Transport phenomena and magnetic/crystalline structure of manganites

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Abstract

The proposal targets are the investigation of magnetoresistive complex oxides, their behavior vs temperature and magnetic field, achivement of new knowlege concerning the magnetic structure and mechanisms which govern the transport propreties. In the frameworks of the project will be presended shortly the synthesis methods of new colosal magnetoresistance stoichiometric manganites. Manganites structure will be characterized by using electronic or optical microscopy and X-ray or neutron diffraction (XRD or ND). Phase composition, unit cell structure parameters, the position of cations/anions in the unit cell, average size of the mosaic blocks, microstrains, crystalline phase diagram will be determinate. The magnetic properties as specific/molar magnetization with temperature and transport phenomena (resitivity vs temperature) will be determined in the temperature and magnetic field intensitiy ranges 10 – 400 K and, respectively, 0 – 1.5 T. We will test the transport mechanisms observed at low and high temperature.

General objectives of the project

The aims of the project are to (1) establish the crystalline and electronic partial phase diagrams of some manganites; (2) determine the variation of the resistance with the temperature (and magnetic field).

1.Synthesis of manganites.

In the **standard ceramic** method the precursors are oxides or carbonates, mixed in a ratio corresponding to the nominal chemical composition. The mixture should be heated at 700 - 900°C few hours, milled and finally sintered between 1200 - 1300°C for 10-24 h. The sintering atmosphere must be chosen in agreement with the necessary oxygen concentration in the samples.

Combustion synthesis is a self-sustaining synthesis reactions used to produce a variety of materials. An exothermic chain reaction is initiated in a part of the product, when it is encapsulated in a highly exothermic atmosphere and heated. Wet chemical methods utilize the exothermic redox reaction initiated in an aqueous precursor solution of metal nitrates (oxidizers) and carbonaceous fuels (reducing agents) to produce a multicomponent oxide powder. Combustion synthesis yields crystalline, fine particle size, porous powders at low temperature, in few minutes.

Mechanical alloying allows the obtaining of the various simple perovskites, which have the unique physico-chemical properties, depending on the constituent elements of the perovskites. Almost all properties could be improved by mechanochemical synthesis, because this process produces very fine samples. Rare earth oxides as La_2O_3, with La in A-site, may react with many trivalent transition metal oxides, M_2O_3, to form various $LaMO_3$ manganites.

We will use the **standard ceramic method** to obtain manganites.

2. Colossal magnetoresistive (CMR) manganites properties

Structure The ABO_3 perovskite structure can be described in terms of a close packed arrangement of AO_3 layers with B cations in the octahedral sites (s. Fig.1). The stacking sequence can be cubic ($3C-ABO_3$), hexagonal ($2H-ABO_3$) or a combination of both (hexagonal polytype).
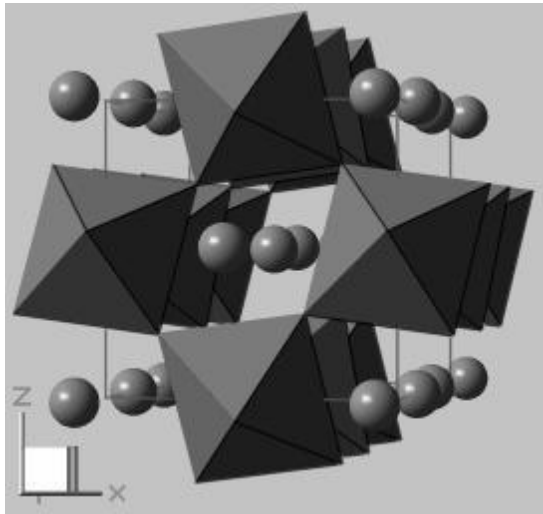

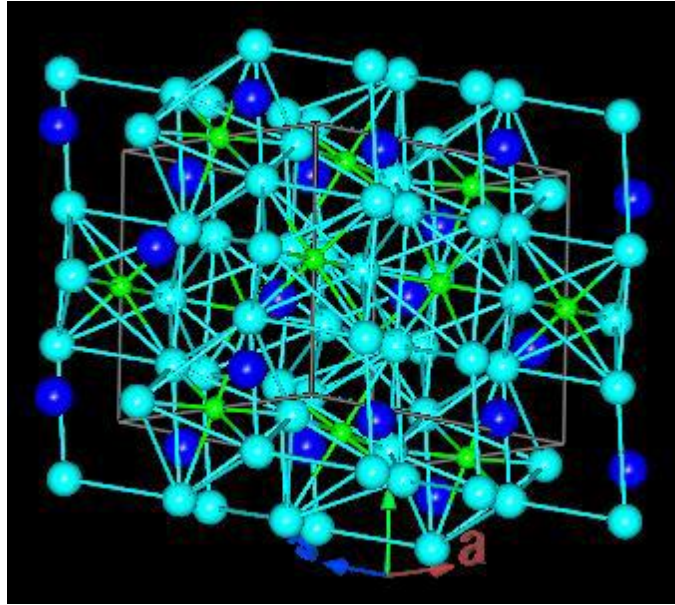*Figure 1a BO_6 octhaedra chains orthorhombic structure of LHSMCO manganite*

Figure 1b Unit cell of $LaMnO_3$ (FullProf)

The ***transport properties*** are based on the transfer of electrons between Mn^{3+} and Mn^{4+} cations, via oxygen 2p orbitals and depend on the relative Mn^{3+}/Mn^{4+} concentrations. Taking account of Hund rule, between t_{2g} and e_g electrons there is a strong coupling. On other hand, e_g electrons of Mn^{3+} cations are very strong hybridized with oxygen 2p orbitals. These electrons become itinerants, if a corresponding amount of Mn^{4+} exists in the $AMnO_3$ lattice. Transport properties are controlled by the effective transfer integral t=bcos(Θ/2), where the electronic transport is associated with Θ the angle Mn-O-Mn of nearest cations: the maximum of probability transfer takes place when Θ is close to 180°. Some compounds from series $Ln_{1-x}Alk_xMnO_3$ (Alk=Ba, Ca, Sr) form a boundary region between FM – metallic and AFM – insulator state, where metallic and insulator states coexist. The substitution of Mn with Ni, Cr, Co, Cu etc can destroy the charge ordering (CO) and induce an insulator-metal transition. For $La_{0.5}Ca_{0.5}Mn_{0.97}Ni_{0.03}O_3$ was observed a broad paramagnetic-ferromagnetic transition. At low temperature (> 50 K) an antiferromagnetic insulator phase was observed, while at temperature ~ 150 K a contribution to ferromagnetism was put in evidence by the neutron diffractometry. The presence of various cations on B places has different consequences concerning the ***magnetic structure*** and transport properties. We have made preliminary calculations, concerning the average radii of A and B places, of tolerance factor and of chemical degree disorder, starting from a few perovskites as:

$$La_x^{3+} Sr_{1-x}^{2+} Mn_z^{4+} Mn_{1-y-z}^{3+} T_y^{3+} O_{3-\delta}^{2-}$$
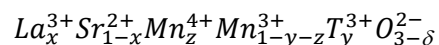
where T represents a transition element. For a small Sr content, $La_{1-x}Sr_xMnO_{3-\square}$ manganites have a rhombohedral structure, with T_C near room temperature (250 K). Variation of oxygen concentration can induce a large change of the electronic phase composition of manganites, implicitly of variation of ferromagnetic metallic (FMM) and antiferromagnetic insulator (AFMI) phase concentration.

3. Measurement methods

Optical Microscopy will be used to put in evidence the presence of the foreign phase in the ceramic samples, to evaluate the decomposition temperature of the sol gel or to evaluate the results of mechanical alloying (see Fig. 2). The samples for optical microscopy or XRD will be prepared by using a high speed diamond cut-off saw and a EQ-Unipol-300 econnomic 3" grinder / polishing.

Figure 2 Some instruments used to obtaining manganites and determining their transport properties. 1. General view of installation for magnetoresistance measurements (photo 2008, on YUMO electromagnet; today (2018) installation is in FLNP building); 2. High Speed Vibrating Ball Mill; 3. Electric Hydraulic Laboratory Press; 4. EQ-Unipol-300 Econnomic 3" Grinder / Polishing; 5. Metallurgical microscope; 6) High Speed Diamond Cut-off Saw

Some sintered or treated bulk or thin solid films will be investigated first by optical microscopy. For optical microscopy the bulk samples will be prepared by standard metallographic methods (ASTM). The metallography was performed by means of a metallurgical microscope, with an image system acquisition (see Fig. 2).

X-Ray analysis All the samples will be investigated by means of X-Ray analysis. A part of recorded data will be processed by Dicvol, Treor and FullProf codes (s. Fig. 3), in order to determine the phase composition, lattice constants, the distribution and the positions of atoms in the unit cell, other microstructural parameters.
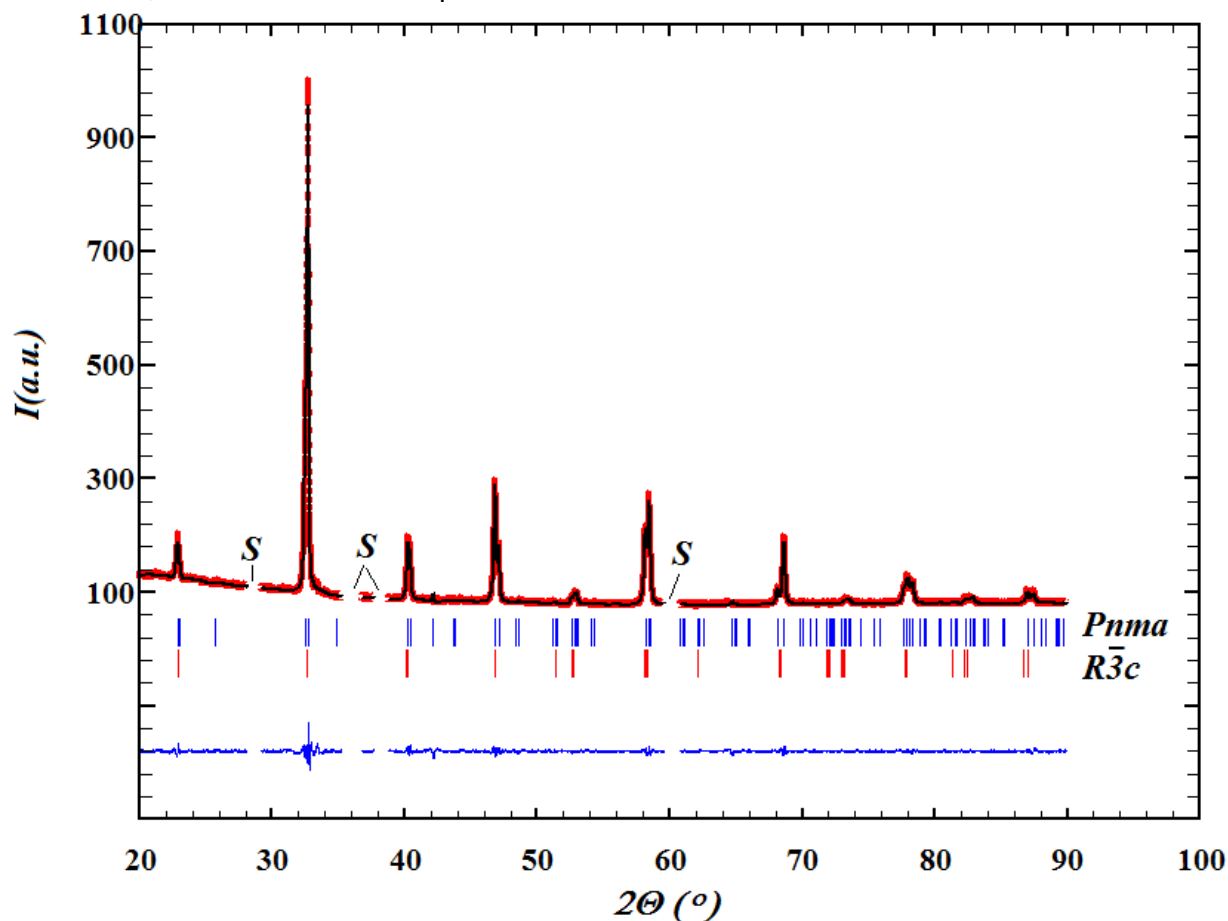

Figure 3. *Observed (black) and calculated (red) XRD diffractograms of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{0.90}Cr_{0.10}O_3$ using FullProf software; bottom (blue) – the difference between the calculated and observed diffractograms. S - foreign phase*

The used programs allow as to check more variants of unit cells and to make the corresponding chose. Each program evaluates the total error, as a sum of experimental and processing errors. The distances between the cations and anions and the Mn-O-Mn or Ln-O-Mn etc angles will be determined by using the PowderCell or GRETEP or similar programs. The observed tolerance factor (t_{obs}) and the chemical disorder degree (σ^2) will determined also.

Magnetic methods. The magnetic measurements have been performed with vibrating sample magnetometer, with data acquisition systems, between 77 and 870 K, in the magnetic fields up to 2.2 T (see Fig. 4). We will determine the Curie temperature, specific/

molar magnetization, magnetic state (ferromagnetic, spin glass type etc) data which will contribute to the establishing of electronic phase composition diagram.
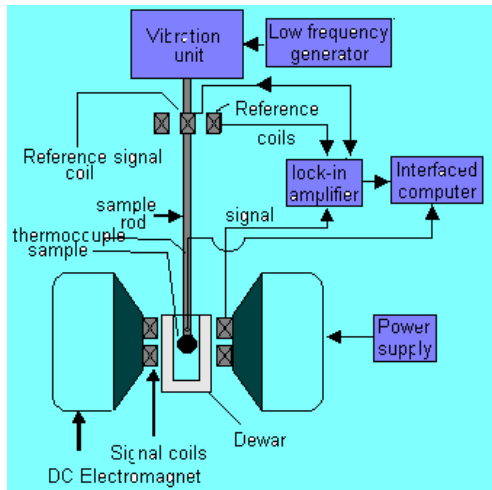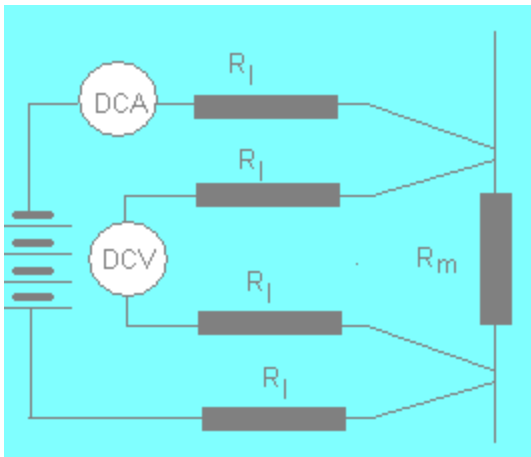

Figure 4 *The simplified schema of vibrating sample magnetometer*
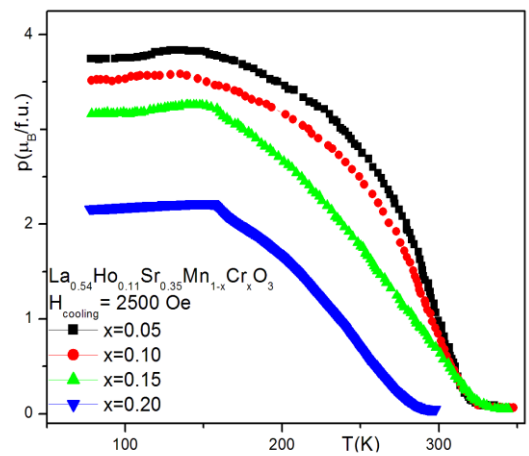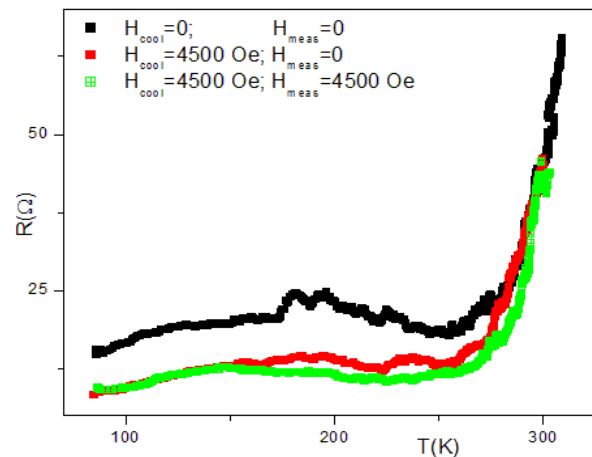

Figure 5 *Variation of specific magnetization with the Cr concentration manganites; $H_{cool}=H_{measurement}=2500$ Oe*

Electrical measurements will be performed by using a four points method (see Fig. 6).

Figure 6 The simplified schema electrical measurements (environment and computer connections are not presented)

Figure 7 Variation of the resistance with temperature and applied magnetic field for $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{0.95}Cr_{0.05}O_3$.

We need 4 students with the knowledge concerning the electricity and magnetism (high level) and crystalline structure (basic level). We appreciate that the measurements and data handling will be finished in three weeks.

References
1) C. Hammond, The Basic of Crysatallography and Diffraction, Oxford University Press, 2001
2) B.K.Vainstein, Modern Crystallography, Springer-Verlag, 1995

3) E. Dagotto, Nanoscale Phase Separation and Colossal Magnetoresistance: The Physics of Manganites and Related Compounds, Springer-Verlag, 2003

Nr. crt.	Subject	Lecture (hours)	Laboratory (hours)
1	Synthesis of manganites	2	
	1) calculating the chemical composition of a series of manganites		1
	2) weighing, mixing and grinding a few samples of the calculated series of manganites		3
	3) pressing the samples as discs, treatment at low temperatures, the intermediate ball mill grinding, pressing and final treatment		3+3
2	Colossal magnetoresistive (CMR) manganites properties: structure, magnetic and transport properties	2	
3	Measurement methods	4	
	Optical metallography		4
	XRD and ND (Dicvol and FullProf methods)		10
	Handling of magnetic measurements		6
	Transport properties measurements		10
4	Data evaluation		2
5	Total		50