



**KIRENSKY INSTITUTE
OF PHYSICS**



WORKSHOP
WORKSHOP
INTAS – Siberian Branch of the Russian Academy of Sciences
Scientific Cooperation on the Research Project
“NEW LAYERED 3d MATERIALS FOR SPINTRONICS”
“NEW LAYERED 3d MATERIALS FOR SPINTRONICS”
(Book of Abstracts)

March 20-23, 2007
March 20-23, 2007
Krasnoyarsk
Krasnoyarsk

L. V. Kirensky Institute of Physics SB RAS

ETH Zurich and Paul Scherrer Institute, Condensed Matter Research with Neutron and Muons Department

Institute of Physics of Polish Academy of Sciences

Institute Laue Langevin, Three–Axis Spectrometer Group

A. V. Nikolaev Institute of Inorganic Chemistry SB RAS, Chemistry Functional Materials Department

**Workshop INTAS – Siberian Branch of the Russian Academy of Sciences
Scientific Cooperation on the Research Project
“New Layered 3d-Materials for Spintronics ”,**

March 20–23, 2007

Krasnoyarsk, Russia

Local Organizing Committee

- **G. Petrakovskii – chairman of committee** e-mail: gap@iph.krasn.ru
- **N. Volkov** e-mail volk@iph.krasn.ru
- **G. Abramova – Secretary of the Organizing Committee** e-mail: agm@iph.krasn.ru
- **E. Bondareva – Assistant Administrator in International Contacts**
e-mail: mainoffice@iph.krasn.ru
- Address: L. V. Kirensky Institute of Physics SB RAS, 660036, Krasnoyarsk, Russia
Tel: +(3912)43-26-35
Fax: +(3912)43-26-35

WORKSHOP PROGRAM

20 March, Tuesday

- 10⁰⁰ – Chairman
G.Petrakovskii **Welcome to Krasnoyarsk.**
- 10³⁰ – J. Schefer **Magnetic structure investigations with neutrons using the instrumentation at SINQ and at ILL**
- 11⁰⁰ – N. Volkov **Mixed-valence manganese oxide $\text{Pb}_3\text{Mn}_7\text{O}_{15}$: structure, magnetic and dielectric properties**
- 11³⁰ – 12³⁰ Coffee-break
- 12³⁰ – V. Val'kov **Double exchange model in the problem of the colossal magnetoresistance manganites**
- 13⁰⁰ – I. Vasilyeva **Chemical aspect of layered compounds $\text{CuCr}_{1-x}(\text{V or Fe})_x\text{S}_2$ ($0 < x < 1.0$)**
- 14⁰⁰ – Welcome party

21 March, Wednesday

- 10⁰⁰ – M. Boehm **Determination of magnetic exchange interactions by inelastic neutron scattering on the example of CuB_2O_4**
- 10³⁰ – G.Petrakovskii **Orbital ordering**
- 11⁰⁰ – 12⁰⁰ Coffee-break
- 12⁰⁰ – G. Abramova **Physical properties and colossal magnetoresistance in 3d-sulfides**
- 12³⁰ – A. Vorotynov **Magnetic structure and magnetic interactions in terbium iron borate $\text{TbFe}_3(\text{BO}_3)_4$**
- 12³⁰ – 14⁰⁰ – Dinner
- 14³⁰ – Visiting L.V. Kirensky Institute of Physics SB RAS, Krasnoyarsk State University

22 March, Thursday

- 10⁰⁰ – V.I. Zinenko **Lattice dynamic and structure phase transition in $\text{La}_x\text{Ca}_{(1-x)}\text{MnO}_3$ ($x=0, \dots, 1$) crystals.**
- 10³⁰ – K. Patrin
- 11⁰⁰ – 12⁰⁰ Coffee-break

12⁰⁰ – Round table (Team tasks management to fulfill INTAS project)

13⁰⁰ – 14³⁰ – Dinner

15⁰⁰ – Excursion to the Krasnoyarsk city, Bobrovyi Log.

23 March, Friday

10⁰⁰ – H. Szhymszak

10³⁰ – V. Sokolov **Synthesis of powder $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ (M= V, Fe), preparation of polycrystal and crystal samples**

11⁰⁰ – V. Varnek **Use of mössbauer spectroscopy for determining the state of iron atoms in $\text{CuCr}_{0.7}\text{Fe}_{0.3}\text{S}_2$**

11³⁰ – 12⁰⁰ Workshop Closing

16⁰⁰ – Banquet

CONTENTS
(Abstracts are published in author's redaction)

J. Schefer	Magnetic structure investigations with neutrons using the instrumentation at SINQ and at ILL	6
N. Volkov	Mixed-valence manganese oxide $\text{Pb}_3\text{Mn}_7\text{O}_{15}$: structure, magnetic and dielectric properties	7
V. Val'kov	Double exchange model in the problem of the colossal magnetoresistance manganites	8
I. Vasilyeva	Chemical aspect of layered compounds $\text{CuCr}_{1-x}(\text{V or Fe})_x\text{S}_2$ ($0 < x < 1.0$)	9
M. Boehm	Determination of magnetic exchange interactions by inelastic neutron scattering on the example of CuB_2O_4	10
G. Petrakovskii	Orbital ordering	11
G. Abramova	Physical properties and colossal magnetoresistance in 3d-sulfides	12
A. Vorotynov	Magnetic structure and magnetic interactions in terbium iron borate $\text{TbFe}_3(\text{BO}_3)_4$	13
V. Zinenko	Lattice dynamic and structure phase transition in $\text{La}_x\text{Ca}_{(1-x)}\text{MnO}_3$ ($x=0, \dots, 1$) crystals.	14
K. Patrin		15
V. Sokolov	Synthesis of powder $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ ($\text{M} = \text{V, Fe}$), preparation of polycrystal and crystal samples	16
V. Varnek	Use of mössbauer spectroscopy for determining the state of iron atoms in $\text{CuCr}_{0.7}\text{Fe}_{0.3}\text{S}_2$	17
L. Mazalov	The study of CMR solid solutions by X-ray spectroscopy methods	18
H. Szhymsczak		19

MAGNETIC STRUCTURE INVESTIGATIONS WITH NEUTRONS USING THE INSTRUMENTATION AT SINQ AND AT ILL

J. Schefer¹, M. Boehm², B. Roessli¹, L. Keller¹, M. Janoschek³, P. Fischer¹, M. Medarde⁴, A. S. Wills⁵, B. Ouladdiaf², E. Lelèvre-Berna², G. A. Petrakovskii⁶, L. Bezmaternikh⁶, V. Temerov⁶ and D. Velikanov⁶

¹ *Laboratory for Neutron Scattering, ETH Zurich & Paul Scherrer Institut, CH-5232 Villigen, Switzerland, E-mail: Jurg.Schefer@psi.ch*

² *Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, Cedex 9, France*

³ *Physik Department E21, TU München, D-85748 Garching, Germany*

⁴ *Laboratory for Developments, Paul Scherrer Institute, CH-5232 Villigen PSI*

⁵ *Department of Chemistry, University College London, WC1H 0AJ London, United Kingdom*

⁶ *Institute of Physics, SB RAS, 660036 Krasnoyarsk, Russia*

We present the instrumentation operated by at PSI/SINQ and ILL which will be used in the Spintronics project. The instruments presented will be TriCS, TASP including the polarimetry option MUPAD, the powder instruments HRPT and DMC as well as the low temperature single crystal diffractometer D10 at ILL.

The potential of the instruments is outlined by presenting three systems studied. The first example is the magnetic ground-state of copper metaborate CuB_2O_4 , which has been investigated with unpolarized and polarized neutron scattering as well as Muon-spectroscopy at PSI (TASP, TriCS and MuSR instruments) and ILL (D10,D3) [1]. In this oxide, a phase transition to a commensurate weakly ferromagnetic state was found at $T_N=21$ K, followed by a second transition at $T^*=10$ K to an incommensurate magnetic structure. The second example is TbMnO_3 , an orthorhombic insulator where incommensurate spin order for temperature $T_N < 41$ K is accompanied by ferroelectric order for $T < 28$ K. In this compound, magnetic inversion symmetry breaking and ferroelectricity was observed by single crystal diffraction on TriCS [2]. The last example is simultaneous antiferromagnetic ordering of Fe^{3+} and Nd^{3+} studied in $\text{NdFe}_3(\text{}^{11}\text{B}\text{O}_3)_4$ [3].

Based on this examples, we will outline the possibilities and the expected results for the Spintronics project.

- 1 B. Roessli, J. Schefer, G. Petrakovskii, B. Ouladdiaf, M. Boehm, U. Staub, A. Vorontinov and L. Bezmaternikh, Formation of a Magnetic Soliton Lattice in CuB_2O_4 Metaborate, Physical Review Letters **86,9** (2001) 1885-1889
- 2 M. Kenzelmann, A.B. Harris, S. Jonas, C. Broholm, J. Schefer, S.B. Kim, C.L. Zhang, S.-W. Cheong, O.P. Vajk and J.W. Lynn Magnetic Inversion Symmetry Breaking and Ferroelectricity in TbMnO_3 Phys. Rev. Lett. **95**, 087206-1-087206-4 (2005)
- 3 P. Fischer, V. Pomjakushin, D. Sheptyakov, L. Keller, M. Janoschek¹, B. Roessli, J. Schefer, G. Petrakovskii, L. Bezmaternikh, V. Temerov and D. Velikanov Simultaneous antiferromagnetic Fe^{3+} and Nd^{3+} ordering in $\text{NdFe}_3(\text{}^{11}\text{B}\text{O}_3)_4$ J. Phys.: Condens. Matter **18** (2006) 7975–7989

MIXED-VALENCE MANGANESE OXIDE $Pb_3Mn_7O_{15}$: STRUCTURE, MAGNETIC AND DIELECTRIC PROPERTIES

N. Volkov¹†, G. Petrakovskii¹, K. Sablina¹, O. Bayukov¹, E. Eremin¹, D. Velikanov¹, A. Balaev¹,
A. Vasiliev¹, A. Bovina¹, P. Böni², and E. Clementyev³

¹ *L.V. Kirensky Institute of Physics SB RAS, 660036, Krasnoyarsk, Russia*

² *Physics Department E21, Technical University of Munich, D-85747 Garching, Germany*

³ *RFNC - Institute of Technical Physics, 456770 Snezhinsk, Russia*

† E-mail: volk@iph.krasn.ru

Currently novel materials based on manganese oxides with the mixed valence of manganese ions Mn^{3+}/Mn^{4+} are being intensively studied. Here we present and discuss the results of extensive study of the structural and magnetic properties of a $Pb_3Mn_7O_{15}$ single crystal. $Pb_3Mn_7O_{15}$ single crystals were grown using the flux method. The crystals obtained have the plate-hexagonal form with a size up to 40 mm in “diameter”. The $Pb_3Mn_7O_{15}$ crystal structure was determined from single-crystal x-ray diffraction patterns. All the reflections were indexed in the hexagonal $P6_3mcm$ space group with lattice parameters $a = 10.0287(4)$ Å and $c = 13.6137(6)$ Å. There are four formula units per unit cell. It should be noted that the $Pb_3Mn_7O_{15}$ crystal structure found by us coincides with that of a mineral known as zenzenite [1]. The observed minor differences in lattice parameters, bonding distances and angles are, apparently, related to the presence of Fe ions in the mineral. The chemical formula of the crystal is consistent with the presence of Mn cations in different valence states, with the two variants possible: the presence of Mn^{3+}/Mn^{4+} ions in a ratio 4:3 or Mn^{2+}/Mn^{4+} ions in a ratio 2:5. At present, the question about the valence state of the manganese ions remains open. The $Pb_3Mn_7O_{15}$ crystallographic structure has the pronounced layered origin that strongly influences the magnetic structure formation.

Magnetic properties of the crystal were studied using ac and dc magnetization measurements in a temperature range 2–900 K and magnetic fields up to 9 T. The study was supplied with specific-heat measurements. They suggest that some different magnetic phases can be distinguished in the temperature region of interest. The PM behavior is observed at high temperatures down to ~250 K. On further cooling, the short range correlations appear in the system, and the extensive antiferromagnetic clusters start forming at ~160 K. At 70 K the long range magnetic order is established, and low spontaneous magnetization is observed in all the ordered regions. At ~20 K one more magnetic transition occurs in the crystals, which can be related to reorientation of a magnetic moment due to the magnetic anisotropy variation with temperature. The analysis of exchange interactions in the framework of the indirect coupling model [2] allowed us to describe the exchange magnetic structure of the crystal, which represents ferrimagnetically ordered Mn layers coupled antiferromagnetically via a “bridging” Mn cation. The weak ferromagnetism of $Pb_3Mn_7O_{15}$ observed in the ordered region is believed to be of the Dzialoshinskii-Moriya type, with its origin being associated with anisotropic relativistic interactions.

It is well known that Pb ions reveal a tendency to high electrical polarizability in oxide compounds. This leads to the appearance of local dipoles, which can be finally ordered in ferroelectric or antiferroelectric fashion. A preliminary measurement of the complex dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$ suggests the appearance of ferroelectric properties. Specific features in the behavior of the dielectric constant are observed at temperatures where peculiarities of magnetic susceptibility appear. As a result, we suggest coexistence of the ferro(antiferro)-electric and magnetic ordering state, along with the coupling between the magnetic and ferro(antiferro)-electric subsystems in $Pb_3Mn_7O_{15}$.

1. D. Holtstam, B. Lindqvist, M. Johansson, R. Norrestam, *Canad. Mineral.* **29**, 347 (1991).
2. O.A. Bayukov, A.F. Savitskii, *Phys.stat.sol.(b)* **155**, 249 (1989).

DOUBLE EXCHANGE MODEL IN THE PROBLEM OF THE COLOSSAL MAGNETORESISTANCE MANGANITES

V.V. Val'kov

L.V. Kirensky Institute of Physics SB RAS, 660036, Krasnoyarsk, Russia
vvv@iph.krasn.ru

In this review we would like to discuss the main peculiarities of the so-called double exchange (DE) model. This model is actively used in the physics of manganites. The experimental data on transport in $\text{La}_{1-x}\text{B}_x\text{MnO}_3$ (B=Ca, Ba, Sr) is analyzed. The phase diagram and the temperature dependence of the resistivity in such materials are discussed.

To derive the expression for the effective Hamiltonian of the DE-model two approaches are used. In the first case the localized spins of the systems are considered as classical values. In the second case the effective Hamiltonian is obtained on the operator form of the perturbation theory when quantum aspects of localized spins are taken into account. Atomic representation is used for a description of the s-d- model in the regime of the strong coupling. The Hubbard operators are introduced on the basis of the eigenstates of the one-site Hamiltonian describing the exchange coupling between local spin and conduction electron spin [1,2]. In this representation the effective Hamiltonian H_{eff} of the system is derived on the basis of the unitary transformation. We will discuss the H_{eff} not only for the strong coupling regime of but also in the intermediate one.

Using effective Hamiltonian of the DE-model physical properties are analyzed in the framework of several approaches. One method is founded on a dynamic mean-field approximation. The second one is built upon numerical calculations.

In short form we would like to discuss limitations of the DE-model and questions of an orbital and charge ordering.

1. M.Sh.Erukhimov and S.G.Ovchinnikov, Phys.Stat.Sol. B **123**, 105 (1984).
2. S.G.Ovchinnikov, V.V.Val'kov. Hubbard Operators in the Theory of Strongly Correlated Electrons, Imperial College Press, 57 Shelton Street, Covent Garden, London WC2H 9HE, 2004.

CHEMICAL ASPECT OF LAYERED COMPOUNDS $\text{CuCr}_{1-x}(\text{V or Fe})_x\text{S}_2$ ($0 < x < 1.0$)

Vasilyeva I.G.

*Nikolaev Institute of Inorganic Chemistry, SB RAS
Ac. Lavrentyeva ave., 3, Novosibirsk, 630090 Russia
E-mail: kamarz@che.nsk.su*

In spite of the considerable current interest in the Van der Waals bonded transition metal dichalcogenides and their intercalations, the nature of intercalates for the group VI chalcogenides CrS_2 and CrSe_2 with Cu and Ag with general formula AMS_2 are yet less well studied and understood. Recently interest to unusual properties and a possibility to modify them by substitution process was resumed to use the compounds as spintronic materials. Some new papers on structure and physical properties of CuCrS_2 and $\text{Cu}_{1-x}\text{V}_x\text{S}_2$ have appeared with attempt to clarify the localized-delocalized behavior of 3d electrons of Cr metal leaving aside problems far from localized yet. However the existing always danger of the measurements being performed on ill-defined materials send us to cover the chemical aspect of the layered compounds $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$ and $\text{CuCr}_{1-x}\text{Fe}_x\text{S}_2$. The goal of the report is to show that such approach may provide the base for the correct interpretation of unusual properties of the compounds.

The report consists of three parts. In the first part structural types of the $\text{M}^{1+}\text{T}^{3+}\text{S}_2^{2-}$ compounds are considered going through the series Ti, V, Cr dichalcogenides to select the compounds isostructural to CuCrS_2 that is an infinite 2D intercalation compound where about one electron transferring to the host matrix ensures the stability of the slabs CrS_2 . The stability of known 2D intercalates with respect to changes in the amount of intercalate, composition and deformation of matrix layers due to doping reactions are analyzed to suggest the most credible defect models for the $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$ and $\text{CuCr}_{1-x}\text{Fe}_x\text{S}_2$ compounds taking into account anionic/cationic non-stoichiometry, the level of the filling van der Waals gaps, and nature of cationic disordering. The high probability to realize the defect states for $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$ and $\text{CuCr}_{1-x}\text{Fe}_x\text{S}_2$ compounds is shown.

The second section deals with synthetic chemistry taking account a metastable character of CrS_2 compound. Different solid state reactions are considered in the context of thermodynamics and kinetics (temperature, pressure of sulfur, duration of procedure, nature and state of starting products) to find the best way of preparation of these compounds. Integral analytical and x-ray powder techniques determining total chemical, phase composition and interlayer spacing are shown as incapable to explain the scattering observed in physical properties for compounds of identical composition prepared by different routes.

In the third part new principles and a specified approach to characterization of the layered compounds are developed. Attention focuses on techniques that are able to control spatial chemical inhomogeneity of the solids with high resolution. Advantages of differential dissolution method combined with ICP AE spectroscopy over classical techniques as EMPA, AES, EDXA, and ESCA are illustrated due to its ability to determine precisely without any requirements to sample form (powders, small crystals, pellets) real stoichiometry of the main phase as a function of the sample depth with resolution as 30\AA as well as amounts of impurity microphases. Our first results that the $\text{CuCr}_{1-x}\text{V}_x\text{S}_2$ and $\text{CuCr}_{1-x}\text{Fe}_x\text{S}_2$ compounds are considerably more complex than assumed by the average models are presented.

At the end a thesis that prerequisite for a thorough understanding of the physics of these complex structures is certainly an adequate chemical characterization revealing microscopic compositional anomalies in the solids will be covered.

DETERMINATION OF MAGNETIC EXCHANGE INTERACTIONS BY INELASTIC NEUTRON SCATTERING ON THE EXAMPLE OF CuB_2O_4

M. Boehm¹, J. Rasch^{1,2}, J. Schefer², B. Ouladdiaf¹, B. Roessli², L. Keller²,
L. Bezmaternikh³ and G.A. Petrakovskii³

¹*Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, Cedex 9, France.*

E-mail: boehm@ill.fr

²*Laboratory for Neutron Scattering, ETH Zurich & Paul Scherrer Institut, CH-5232 Villigen.*

³*Institute of Physics, SB RAS, 660036 Krasnoyarsk, Russia.*

In the framework of the common Spintronics project, the evaluation of the magnetic structures and interactions within the so-called task 4 implies the use of neutron three-axis spectroscopy. We want to present this well-established neutron scattering technique by means of the cold three-axis spectrometer IN14 at the ILL. We show the interest of this kind of instrument for the Spintronics project with the example of the exchange interactions in the complex copper-oxide system CuB_2O_4 , intensively studied both from the theoretical [1-4] as well as experimental point of view [5,6].

The analysis of the magnetic excitations by inelastic neutron scattering allows identifying the nature and the strength of magnetic interactions in single crystals. Using three-axis spectroscopy we can selectively explore dispersion relation in different crystallographic directions and explore the nature and anisotropy of different types of interactions involved to stabilize the magnetic ground-states. IN14 provides a technically challenging sample environment like dilution fridges (down to 50 mK), high field magnets (up to 15T) and neutron polarization techniques (standard spin-flip and neutron spherical polarimetry).

The spin dynamics in the insulating cuprate CuB_2O_4 is determined by the interplay of two magnetic Cu^{2+} subsystems, a so-called magnetic ‘cage’ with predominant 3d Heisenberg exchange and quasi 1d zig-zag chains. While the magnetic excitations of the cage are well understood by classical spin-wave excitations, some aspects of the weak dispersive, broadened zig-zag excitations remain still unclear. For a better understanding of the spin dynamics of the zig-zag chains and their influence on the cage, we performed a series of measurements as a function of temperature (down to 100 mK) and magnetic field (up to 6T).

- 1 S. Martynov, G. Petrakovskii, M. Boehm, B. Roessli and J. Kulda, *JMMM* **299** (2006), p. 75.
- 2 O. Bolsunovskaya, M. Popov, G. Petrakovskii, M. Boehm, B. Roessli, *JMMM* **300**, e392-e394 (2006).
- 3 S. Martynov, G. Petrakovskii and B. Roessli, *JMMM* **269** (2004), 106.
- 4 M. Boehm, S. Martynov, B. Roessli, G.A. Petrakovskii, J. Kulda, *JMMM* **250** (2002), 213.
- 5 B. Roessli, J. Schefer, G.A. Petrakovskii, B. Ouladdiaf, M. Boehm, U. Staub, A. Vorotinov and L. Bezmaternikh, *Phys. Rev. Lett.* **85** (2001), 1885.
- 6 M. Boehm, B. Roessli, J. Schefer, A. Wills, B. Ouladdiaf, B. Lelievre-Berna, U. Staub and G.A. Petrakovskii, *Phys. Rev. B* **68** (2003), 024405.

ORBITAL ORDERING

G. Petrakovskii

Institute of Physics SB RAS, Krasnoyarsk 660036, Russia

E-mail: gap@iph.krasn.ru

In the magnetic substances containing the ions with the orbital degeneracy, the orbital ordering may take place together with the spin ordering. This results to numerous physics effects, including the conductivity behavior of the compounds. Usually in such substances the lattice phase transition takes place with decreasing of symmetry (collective Jahn-Teller phase transition), the magnetic properties are more complicated, and the low energy branch in the spectrum of the elementary excitations may appears due to the transitions between the orbital states. The second mechanism of the orbital ordering is the double exchange interaction, when the decreasing of the energy of the virtual transitions of d-electron to the neighbor center depends on the mutual orientation of spins of these centers. Similar, at the orbital degeneracy the energy contribution depends both on magnetic structure and type of the orbital states of the neighbor centers which are occupied. So, the usual super-exchange interaction results both in the magnetic and orbital ordering and it determinates the magnetic and orbital structure of the ground state.

The electrical resistance of the manganese compound like $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.16 < x < 0.4$) at the magnetic phase transition from the high temperature paramagnetic state to the ferromagnetic state is decreased on the order of magnitude. With the double exchange interaction mechanism of the orbital ordering at one hand the orbital ordering depends on the spin ordering, and the orbital order changes the exchange interaction on the other hand. So, by changing of the magnetic state (for example, by external magnetic field) due to the mechanism of the orbital ordering it is possible to change the exchange interaction and the temperature of the magnetic ordering. This fact gives the strong dependence of the resistance on magnetic field (colossal magnetoresistance phenomena) near the magnetic phase transition point.

1. K.Kugel, D.Khomskii. UFN136,621(1982)
2. L.Gor'kov. UFN168,665(1998)
3. Y.Tokura.Rep.Progr.Phys.69,797(2006)

PHYSICAL PROPERTIES AND COLOSSAL MAGNETORESISTANCE IN 3d-SULFIDES

G. Abramova, G. Petrakovskiy, N. Volkov, O. Bajukov, A. Vorotynov,
D. Velikanov, N. Kiselev, A. Bovina, V. Vasiliev,
V. Sokolov¹, M. Boehm², R. Szymczak³, B. Roessli⁴

L.V. Kirensky Institute of Physics SB RAS, Russia

E-mail: agm@iph.krasn.ru

¹ *Nikolaev Institute of Inorganic Chemistry, Russia*

² *Institute Laue Langevin, France*

³ *Institute of Physics PAS, Warsaw, Poland*

⁴ *Paul Scherrer Institute, Switzerland*

The phenomenon of the colossal magnetoresistance (CMR) produces new opportunities for the solid state electronics [1]. Searching for and investigation of a new materials with CRM are the high-priority directions of the magnetism and solid state physics. We used the method of direct cation substitution in the 3d-monosulfides and layered 3d-sulfides as the technology for designing and synthesizing substances with qualitatively new physical–technical parameters [2]. For example, in the ceramic $Mn_{1-x}Fe_xS$ samples at $x=0.29$ the colossal magnetoresistance about – 450% was found at 50 K and the magnetic field 30 kOe [3]. In this report the some properties of the $Mn_{1-x}Fe_xS$ and $CuV_xCr_{1-x}S_2$ solid solutions in the range of 4.2-300 K are presented. The parent materials for $Mn_{1-x}Fe_xS$ and $CuV_xCr_{1-x}S_2$ solid solutions are the antiferromagnetic semiconductors MnS and CuCrS₂. The $Mn_{1-x}Fe_xS$ samples were investigated in two forms: ceramic and single-crystals. It was found that the Fe-substitution in the $Mn_{1-x}Fe_xS$ single crystals results in the decreasing of the cubic lattice parameter and the deformation of the octahedral sites. The lattice compression with increasing of X in the $Mn_{1-x}Fe_xS$ sulfides is accompanied with the resistance decreasing of 6-order of magnitude and the change of the magnetic order from antiferromagnetic to ferromagnetic one. The CuCrS₂ compound belongs to the layered double sulfides of 3d elements [3]. The double sulfides of 3d elements (for example, TiS₂, CrS₂, VS₂) can be used to create three-dimensional structures in which the intercalated atoms (for example Cu, Ag) form the distinguished layers in the lattice. This gives a method of growing a new type of multiplayer structures. We found that the solid solutions with the R3m rhombohedral structure are formed with the V-substitution in $CuV_xCr_{1-x}S_2$ system. With the temperature decreasing, the compounds with $x \sim 0.1$ undergo a sequence of phase transitions: structural transition at $T_S = 160$ K, electronic transition at $T_C \sim 95$ K, and magnetic transition at $T_{max} = 20$ K. Colossal magnetoresistance is observed for temperatures below 160 K and reaches a value of about 60% in a magnetic field 7 kOe near the electronic transition at $T_C \sim 95$ K.

1. G.A. Prinz, Physics Today, **48**, №4, 353 (1995); Flederling R., Kelm M., Reuseher G. Nature, **402**, 787 (1999); A-M Haghiri-Gosnet 1 and J-P Renard, J. Phys. D: Appl. Phys. **36**, R127(2003)
2. G. M. Abramova and G. A. Petrakovskii, Metal-insulator transition, magnetoresistance, and magnetic properties of 3d-sulfides (Review), Low Temperature Physics, **32**, 725 (2006).
3. J.A. Wilson, A.D. Yoffe. Adv. Phys. 18, 193 (1969)

MAGNETIC STRUCTURE AND MAGNETIC INTERACTIONS IN TERBIUM IRON BORATE $\text{TbFe}_3(\text{BO}_3)_4$

A. Vorotynov, C. Ritter¹, G. Petrakovskii, A. Balaev, V. Temerov, I. Gudim

L.V. Kirenskiĭ Institute of Physics, Siberian Branch of RAS, Krasnoyarsk, 660036 Russia

E-mail: sasa@iph.krasn.ru

¹ *Institute Laue-Langevin, Boite Postale 156, F-38042 Grenoble, France*

Borates of general formula $\text{RM}_3(\text{BO}_3)_4$ with R being a rare earth and $\text{M}=\text{Al, Ga, Sc, Cr, Fe}$ have recently been studied intensively due to the interesting optical properties shown by the Al compounds and the expected interesting magnetoelectric properties of the iron borates [1,2]. The combination of a strongly anisotropic nuclear structure with the presence of highly anisotropic magnetic rare earth ions characterizes these compounds and it was suspected to be at the origin of a magnetic behavior dominated by polarization and spin reorientation phenomena. The fact that all the information on the magnetic structure in the $\text{RFe}_3(\text{BO}_3)_4$ compounds is coming from macroscopic measurements motivated our study on $\text{TbFe}_3(\text{BO}_3)_4$ using the microscopic method of neutron diffraction. The Tb compound was chosen as the starting point of a more general study as Tb is not strongly absorbing (as e.g. Gd, Eu and Dy) and possesses normally a rather big magnetic moment easily seen in magnetic neutron diffraction. We have determined the nuclear and the magnetic structure of $\text{TbFe}_3(\text{BO}_3)_4$ as a function of temperature using neutron diffraction. A nuclear phase transition from R32 to P3_121 takes place at $T=192$ K. An antiferromagnetic coupling along the helicoidal chains of Fe atoms with a magnetic propagation vector $\kappa = 0\ 0\ \frac{1}{2}$ sets in at about 40 K. Within the ab-planes of the structure all Fe spins are parallel but antiparallel to the Tb spins which are as well antiferromagnetically ordered in c-direction. At the external magnetic field parallel to the c axis the metamagnetic transition occurs at $H=H_t$ with the parallel Tb spin orientation and spin-flop transition of Fe spins. At 2 K the magnetic moment values amount are about $\mu_{\text{Fe}} = 4.4\ \mu_{\text{B}}$ and $\mu_{\text{Tb}} = 8.6\ \mu_{\text{B}}$. Our study does confirm the polarization effect of the long-range ordered Fe-sublattice on the Tb spins. The detailed analysis of the temperature dependence of the magnetic moments shows that this polarization leads in the case of the Tb-compound to an immediately at T_N induced magnetic moment on the Tb-site. Starting at about 35 K the indirect Tb-Tb interactions become important and lead to an increasing of the Tb-sublattice magnetization uncoupled from the Fe-sublattice magnetization. The symmetry reduction from R32 to P3_121 at high temperatures does not seem to play any important influence on the magnetic structure formed: The two inequivalent Fe-sites behave similarly, and for the magnetic coupling decisive bond-lengths and bond-angles are nearly identical. Bond valence calculations give a valence of about +3 for both Fe-sites. The Fe-Fe distances within the two helicoidal chains along the c-direction are with $\text{Fe1-Fe1} = 3.170(6)\ \text{\AA}$ and $\text{Fe2-Fe2} = 3.186(6)\ \text{\AA}$ only different by 0.5% whereas in the Gd-compound this difference amounts to 0.9%. Further studies on the related compounds $\text{YFe}_3(\text{BO}_3)_4$, $\text{NdFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ are underway and will clarify further the role played by the rare earth sublattice, the interatomic bond distances and by the nuclear symmetry.

1. A. Brenier, C. Tu, Z. Zhu, B. Wu, *Appl. Phys. Lett.* **84**, 2034 (2004)
2. A.K. Zvezdin, S.S. Krotov, A.M. Kadomtseva, G.P. Vorob'ev, Y.F. Popov, A.P. Pytakov, L.N. Bezmaternykh, E. Popova, *JETP Lett.* **81**, 272 (2005)

LATTICE DYNAMIC AND STRUCTURE PHASE TRANSITION IN $\text{La}_x\text{Ca}_{(1-x)}\text{MnO}_3$ ($x=0,\dots,1$) CRYSTALS.

V.I. Zinenko, M.S. Pavlovsky

L.V. Kirensky Institute of Physics SB RAS

E-mail: zvi@iph.krasn.ru

The non-empirical calculations of static and dynamic properties of solid solution $\text{La}_x\text{Ca}_{(1-x)}\text{MnO}_3$ ($0 \leq x \leq 1$) with perovskite structure in cubic, rhombohedral and orthorhombic phases are presented. The microscopic model of ionic crystal, which taking into account deformability and polarizability of ions, was used for this calculation.

Unstable vibration modes were found in phonon spectrum of lattice in cubic phase, and these modes occupied phase space in whole Brillouine zone (Fig. 1). Eigenvectors of most unstable mode in boundary point R of Brillouine zone, which are related with displacements of oxygen ions, correspond to “tilt” MnO_6 octahedra. Condensation of one, two or three components of this mode results to tetrahedral, orthorhombic or rhombohedral structure distortions. Doubling perovskite unit cell, where whole MnO_6 octahedra are single out, are used for description of phase transition in local mode approximation. Parameters of model Hamiltonian were found and statistical properties are investigated by Monte-Carlo method. Calculated long-wave frequencies of lattice vibration in experimentally observed phase are in good agreement with experimental data.

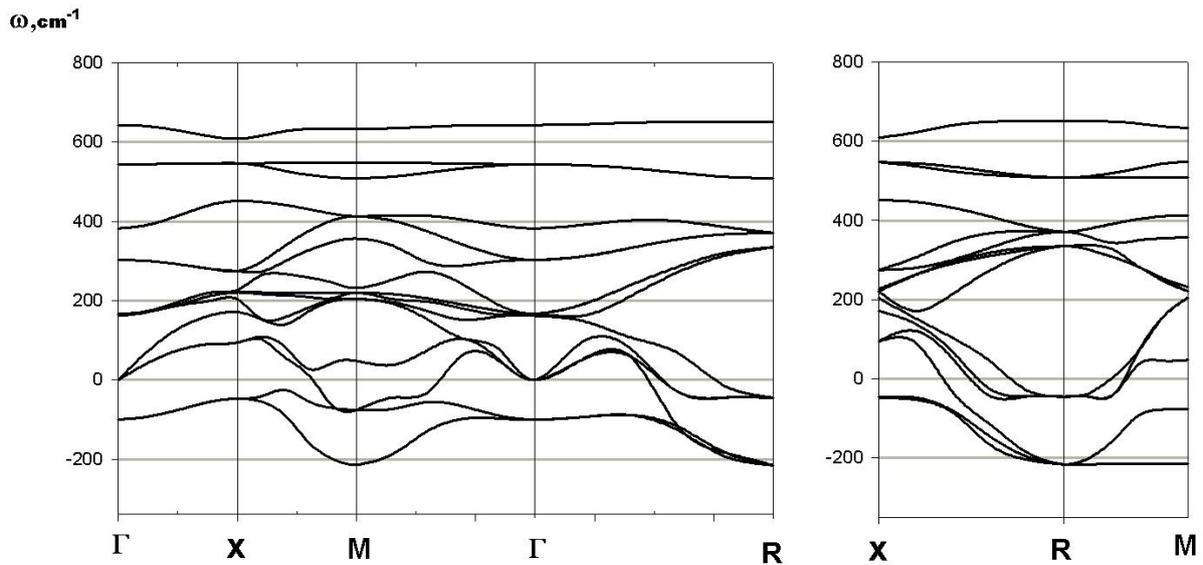


Fig. 1. Phonon spectra of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ crystal in cubic phase.

**(La_{0.4}Eu_{0.6})_{0.7}Pb_{0.3}MnO₃ SINGLE CRYSTAL:
MAGNETIC AND TRANSPORT PROPERTIES;
ELECTRON MAGNETIC RESONANCE MEASUREMENTS**

K. Patrin¹†, N. Volkov¹, G. Petrakovskii¹, P. Böni², E. Clementyev², K. Sablina¹, E. Eremin¹,
V. Vasiliev¹, A. Vasiliev¹, M. Molokeev¹

¹*L.V. Kirensky Institute of Physics SB RAS, Krasnoyarsk, 660036, Russia;*

²*Technical University of Munich, D-85747, Garching, Germany*

† E-mail: patrinkg@gmail.com

The study of magnetic and magnetotransport properties of the crystals of (La_{1-y}Eu_y)_{0.7}Pb_{0.3}MnO₃ system has been carried out. Eu ions enter the crystals being in trivalent nonmagnetic state. Europium ions possessing of smaller ionic radius in comparison with La ions, induce local distortions of Mn-O-Mn bonds in the system that cause random distribution of magnetic exchange interactions in magnitude and, probably, in sign. The competition of magnetic interactions leads to the appearance of the inhomogeneous magnetic state in the crystals. The enhancement of concentration of Eu ions results in decrease of the Curie temperature and broadening of the inhomogeneous magnetic state area. For all investigated compositions $y = 0 - 0.6$ the CMR effect is observed in the area where the inhomogeneous magnetic state exists. The effect is determined by different conductivity of the coexisting phases and by sensitivity of the inhomogeneous state to external magnetic field. Conventional magnetic and transport measurements have been supplemented by a magnetic resonance study. The experimental data support the model of two magnetic phases coexisting in the crystal volume. At a temperature T^* , which is well above Curie temperature T_C , ferromagnetic clusters appear in the sample. These ferromagnetic regions possess a higher conductivity in comparison with the paramagnetic background (majority phase). On cooling through T_C , the magnetization of the spatially confined ferromagnetic clusters of the minority phase freeze in random directions due to the frustrated exchange interactions at the phase boundaries with the ferromagnetic majority phase. Such a mixed state is responsible for the observed magnetic glassy behavior of the system. The frustration between antiferromagnetic and ferromagnetic exchange interactions results from a quenched disorder caused by the random chemical replacement of the perovskite A site of the manganite. A phase separation state comprised of two different ferromagnetic phases has been used to account for the colossal magnetoresistance phenomenon and the magnetic-field-driven nonlinear conduction found in the crystal.

SYNTHESIS of POWDER $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ (M= V, Fe), PREPARATION of POLYCRYSTAL and CRYSTAL SAMPLES

V.V.Sokolov, I.Yu.Filatova, Yu.M.Zelenin, A.Yu.Pichugin, Yu.A.Stonoga, O.V.Matveev

*Nikolaev Institute of Inorganic Chemistry SB RAS,
Ave. ac.Lavrentyuev, 3, Novosibirsk, 630090, Russia
e-mail: sokolov@che.nsk.su*

Initial reagents. CuO , Cu_2O , Cr_2O_3 , FeO , Fe_2O_3 , Fe , V_2O_3 , V_2O_5 of 99 - 99,9% purity, NH_4CNS - sulfidizing reagent, Ar, He gas – carriers.

Method of synthesis of powders: Synthesis of sulfides by use of NH_4CNS was proposed in NINC. Calculated mixture in glasscarbon boat is placed in quartz reactor with furnace (1). After removing of air by inert gas the heating is switch on and sulfidizing by products of NH_4CNS termolysis is began. Usually synthesis is ended after 2-3 time grinding at 680, 800, 870⁰ C . Ex-press control of synthesis – constant weight and results of XRD analysis.

Preparation of ceramic samples. It is used the equipment of vacuum recrystallization pressing (2). The conditions of preparation of samples: camera with pressform , fulfilled by prepared sulfide, is pumped up to 5×10^{-3} mm Hg; heating up to 800⁰ C; pressing up to 2 t/sm² ; time under pressure - 30 min; after removing of pressure - the 30⁰/min cooling.



1



3



2



4

Equipments: 1- for synthesis powder sulfides 2- for preparation of ceramics
3- for crystallization in sulphur vapor 4 for crystallization in inert gas

Growth of crystal. Crystallization from the melts of sulfides is carried out with use of induction heating in carbon or glasscarbon containers by low cooling of melt under sulphur vapor (3) or by drawing of reactor across inductor (4) with rate 0.5 -1 sm/h (under Ar gas).

Results. It is prepared the first powder samples of pure CuCrS_2 and $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ (M= V, Fe; x = 0-0.3), iron doped ceramics and crystal samples. Their properties are investigated.

USE OF MÖSSBAUER SPECTROSCOPY FOR DETERMINING THE STATE OF IRON ATOMS IN $\text{CuCr}_{0.7}\text{Fe}_{0.3}\text{S}_2$

V. A. Varnek, V. V. Sokolov, and I. Yu. Filatova

*A.V. Nikolaev Institute of Inorganic Chemistry,
Lavrentiev ave. 3, Novosibirsk, 630090, Russia
E-mail: varnek@che.nsk.su*

Mössbauer spectroscopy was used to study two $\text{CuCr}_{0.7}\text{Fe}_{0.3}\text{S}_2$ samples at 295 K. Sample I was ordinary polycrystalline powder, and sample II was obtained from I by additional recrystallization. The spectrum of I is a superposition of a broadened singlet ($\Gamma_e = 0.70$ mm/s) with an isomer shift $\delta = 0.45$ mm/s relative to $\alpha\text{-Fe}$ and a sextet characterized by the isomer shift $\delta = 0.26$ mm/s, zero-field quadrupole splitting, and effective magnetic field on the iron nuclei $H_{\text{eff}} = 335$ kOe. The relative area was 48% for the singlet and 52% for the sextet, indicating that the two samples have approximately equal amounts of iron atoms.

The spectrum of sample II contains the same singlet (81%) and a sextet with a zero isomer shift (19%) and $H_{\text{eff}} = 330$ kOe, which is due to metallic iron.

In the spectra of samples I and II, the singlet line is attributed to Fe^{3+} ions with octahedral surroundings composed of sulfur atoms, while the sextet in the spectrum of I is assigned to Fe^{3+} ions with tetrahedral surroundings of sulfur atoms.

These results suggest that sample I has iron ions substituted for Cr and Cu, while sample II has iron ions substituted for Cr alone (a small amount of iron is also present in sample II in the form of $\alpha\text{-Fe}$). Future measurements will be performed for samples containing the ^{57}Fe isotope in order to reduce the concentration of the iron impurity atoms to 1%. Work in this direction will allow us to explain the effects of the iron impurity atoms on the properties of sulfides and to optimize the synthetic conditions for the latter.

THE STUDY OF CMR SOLID SOLUTIONS BY X-RAY SPECTROSCOPY METHODS

L.N. Mazalov, lm@che.nsk.su, S.V. Trubina, svt@che.nsk.su

*Nikolaev Institute of Inorganic Chemistry, SB RAS
Ac. Lavrentyeva ave., 3, Novosibirsk, 630090 Russia*

The searching and studying of new materials with particular magnetic and electric properties are the priority directions of development of the magnetic and solid state physics. Spin-dependent electron transport mechanism and correlation of magnetic and electric properties of the magnetic semiconductor solid solutions do not clarify at now [1].

XPS method allows studying electron density distribution on atoms of compounds; to determine oxidation level of atoms; to spy on possible channels of spin density transfer as a result of cationic substitution.

X-ray emission (XES) and absorption (XANES and EXAFS) atomic spectra allow to determine the structure of valence and conduction bands of compounds and to find out the changes in the electron structure at cationic substitutions. Absorption spectra allow studying the space structure of nearest coordination spheres around investigated atom with the increasing of substitution extent. The exploration of X-ray spectra at different temperature (room, liquid nitrogen, helium) allows studying compounds at different phase.

At present time row investigations of CMR solid solutions (CMR – colossal magnetic resistance) by X-ray high energy methods were carried out.

XPS spectra: $C1s$; $O1s$; $S2p_{1/2,3/2}$; $Cu2p_{1/2,3/2}$; $La3d_{3/2,5/2}$; $Cr2p_{1/2,3/2}$; $V2p_{1/2,3/2}$; $Mo3d_{3/2,5/2}$; $Ce3d_{3/2,5/2}$; $Gd4d_{3/2,5/2}$, valence bands are obtained. XES spectra: CuL_{α} ; SK_{α} ; SK_{β} are obtained. XANES spectra: KCu ; KCr ; KMo are obtained.

Table 2. Bond energy of core level electrons (eV) taking into account recharging.

compounds	Cl_s (norm.)	$O1s$	reference	Ce $3d_{5/2}$	reference	Mo $3d_{5/2}$	reference	Gd $4d_{5/2}$	reference
Ce_6MoO_{15}	284,8	529,8 531,9	Углев-ды~532 $Ce_2Mo_4O_{15}$ -530,3	881,8	Ce-883,5 $Ce_2Mo_4O_{15}$ - 882,28 Ce_2O_3 -883,3 CeO_2 -882,2	232,5	Mo-228,0 $Ce_2Mo_4O_{15}$ -232,55 Mo_2C -228,3 MoO -228,3 MoO_2 -229,8 MoO_3 -232,6	-	Gd-141,55 Gd_2O_3 -142,8
$Ce_{6-x}Gd_xMoO_{15-\delta}$ $x=1,0$	284,8	530,1 532,7	Ce_2O_3 -529,7 CeO_2 -529,2 Gd_2O_3 -531 MoO -530,5 MoO_2 -530,4 MoO_3 -530,8	881,7		232,9	143,5		
$Ce_{6-x}Gd_xMoO_{15-\delta}$ $x=1,8$	284,8	529,8 532,6		881,3		232,7	143,1		

compounds	Cl_s (norm.)	$O1s$	reference	La $3d_{5/2}$	reference	Cu $2p_{3/2}$	reference	S $2p_{3/2}$	reference	V $2p_{3/2}$	reference
$LaSCuO$	284,8	531,4	La_2O_3 -530,0 Cu_2O -530,6 CuO -529,9 Na_2SO_3 -531,2	834,9 838,1	La-835,9 La_2O_3 -834,0 LaH_3 -838,8	931,8	160,7 168,7	S-163,9 SO_2 -167,8 CuS -162,1 Cu_2S -161,8 $CuSO_4$ -168,8 VS-163,5 Cr_2S_3 -162,7	521,0	V-512,5 V_2O_3 -516,1 V_2O_4 -516,2 V_2O_5 -517,4 VO_2 -516,3 VS-513,9	
$CuV_{0,05}Cr_{0,95}S_2$	284,8	531,5		Cr $2p_{3/2}$	reference	932,5 934,8					
$CuV_{0,1}Cr_{0,9}S_2$	284,8	531,2		576,0	Cr-574,2 Cr_2O_3 -576,5 CrO_2 -576,3 CrO_3 -579,2 Cr_2S_3 -575,1 $CrCuO_2$ -576,4 $CuCr_2O_4$ -577,1	932,1 934	161,3				

H. Szymczak

