to 5 T. In the case of measurements under pressure the hydrostatic pressure up to 1.4 GPa was generated by a piston cylinder type of the CuBe pressure cell for MPMS based on Teflon container (Easy Lab). A mixture of mineral oils served as hydrostatic pressure transmitting medium. Resistivity measurements were performed in the temperature range from 300 K to 50 K in VERSALAB equipment.

3. Results and discussion

TEM study confirmed that all samples consist from agglomerates of nanoparticles as it is shown for sample annealed at 300 °C for 2 h (Fig. 1). The size of particles depends on annealing and corresponds with size of nanoparticles determined by scanning electron microscopy [5]. The smallest particles have size approximately from 10 to 15 nm and typically have character of single crystals as it was revealed by HRTEM study (Fig. 2).

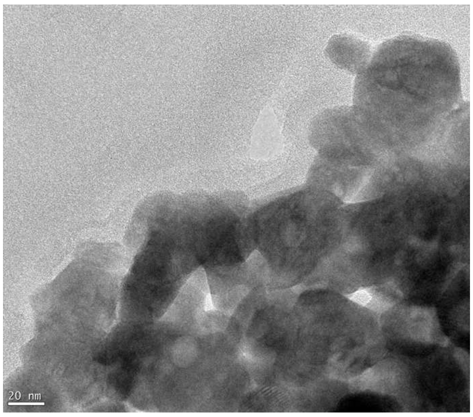

Fig. 1. TEM image shows an agglomerate of nanoparticles. The white line represents the distance of 20 nm.

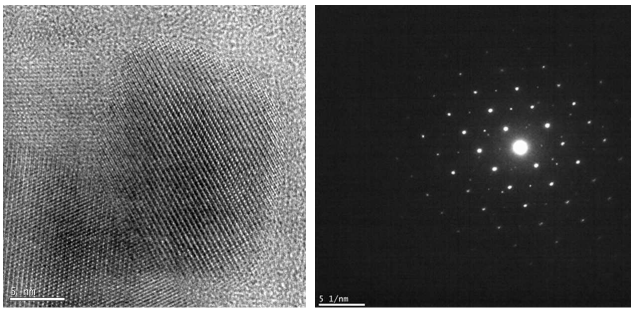

Fig. 2. HRTEM image of as prepared sample shows an individual particle. The white line represents the distance of 5 nm. Second photo shows the electron diffraction pattern.

Hysteretic behaviour between temperature dependence of magnetization in zero field-cooling (ZFC) and field-cooling (FC) regimes is a characteristic feature of the system with the orthorhombic crystal structure (see Fig. 3). Very large difference between magnetization ZFC and FC curves can indicate structural disorder. Together with

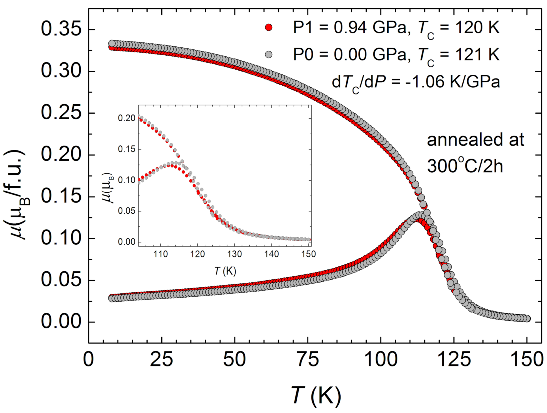

Fig. 3. ZFC and FC magnetization are shown at different pressures for sample with the orthorhombic crystal structure. The inset shows bifurcation and phase transition in detail.

our X-rays diffraction measurements [5] and in analogy with study, which was performed on $La_{0.7}Ca_{0.3}MnO_3$ system of nanoparticles [8], we suppose that the JT distortion of crystal lattice is mainly responsible for this disorder. Pressure effect on the Curie temperature T_C is very small and even T_C decreases with pressure with rate −1.06 K/GPa (see Fig. 3). Such behaviour is unusual for hole-doped manganites with dominant DE interaction, where pressure stabilises ferromagnetic (FM) ordering and increases T_C [9]. It was shown theoretically that the JT coupling drastically reduces the Anderson–Hasegawa double exchange (DE) [6] and in this context our pressure measurements correspond with theoretical prediction [6]. We associate small increase of T_C, i.e. the increase of FM interactions with annealing [5], with reduction of JT distortions.

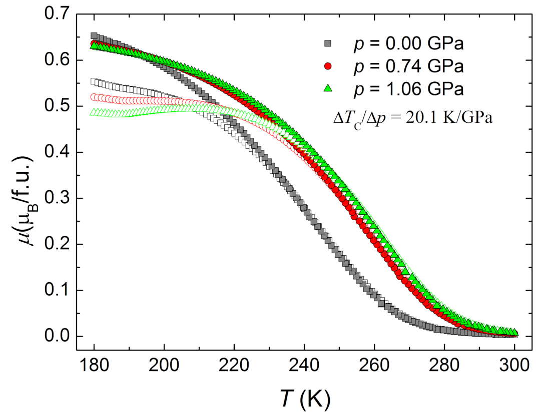

Fig. 4. ZFC and FC magnetization in vicinity of magnetic phase transition are shown at different pressures for sample with rhombohedral crystal structure.

The crystal structure changes from orthorhombic to rhombohedral [5], by annealing at 600 °C/2 h, and T_C increases from 112.0 K to 245 K (Fig. 4). Doubling of T_C is mainly due to the increase of bonding angle Mn–O–Mn from 171 to 180 degrees since the strength of DE

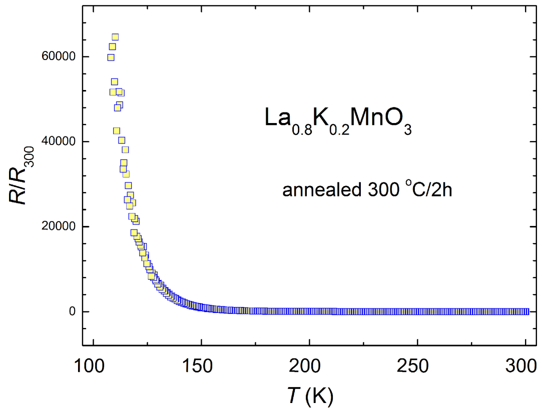

Fig. 5. Temperature dependence of the electrical resistance. The insulator type of resistivity was observed on the sample with the orthorhombic crystal structure.

is proportional to the cosine of this angle [6]. The rhombohedral crystal structure is practically free from JT distortions of lattice, DE interaction is strong and pressure increases T_C with rate 20.1 K/GPa (Fig. 4). Pressure experiment can be used as an indirect indicator of JT distortion in such type of material. JT reduces mobility of electrons, which is expected to be high in the case of DE interaction.

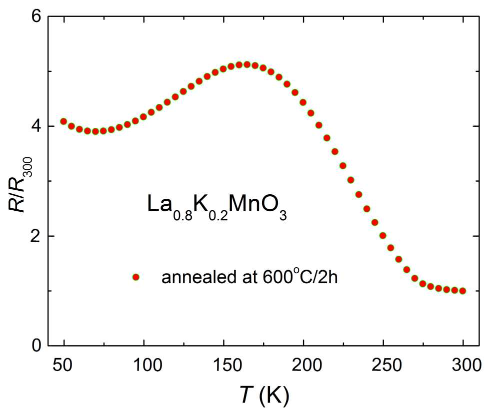

Fig. 6. Temperature dependence of the electrical resistance on the sample with rhombohedral crystal structure.

Measurements of electrical resistivity proof mobility of electrons and can be used as indirect indication of JT distortion in the sample. The insulator type of resistivity was observed on sample with orthorhombic crystal structure which contains JT distortions (Fig. 5). Such a behavior indicates reduction of electron mobility. The insulator–metal transition, which is characteristic feature of hole-doped ferromagnetic manganites with dominant DE interaction, was observed on sample with rhombohedral structure (Fig. 6). At lower temperatures a reentrant transition is present. The JT distortions reduce mobility of electrons and affect the type of electrical resistance in this material.

4. Conclusions

Our study of electrical resistance and pressure effect on magnetic properties of the $La_{0.8}K_{0.2}MnO_3$ system of nanoparticles with orthorhombic (space group *Pnma*) and rhombohedral (space group *R-3c*) crystal structure confirmed theoretical prediction that JT distortion reduces mobility of electrons and DE interaction, which is responsible for ferromagnetic state in this system. Moreover, the reduction of electron mobility due to JT distortion of lattice supports insulator type of resistance.

Acknowledgments

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