Palacký University
Olomouc

JOINT INSTITUTE
FOR NUCLEAR RESEARCH

Transport phenomena and magnetic/crystalline structure of some manganites

- Student:

Viktorie Vichova

Nanotechnology, Master Course
Regional Centre of Advanced Technologies and Materials
Palacky University in Olomouc, Czech Republic

- Laboratory:

Frank Laboratory of Neutron Physics

- Project Coordinator:

Dr. Mihail - Liviu Craus

Aim

The samples preparation:

- Precursors for manganites will be calculated, weighted and mixed.
- $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites will be prepared by ceramic method using oxides and acetates and sintered in air at 1250^o C for 15 h.

X-ray diffraction:

- The synthetized samples will be investigated to determine the phase composition and the crystalline structure parameters.
- A part of X-ray data for samples mentioned was obtained with a Philips diffractometer ($CuK_{\alpha 1 \alpha 2}$ radiation) and was handled using FullProf Suite and PowderCell codes.

Aim

Magnetic measurements (NIRDTP Iasi, Romania):

- Magnetic measurements were performed by using a magnetometer type Foner.

Transport measurements (FLNP JINR Dubna, Russia):

- The electrical characteristics (resistance) were obtained by using a Cryomech cryocooler.

Work Within the Project

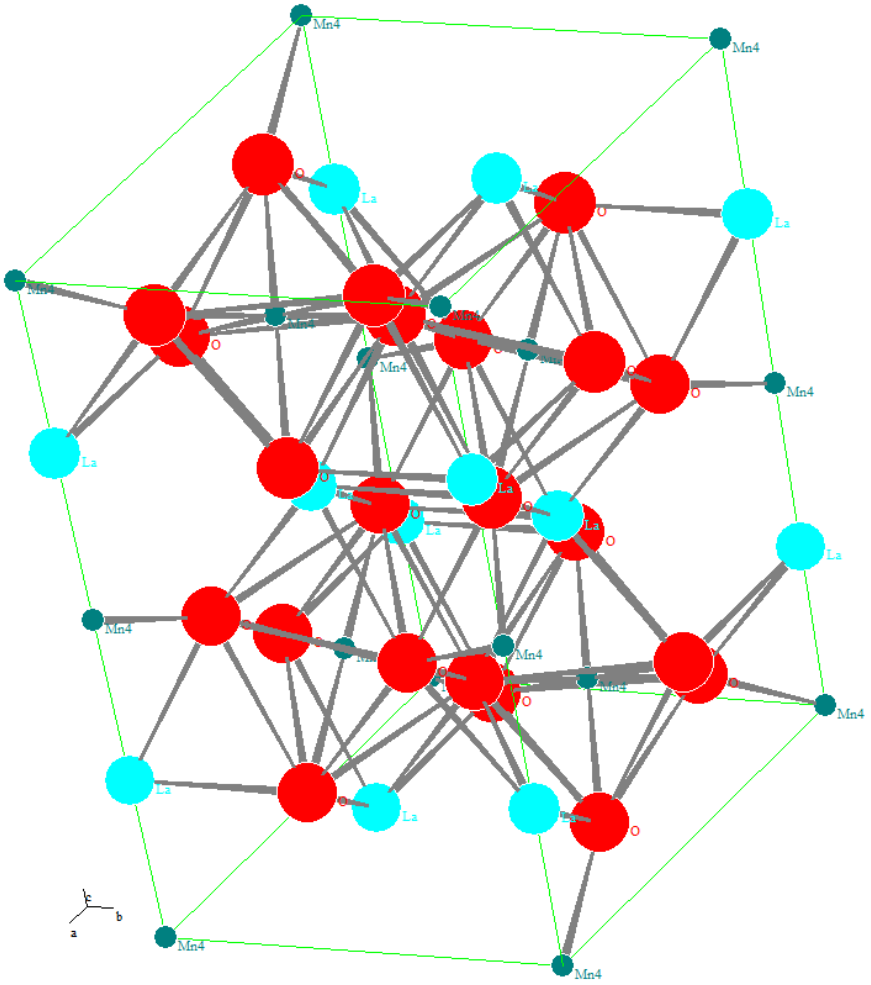
- XRD data of manganite samples with the general chemical formula $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ have been handled using FullProf Suite, PowderCell, CellRef codes.
- We received the variation of lattice constant value, microstrains and crystallite average size dependence with Mn/Co concentration.
- We also have received the variation of magnetic properties and transport characteristics with Co concentration.

Part 1:

Difraction analysis of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites

Unit cell of manganite $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$

- Distorted Perovskite ABO_3
- Ortorhombic space group: *Pnma*
- Primitive lattice (*P*)
- A places: La, Ho and Sr cations (blue)
- B places: Mn and Co cations (green)
- Oxygen (red)



Observed and calculated diffractograms of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{0.95}Co_{0.05}O_3$ (FullProf method)

x = 0.05

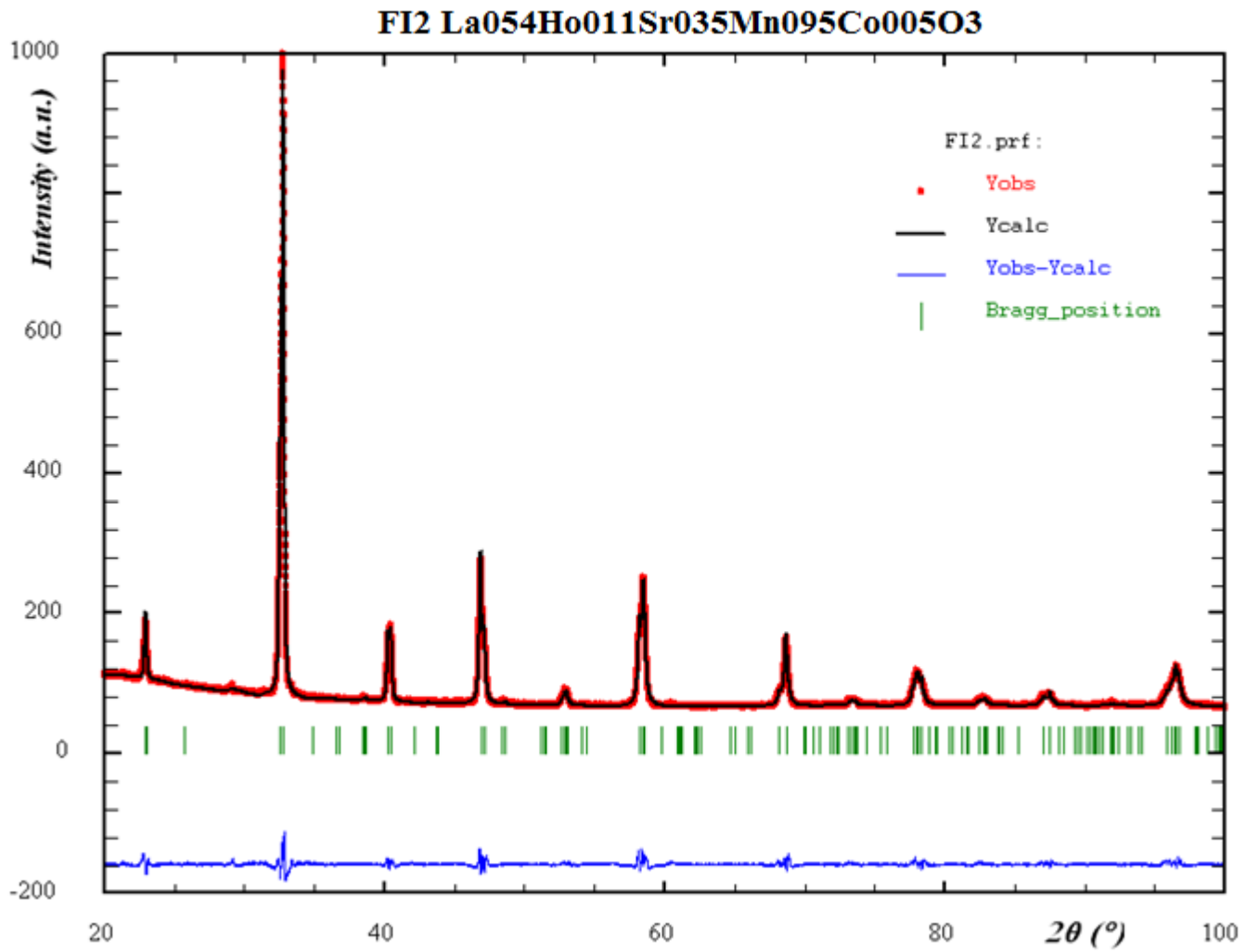


Figure 1

Observed and calculated diffractograms of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{0.90}Co_{0.10}O_3$ (FullProf method)

x = 0.10

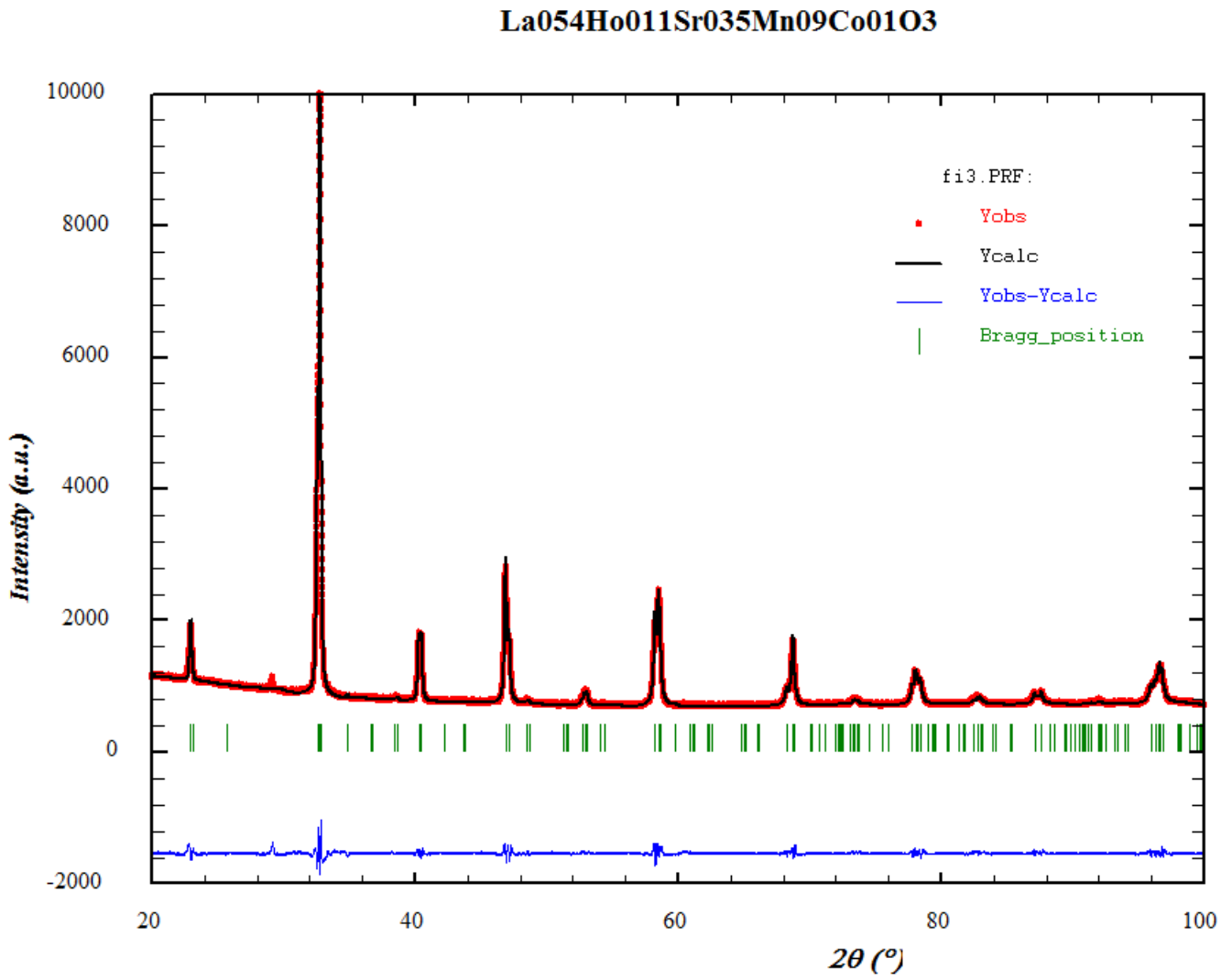


Figure 2

Observed and calculated diffractograms of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{0.85}Co_{0.15}O_3$ (FullProf method)

x = 0.15

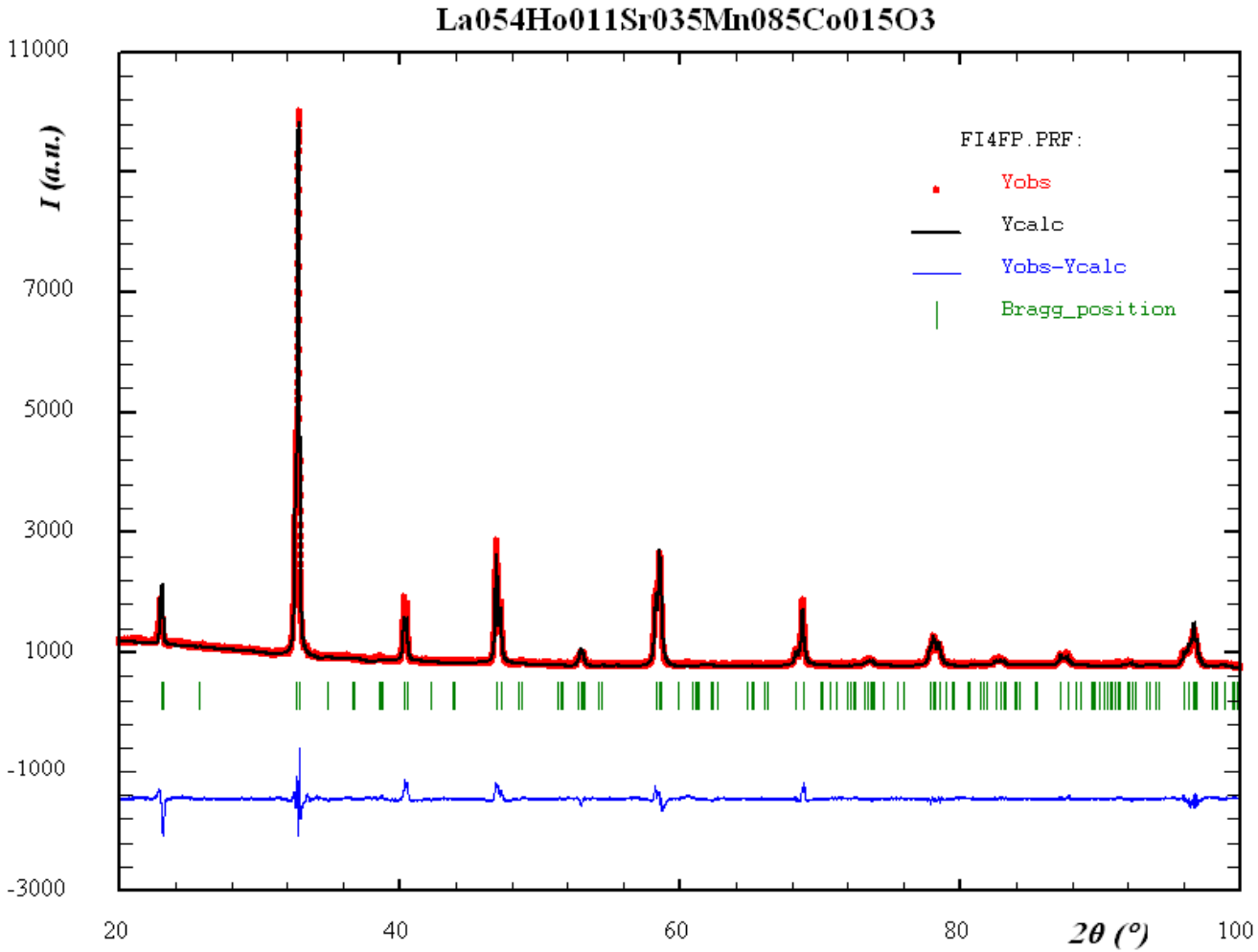


Figure 3

Observed and calculated diffractograms of $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{0.80}Co_{0.20}O_3$ (FullProf method)

x = 0.20

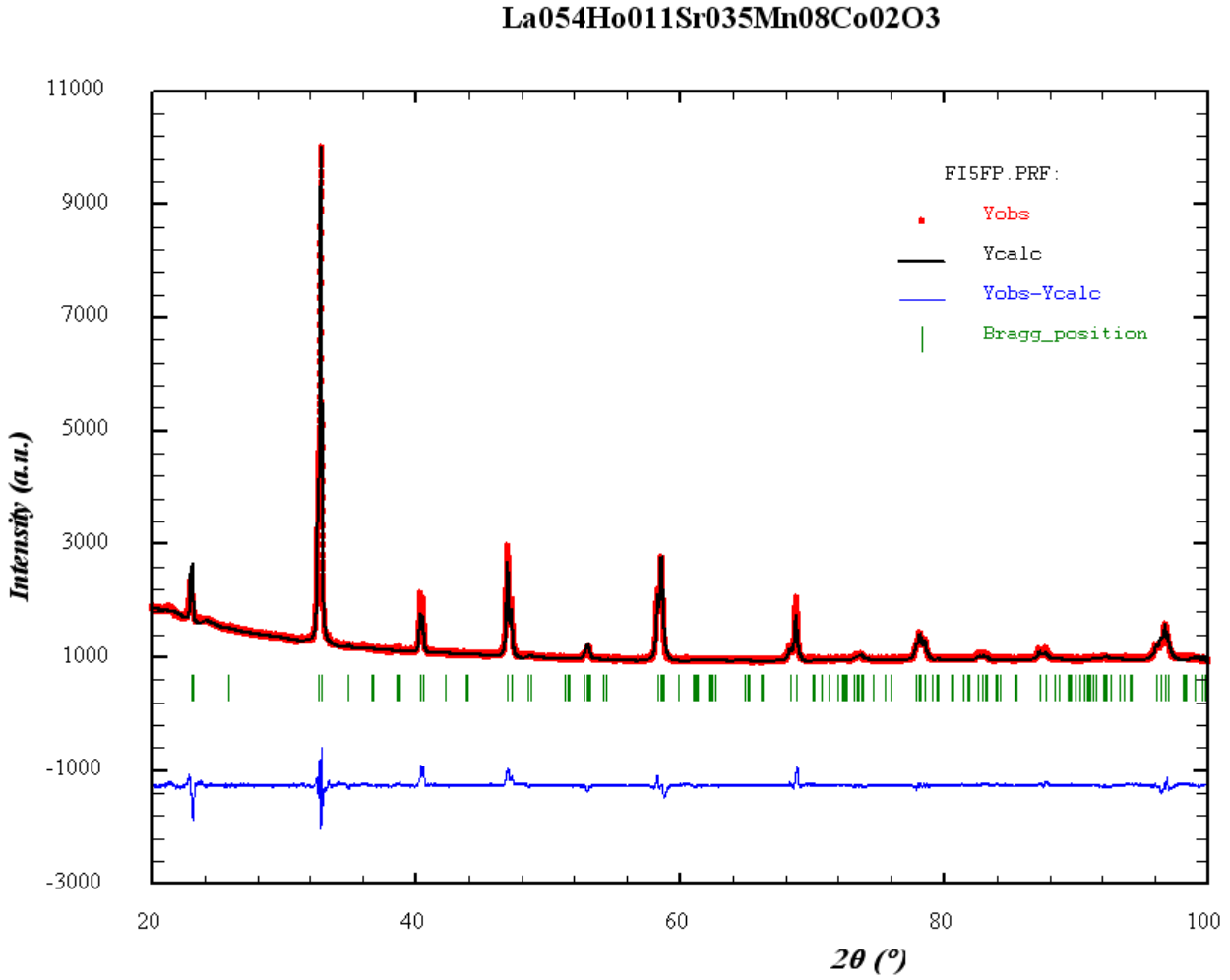


Figure 4

Table 1: Variation of the lattice constants and the unit cell volume (a,b,c,V) *vs.* Co concentration (*x*)

x	a(Å)	b(Å)	c(Å)	V(Å^3)
0.05	5.4946	7.7075	5.4613	231.284
0.10	5.4556	7.7003	5.4922	230.726
0.15	5.4539	7.6929	5.4888	230.290
0.20	5.4516	7.6903	5.4871	230.044

We can observe a small decrease of the unit cell volume with the increase of the Co concentration.

Table 2: Variation of the microstrain ε and of the average size of the mosaic blocks *vs*. Co concentration (*x*)

x	ε	D (Å)	d_{AO} (Å)	d_{BO} (Å)
0.05	0.00055	567	2.564	1.959
0.10	0.00093	1022	2.562	1.958
0.15	0.00076	1285	2.560	1.956
0.20	0.00091	1643	2.559	1.956

- Microstrains have small values and show a **maximum** with Co concentration for x = 0.10.
- The average size of mosaic blocks increases with the Co concentration.
- The distance between A cations and oxygen and the distance between B cations and oxygen decreases with Co concentration.

Part 2:
Magnetism and transport characteristics

Magnetic measurements
(performed at NIRDTP Iasi, Romania)

- Magnetic measurements were performed on the $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites between 77 and 450 K, at various magnetic field intensities.
- Curie temperatures and the specific/molar magnetizations were obtained.
- For some samples a transition from spin-glass to ferromagnetic state was put in evidence.

Some results of magnetic measurements

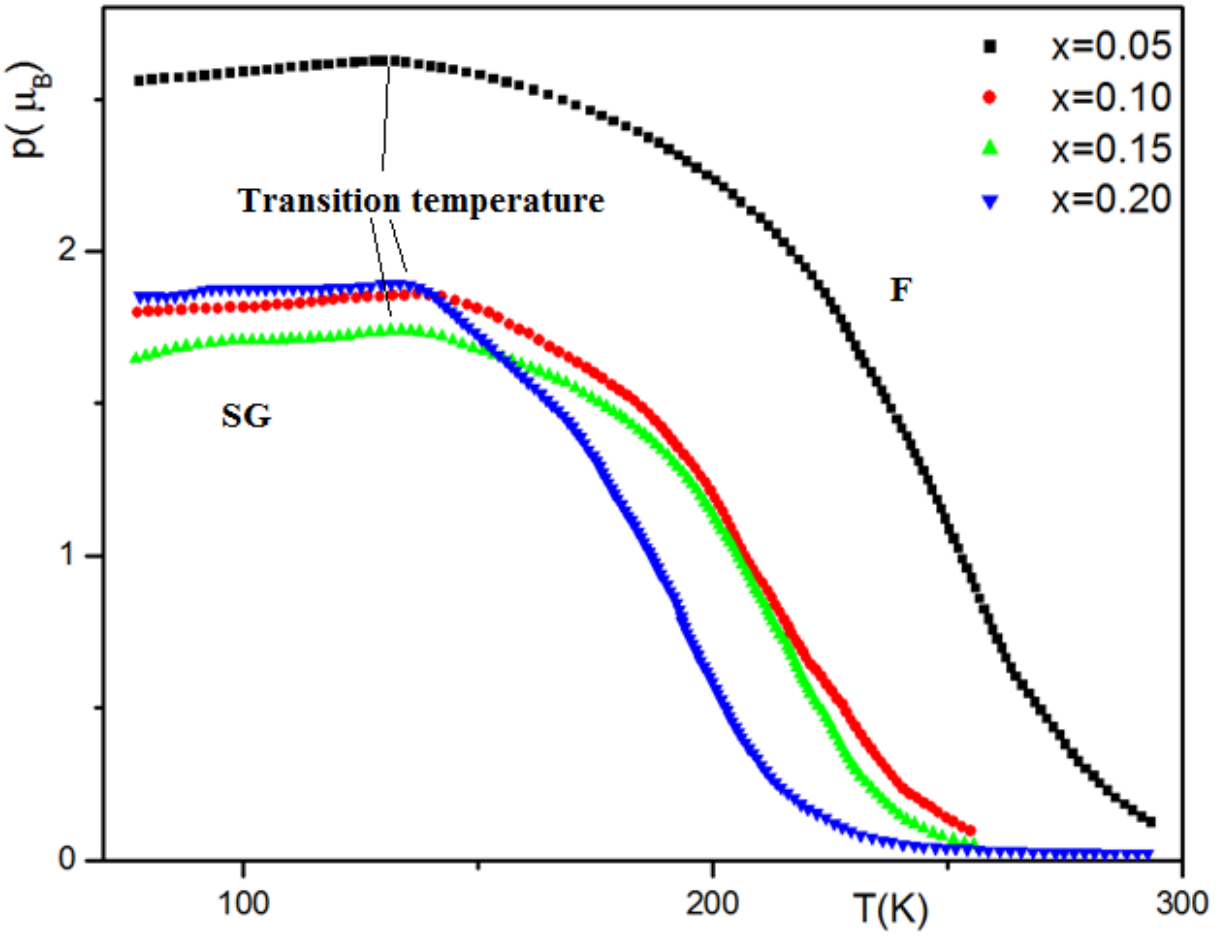


Figure 5

p represents the magnetization of a molecule in μ_B and T is the temperature of the sample

Resistance measurements
(performed at FLNP-JINR , Dubna, Russia)

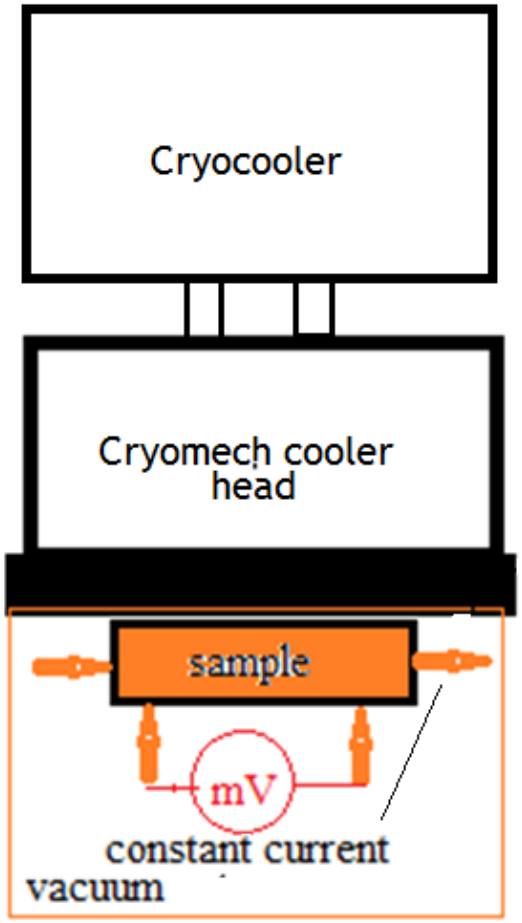


Figure 6 The principal scheme of installation for the determination of the resistance with temperature.

The resistance measurements were performed by four probes method. The samples can be cooled by using cryogenic installation to temperatures between 30 and 300 K.

The sample is located inside a room, evacuated with a vacuum pump. A constant current will pass through the sample. This current will be generated by a constant current source. The voltage droped by the sample will be measured using the nanovoltmeter.

Results of transport measurements

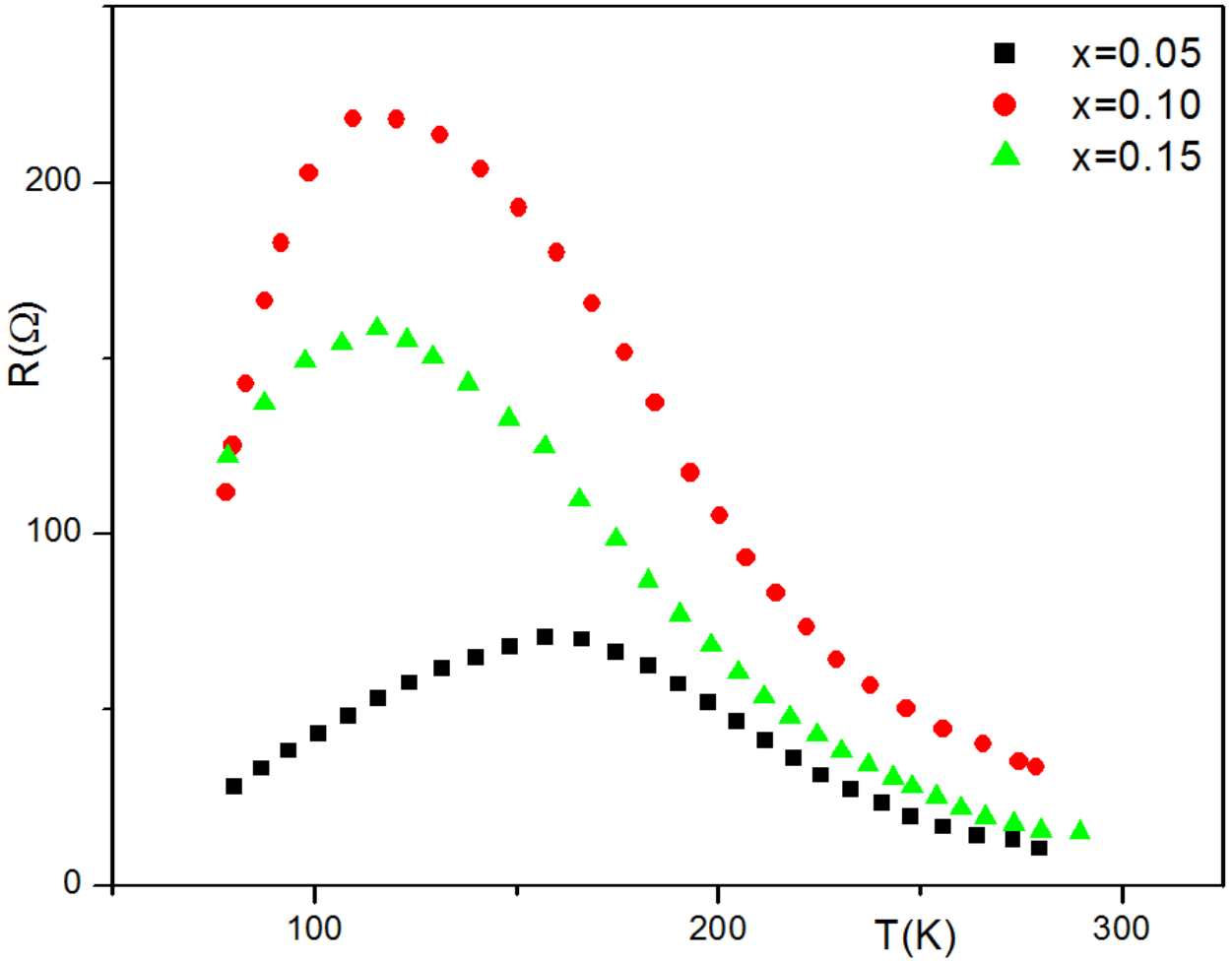


Figure 7 Variation of the resistance with the Co concentrations (x) in the absence of the magnetic field.

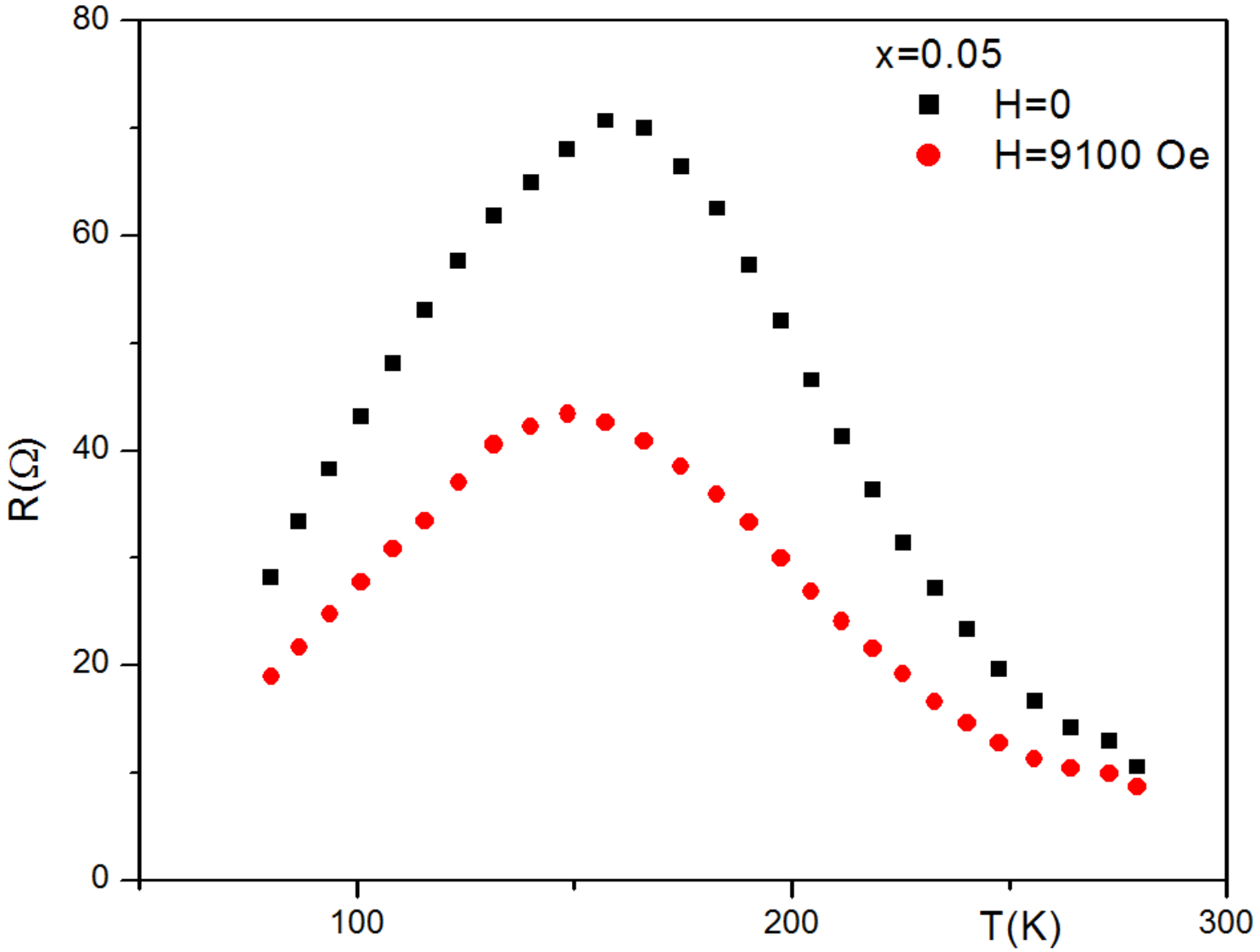


Figure 8 Variation of the resistance with the magnetic field intensity.

Conclusion

1) The structure of the obtained samples is characterized by space group Pnma. The unit cell volume decreases with the increase of Co concentration. We have attributed this behavior to the difference between crystalline radii of Co^{3+} (0.75 Å) and Mn^{3+} (0.785 Å).
2) Average size of the crystalline blocks increase with the Co concentration. The microstrains have small values, with a maximum corresponding to x = 0.10.
3) The variation of the magnetization with the temperature indicates the appearance of the spin glass state at temperature lower than 150 K. The Curie temperature decreases with the Co concentration, indicating a decrease of Mn-O-Mn interaction.
4) Transition temperature from the metallic to semiconductor/insulator state decreases with the increase with the Co concentration.

References

- "Transport phenomena in $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Cu_xO_3$ manganites" Mihail-Liviu Craus[1,2], Nicoleta Cornei [3], Ahmed Islamov[2] and Vasyl M. Garamus[4]
- http://www.ill.eu/sites/fullprof/
- www.flnr.jinr.ru
- Neutron Scattering, Thomas Brückel, Gernot Heger, Dieter Richter and Reiner Zorn, RWTH Aachen, University of Münster
- Magnetoresistive Perovskites: sinthesys, properties and applications, Mihail-Liviu Craus, Nicoleta Cornei, Mihai Lozovan, Viorel Dobrea, Iassy:Alfa, 2008
- An introduction to the program FullProf, Juan Rodríguez-Carvajal, Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay, 91191 Gif sur Yvette Cedex, FRANCE

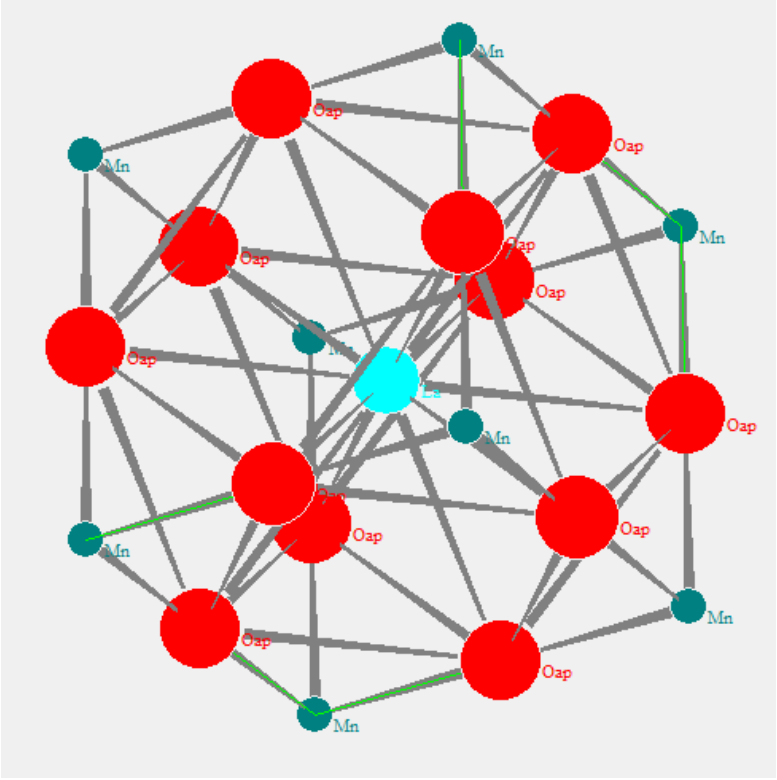
Palacký University
Olomouc

JOINT INSTITUTE
FOR NUCLEAR RESEARCH

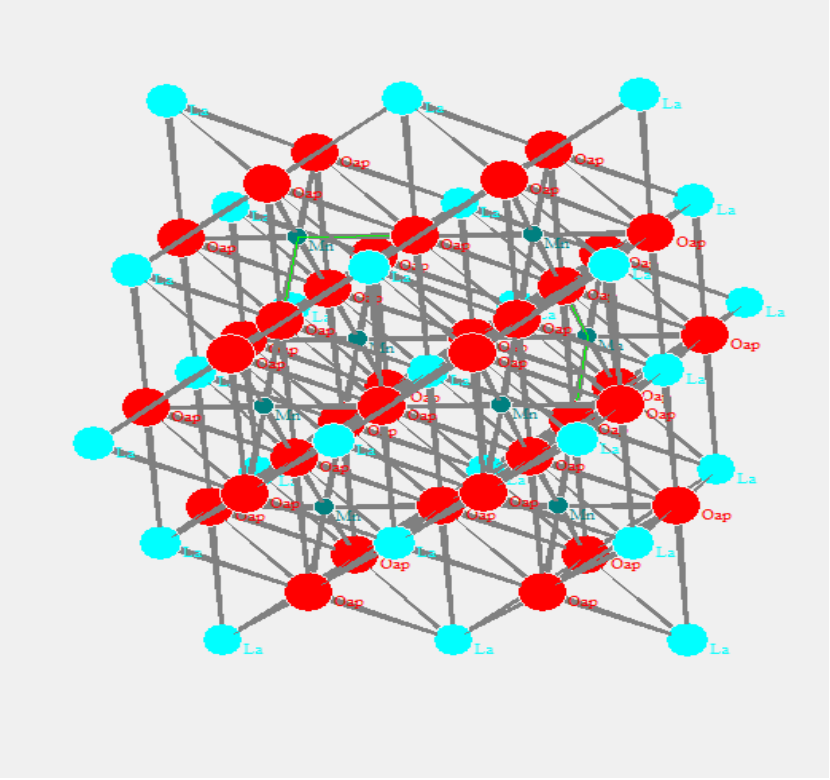
Thank you for your attention!

Unit cell of manganite

$La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$



Cubic unit cell



Cubic supper cell

FullProf Main Features

- **The program has been mainly developed for Rietveld analysis (structure profile refinement) of neutron** (nuclear and magnetic scattering) **or X-ray powder diffraction data** collected at constant or variable step in scattering angle 2θ

  • X-ray diffraction data: laboratory and synchrotron sources.

  • The scattering variable 2θ in degrees,

  • Background: fixed, refinable, adaptable, or with Fourier filtering.

  • Choice of peak shape for each phase: Gaussian, Lorentzian, modified Lorentzians, pseudo-Voigt, Pearson-VII, Thompson-Cox-Hastings (TCH) pseudo-Voigt, numerical, split pseudo-Voigt, convolution of a double exponential with a TCH pseudo-Voigt for TOF.

  • Multi-phase (up to 16 phases).

  • Absorption correction for a different geometries. Micro-absorption correction for Bragg-Brentano set-up.

FullProf Main Features

- Choice between automatic generation of hkl and/or symmetry operators and file given by user.
- Magnetic structure refinement (crystallographic and spherical representation of the magnetic moments).
- hkl-dependence of the position shifts of Bragg reflections for special kind of defects.
- Profile Matching. The full profile can be adjusted without prior knowledge of the structure (needs only good starting cell and profile parameters).
- Quantitative analysis without need of structure factor calculations.
- Chemical (distances and angles) and magnetic (magnetic moments) slack constraints. They can be generated automatically by the program.
- The instrumental resolution function (Voigt function) may be supplied in a file. A microstructural analysis is then performed.
- Neutron (or X-rays) powder patterns can be mixed with integrated intensities of X-rays (or neutron) from single crystal or powder data.
- Full Multi-pattern capabilities. The user may mix several powder diffraction patterns (eventually heterogeneous: X-rays, TOF neutrons, etc.) with total control of the weighting scheme.

Four probes method

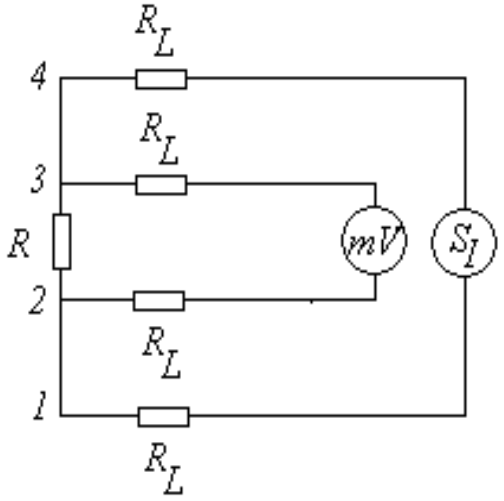


Figure 8

When the four probes method is used, current is supplied via a pair of connections through the current leads, 1 and 4 contacts, from constant current source, S_I (s. Fig.8). These generate a voltage drop across the impedance to be measured according to the Ohm law *V=R*I,* by using a milivoltmeter mV (s. Fig.8) . This current also generates a voltage drop across the wires themselves. To avoid including that in the measurement, a pair of **sense** connections (voltage leads) are made immediately adjacent to the target impedance.

The accuracy of the technique comes from the fact that almost no current flows in the sense wires, so the voltage drop *V=R I* is extremely low. It is conventional to arrange the sense wires as the inside pair, while the force wires are the outside pair. If the force and sense connections are exchanged, accuracy can be affected, because more of the lead resistance is included in the measurement. In some arrangements, the force wires are very large, compared to the sense wires which can be very small. If force and sense wires are exchanged at the instrument end, the sense wire could burn up from carrying the force current.

Magnetic measurements
(performed at NIRDTP Iasi, Romania)

With a vibrating sample magnetometer Foner type we can obtain information concerning:

- Variation of specific magnetization with the temperature and the magnetic field intensity;
- Magnetic phase transitions (from ferromagnetic to paramagnetic state; transition between two different ferromagnetic states; transition from spin glass to ferromagnetic state etc);
- Magnetic structure.

Part 2 : Magnetism and transport characteristics

- **Vibrating Sample Magnetometer** is a method of measurements used in research for the determination of the magnetic structures characteristics (specific magnetization, coercitive field, Curie temperature etc).
- The measured magnetic data allow to made a correlation between the crystalline and magnetic structure.
- **Four Probes Method** allow us to perform measurements of the resistance in a large range of temperatures, with minimum of errors.
- From variation of the resistance with the temperature we determined the transition from the metallic to insulator (semiconductor) state and their correlation with chemical composition.

The magnetic measurements were performed by using a Foner type magnetometer. One speaker put in vibration the sample in the middle of four coils (s. Fig.6). The coils signal is send to a lock-in amplifier, together with the signal from the reference coils(s. Fig. 6).

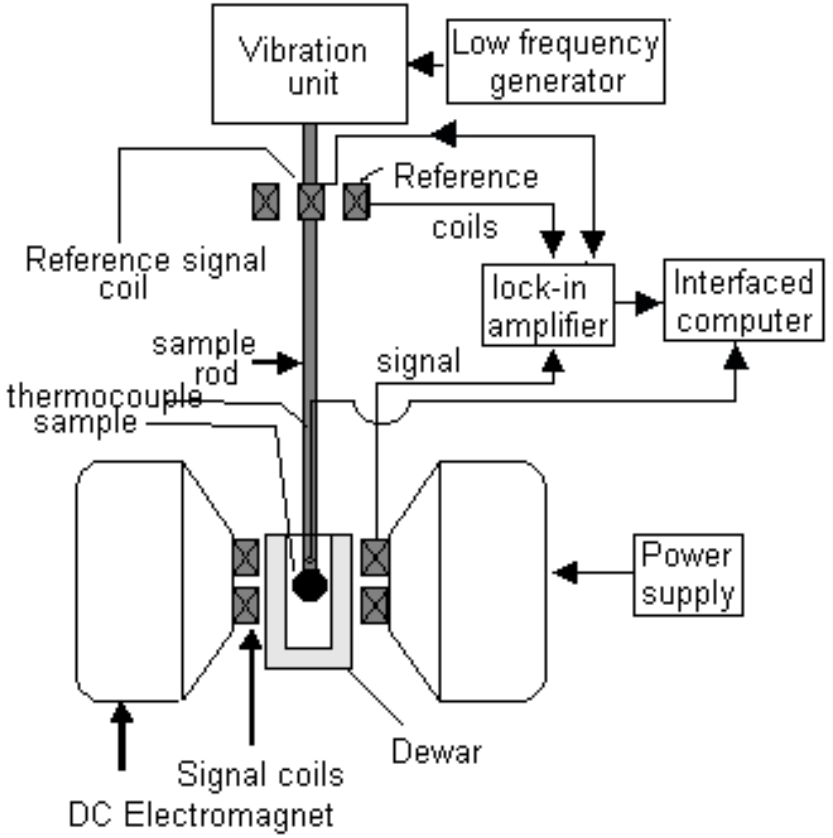


Figure 6 (NIRDTP Iasi Romania)

The difference signal is amplified and send to the reference signal coil. To change the sample temperature can use a Dewar (s. Fig.6) or a oven. The temperature was measured with a thermocouple. The magnetic field is applied with an electromagnet(s. Fig.6). To receive specific magnetization we used the relation:

$$\sigma = k \frac{U}{m}$$

where σ is the specific magnetization, U – the voltage drop across the coils signal, m – sample weight; k - a constant which can be obtained by using a standard.