

Charles University in Prague
Faculty of Mathematics and Physics

AGH University of Science and Technology
Faculty of Physics and Applied Computer Science



DOCTORAL THESIS

Vít Procházka

Study of cobaltites and manganites by NMR and EXAFS

Department of Low Temperature Physics
Department of Solid State Physics

Supervisors: prof. RNDr. Helena Štěpánková, CSc.
and prof. dr hab. Czesław Kapusta

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Název práce: Studium kobaltitů a manganitů pomocí NMR a EXAFS

Autor: Vít Procházka

Školitelé: prof. RNDr. Helena Štěpánková, CSc.

a prof. dr hab. Czesław Kapusta

Školící pracoviště: Katedra fyziky nízkých teplot, MFF UK

a Katedra Fyziky Ciała Stałego, WFiS AGH.

e-mail školitele: stepanko@mbox.troja.mff.cuni.cz

kapusta@agh.edu.pl

Abstrakt : Tato disertační práce je věnována studiu fyzikálních vlastností manganitů a kobaltitů s perovskitovou strukturou. Ke studiu byla použita kombinace makroskopických (měření hysterzních smyček, magnetické susceptibility a práškové difrakce) a mikroskopických metod (NMR a EXAFS), která umožňuje komplexní pohled na magnetické a nábojové uspořádání přechodových kovů ve zkoumaných materiálech. Práce předkládá nové poznatky, které byly rovněž publikovány v mezinárodních časopisech. Hlavními výsledky jsou určení a upřesnění parametrů okolí kationtů kobaltu a manganu a jejich spinového uspořádání pro jednotlivé oxidační stavy ve feromagnetické struktuře studovaných látek.

Klíčová slova: manganity, kobaltity, perovskity, EXAFS, NMR

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and prof. dr hab. Czesław Kapusta

Department: Department of Low Temperature Physics, MFF UK

and Department of Solid State Physics, WFiS AGH.

Supervisors e-mails : stepanko@mbox.troja.mff.cuni.cz

kapusta@agh.edu.pl

Abstract : This Thesis is devoted to a study of physical properties of manganites and cobaltites with perovskite structure. Combination of macroscopic (magnetization measurements and X-ray powder diffraction) and microscopic (NMR and EXAFS) methods was applied in order to get a complex and detailed view on the charge and magnetic ordering of transition metals ions in the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ solid solutions. The Thesis presents new results which were published in international journals. The main result is the determination of details of Mn and Co local environments and the spin arrangement of their individual oxidation states in the ferrimagnetic structure of the compounds studied.

Keywords: manganites, cobaltites, perovskite, EXAFS, NMR

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In Prague August 6, 2009

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Contents

1	Introduction	6
2	Perovskites	9
2.1	Structural properties	11
2.2	Electronic properties	12
2.3	Jahn-Teller distortion	14
2.4	Magnetic interactions	15
2.5	Phase separation	16
2.6	Magnetic and transport properties	16
3	EXAFS	20
3.1	Basic principles of EXAFS	21
3.2	Experimental setup	23
4	EXAFS data elaboration	25
4.1	Pre-edge substraction	26
4.2	Edge step	26
4.3	Free atom background removal	27
4.4	FEFF calculations	29
4.5	Fitting procedure	31
4.6	Path parameters	33
5	Nuclear magnetic resonance	34
5.1	Basic principle	34
5.2	Electric quadrupolar resonance	36
5.3	Interaction of nucleus with electric and magnetic field	39
5.4	Formulation of Bloch equations	41
5.5	Pulse solution of Bloch equations	42
5.6	NMR in magnetically ordered materials	47

<i>CONTENTS</i>	5
6 NMR spectrometer	49
6.1 Description of spectrometer construction	49
7 NMR technique and developed modifications for broad line measurements	53
7.1 Principles of NMR measurement	55
7.1.1 Telegraphic equation	55
7.1.2 Probe head principles, impedance matching	58
7.2 Broad line measurement	60
7.3 Procedures for broad band measurements	61
7.3.1 Calibration and correction of transmitter section	62
7.3.2 Calibration and correction of receiver section	64
7.4 Example of measured spectra	65
8 Software for NMR data elaboration	67
9 Characterization of samples studied	70
9.1 Sample preparation	70
9.2 X-ray diffraction	72
9.3 Magnetization measurements	72
10 EXAFS results and discussion	82
10.1 Absorption spectra	82
10.2 χ functions	86
10.3 Results of the fitting procedures	89
10.3.1 Co:K edge results	92
10.3.2 Mn:K edge results	93
10.4 Discussion of EXAFS results	93
11 NMR results and discussion	98
11.1 LaMnO_3	99
11.2 $\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$	100
11.3 $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$	104
11.4 $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$	104
11.5 $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$	109
11.6 $\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$	117
11.7 Influence of cobalt doping on the NMR spectra	118
11.8 Discussion	121
12 Summary and conclusions	124
Literature	126

Chapter 1

Introduction

Manganites and cobaltites studied in the Thesis belong to a wide family of perovskite materials. Perovskites are oxides described by general formula ABO_3 , where A is a divalent alkali earth or trivalent rare earth and B is a $3d$ transition metal. In the 50ies of the last century many interesting electric and magnetic properties and phenomena were observed in perovskites. The most spectacular one is the colossal magnetoresistance (CMR) which is observed in perovskites with manganese as a transition metal. Colossal magnetoresistance is promising for a large number of possible applications. Magnetic and electronic properties in this family of materials are strongly interconnected due to the same origin which is a result of interactions of transition metals $3d$ electrons. The spin, electric charge and lattice degrees of freedom are strongly coupled and it results in very unique and intriguing properties. Many different ground states such as diamagnetic insulator, antiferromagnetic insulator, paramagnetic metal, ferromagnetic insulator and ferromagnetic metal can be realized in these materials.

With substituting a trivalent cation on A site by a divalent cation, part of $3d$ transition metals on a B site changes their valence state and a mixture of $3d$ metal cations with different valences appears in the material. This has an influence on magnetic, electrical and structural properties, so that they can be effectively controlled by doping. Similar effect on the $3d$ metal valence state can be achieved by controlling oxygen nonstoichiometry.

This work is focused on perovskites where the A site is occupied by lanthanum and the B site is occupied by manganese or cobalt (manganites or cobaltites). In order to study physical properties and phenomena in these compounds we combined macroscopic and microscopic methods. For macroscopic characterization of the samples X-ray powder diffraction and magnetization measurements were carried out. The first microscopic method employed in this Thesis is the Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy which is based on X-ray absorption measurements. EXAFS is a powerful tool for studying the local environment

of a specific element in the material. The second microscopic method used in this work is Nuclear Magnetic Resonance (NMR). It is a nondestructive local probe, element selective method which has been often successfully employed in material research. The NMR method is sensitive to the electronic shell configuration of specific atoms and isotopes and gives information on magnetic and electric hyperfine fields of atom on individual structural and magnetic sites. NMR is useful also for determination of coexistence of two or more different valence states of atom. These two complementary methods provide an interesting and detailed view on materials studied.

NMR studies of magnetically ordered solid states materials (like manganites and cobaltites) create several problems for the experiment. One of the most important issue is a large width of spectral lines and a broad spectral range. To solve these problems a specific methodological approach in NMR measurements has to be undertaken. Such approach is proposed and presented in this work.

The NMR and EXAFS results are combined and analyzed together with X-ray diffraction measurements and magnetization measurements. Combination of local and macroscopic methods gives us a unique opportunity to observe and study these materials. We observed a change of interatomic distances with doping, increase of coercive field with doping and influence of preparation method on macroscopic magnetic properties. We also determined ferrimagnetic character of specific compounds by NMR in external magnetic field.

In the chapter 2 a current knowledge of manganese perovskites properties is briefly presented.

Chapters 3 and 4 introduces the EXAFS method: basic physical principles, experimental setup and analysis are described.

Chapter 5 is a theoretical introduction to NMR method. NMR phenomenon is explained and basics of pulse NMR experiments are presented. Chapter 6 describes Bruker broad band pulse NMR spectrometer which was used for NMR measurements.

In chapter 7 experimental aspects of NMR measurements in a wide frequency range are presented together with a new approach, that we developed, to carry out NMR experiments for broad frequency swept spectra.

Chapter 8 includes description of new software which was developed in order to analyze NMR experiments of magnetically ordered solids and broad lines in general. The software was created especially for evaluation of broad lines which are observed in manganites and cobaltites, but it also provides procedures and tools for high resolution NMR spectra analysis.

Chapter 9 contains information about studied samples. Methods of preparation and the conditions of preparation processes are reported. This chapter includes also X-ray diffraction measurements and results of SQUID experiments.

Measurements and results of the EXAFS experiment are presented in chapter 10.

NMR results are shown in chapter 11. This chapter includes analysis of frequency swept spectra and measurements of relaxation times. NMR frequency swept spectra in external magnetic fields measured for selected samples are presented.

Summary and conclusions are presented in the chapter 12.

Chapter 2

Perovskites

Perovskites are oxides which can be described with a formula ABO_3 , where A is an alkali earth (Ca, Sr, Ba, ...) or a rare earth (La, Gd, Pr, Sm, ...) and B is a 3d transition metal (Mn, Fe, Co, Ti, ...). In perovskite materials the spin, electrical charge and lattice degrees of freedom are strongly coupled which is a source of complex and unusual properties. The compounds where the B site is occupied by manganese and cobalt are usually called manganites or cobaltites, respectively. They have been intensively studied in the last decades. Large interest was devoted mainly to mixed valence manganites, where the A site is occupied by 3+ cations which are substituted with 2+ cations. When the A site is partly occupied by a 3+ cation of a rare earth and partly by a divalent alkali earth cation the resulting change of the electric charge on the A site is compensated by manganese cations on the B site, i.e. part of manganese cations change their valence state from 3+ to 4+. Mixing of valence states can be also introduced by oxygen nonstoichiometry, [Topf1997], [Ritt1997].

Manganites with different element on the A site have been studied using a large number of physical methods. In the studies of manganese perovskites the NMR technique was successfully employed and it provided insight into the micro-, meso- or nanoscopic properties. Measurements of magnetization, resistivity, thermoelectric power, susceptibility and NMR measurements on $Pr_{0.65}Ba_{0.35}MnO_3$ and $Pr_{0.65}Ca_{0.21}Sr_{0.14}MnO_3$ single crystals are presented in [Savo2000a]. For both compounds authors have observed the phase separation into ferromagnetic and paramagnetic regions at temperatures close to T_C . Also for $Ca_{1-x}Pr_xMnO_3$ compound which was studied in [Savo2000b] the phase separation was observed, in the antiferromagnetic matrix ferromagnetic regions were found. NMR results for $Pr_{0.5}Sr_{0.5}MnO_3$ compound have been presented in [Allo2000]. NMR spectra were measured in the external magnetic field and two spectral lines were observed and assigned to inner core and the outer surface layers of the ferromagnetic clusters which are located in the antiferromagnetic matrix, no signal from antiferromagnetically ordered matrix

was detected for this material [Allo2000]. A. A. Livesay studied the Fermi surface in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ which shows larger colossal magnetoresistance effect [Live1999]. Magnetic coupling of the phase separated (ferromagnetic insulating and ferromagnetic metallic regions) $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has been studied in [Dai2001]. In articles [Kapu2000], [Savo2001], [Savo2003], [Shim2004], [Oate2005], [Ribi2007] the effect of substitution of La^{3+} with divalent cations has been studied.

Several papers with EXAFS and XANES studies of perovskite materials were published during the last decade. Monesi et al. [Mone2005], [Rion2006] studied LaMnO_3 and CaMnO_3 by means of XANES and EXAFS, Hass et al. evaluated the inter atomic distances in LaCoO_3 , [Hass2004]. In [Melo2006] EXAFS investigation of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ is reported.

Cobaltites with mixed valence have been also studied in the last years. Many different experimental methods which provide information on a microscopic and macroscopic level have been employed to study their structural magnetic and electronic properties. Kenjiro Muta and co-authors presented measurements of magnetic, electronic and calorimetric properties on $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ in comparison with $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, [Muta2002]. The $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ compound was also investigated by means of NMR in [Kuhn2003], [Hoch2004a] and [Hoch2004b].

Doping on the B site drastically changes properties of compounds and therefore the study of doping can help to understand the processes and interactions responsible for magnetic and charge ordering. Compounds with substitution for manganese cations were studied very rarely with the NMR method [Sono1992], [Nish1995] and additionally the published spectra covered a limited spectral range around 300 MHz. In [Sanc2006] EXAFS and XANES results on $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ for $x > 0.6$ are presented and in [Kyon2003] EXAFS results on $\text{LaCo}_{0.5}\text{Ni}_{0.5}\text{O}_3$ are shown.

There are only a few NMR publications on cobaltites. Field swept NMR spectra of $\text{La}_4\text{Co}_3\text{O}_{10}$ in the range of 3.5–6.5 T, [Miya2002]. Diamagnetic perovskite LaCoO_3 was studied by NMR also. Itoh and coauthors published magnetic field swept NMR spectra of LaCoO_3 measured at 40 MHz in the range of 5.5–7.5 T where an evident quadrupolar splitting can be observed, [Itou1995a]. Itoh's results were confirmed by [Koba2000]. Kuhns and coauthors observed broad NMR spectral lines of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with x from 0.4 to 1 in the range 50–250 MHz. The authors assigned them to Co in ferromagnetic and spin glass regions, [Kuhn2003]. Consistent results with [Kuhn2003] were published by Itoh and Natori, where authors measured NMR spectra of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with $0.2 \leq x \leq 0.5$, [Itou1995b].

Tsuda published NMR spectrum of ^{59}Co in cobalt ferrite ferrimagnetic spinel, which consists of number of lines in the range 260–600 MHz, [Tsud1974]. Latter on, Kovtun published ^{59}Co NMR spectrum of cobalt ferrite also, which consists of two regions of spectral lines, first in the range 340–380 MHz which was attributed to Co^{2+} and second in the range 560–600 MHz attributed to Co^{3+} , [Kovt1982].

This work is focused on samples from the series $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ prepared using

different methods.

2.1 Structural properties

Crystal structure of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds depends on the composition. Compounds with $x > 0.6$ crystallize in a rhombohedral structure with space group $R\bar{3}c$ while compounds with $x < 0.6$ crystallize in a orthorhombic structure with space group $Pbnm$, [Autr2005]. For compounds with $x = 0.6$ a mixture of two phases, orthorhombic and rhombohedral in ratio of 60% orthorhombic and 40% rhombohedral phase was observed [Autr2005].

For both structures the transition metal (Me) is placed inside the oxygen octahedron and this octahedron is in the center of a cube formed by La cations (see Figure 2.1). In Figures 2.2, 2.3 rhombohedral structure with a space group $R\bar{3}c$ and orthorhombic structure of perovskite with a space group $Pbnm$ are shown.

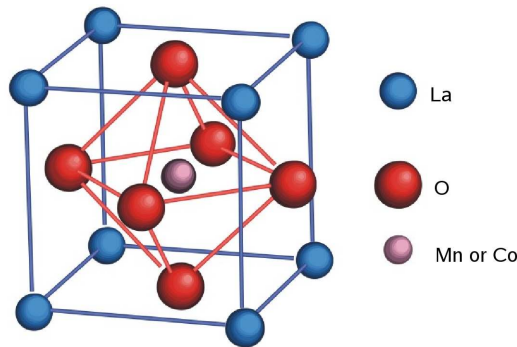


Figure 2.1: Perovskite structure.

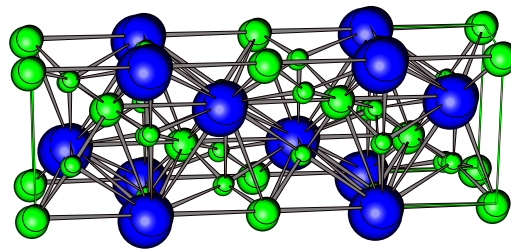


Figure 2.2: Rhombohedral structure with space group $R\bar{3}c$ of compounds with $x > 0.6$, blue ball - La, small green ball - oxygen, big green ball - Me.

For rhombohedral structure oxygen ions form an ideal octahedron (all Me-O bonds have the same length) while for orthorhombic structure the octahedron is distorted due to the Jahn-Teller effect and three different Me-O bond lengths are

observed. A large drop of the unit cell volume between both structures was reported for $x = 0.6$ compound in [Autr2005]. In Figure 2.4 the dependence of lattice parameters on x is plotted, [Autr2005].

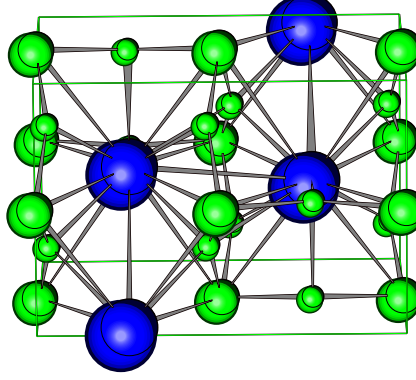


Figure 2.3: Orthorhombic structure with space group $Pbnm$ of compounds with $x < 0.6$, blue ball - La, small green ball - oxygen, big green ball - Me.

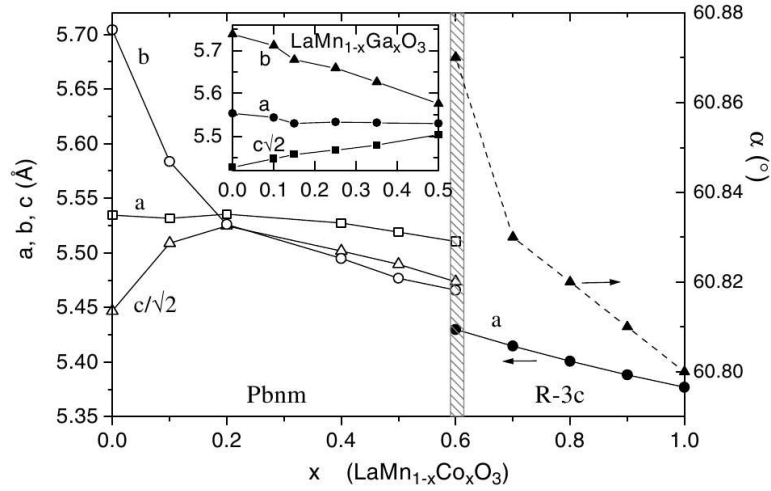


Figure 2.4: Dependence of lattice parameters on Co content in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ series, [Autr2005].

2.2 Electronic properties

Mn and Co are transition metals with valence shell formed also by $3d$ electrons. In the case of free atoms or ions and a negligible spin-orbit interaction the $3d$ orbits are $(2L + 1)(2S + 1)$ degenerated. This situation changes when Mn or Co cations are bound in a solid state material on specific positions in a crystal lattice. In the

presence of a crystal field the orbital degeneracy can be removed and the $3d$ levels are split.

Crystal field theory shows that the splitting of $3d$ energy levels depends strongly on the symmetry of the crystallographic site. As the crystal field is produced by the electric charge distribution around $3d$ metal, the symmetry of the crystal field is given by the symmetry of the lattice site.

In perovskites $3d$ metals (at B site) are coordinated by six oxygens. In the following text, only the octahedral symmetry of the crystal field will be discussed.

Let's define a coordination system xyz which is connected to the oxygen octahedron. The $3d$ orbitals denoted as $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ point directly toward the oxygens (the shapes of $3d$ orbitals are shown in the Figure 2.5). Other three orbitals ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$) are directed between oxygens. According to the crystal field theory the energies of $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ orbitals are higher than those of the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ orbitals. The lower energy levels, i.e. $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ are called t_{2g} and the higher energy levels i.e. $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ are called e_g , see Figure 2.6.

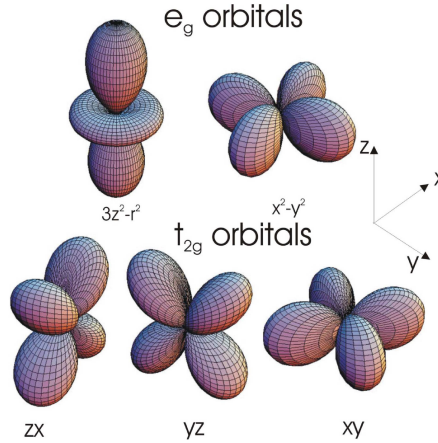


Figure 2.5: Angular wave functions of the e_g and t_{2g} orbitals.

With filling these orbitals with electrons one can obtain different spin states of Me ions. For example Co cations can have valence states $2+$, $3+$, $4+$ [Park1997]. In oxygen octahedron, depending on composition, strength of the crystal field, external conditions etc. [Good1961], for example Co^{3+} can exist in three different spin states i.e. in a low spin state (LS) with $L=0$, intermediate state (IS) with $L = 1$ and in a high spin state (HS) with $L = 2$, [Autr2005], [Siko2006].

The situation of manganese cations is similar to cobalt and manganese can exist also in different valence states ($2+$, $3+$, $4+$) [Good1961] with different spins.

2.3 Jahn-Teller distortion

$3d$ energy levels of cations of transition metals surrounded by oxygens creating octahedron are split by the crystal field into two levels, double degenerated e_g level and triple degenerated t_{2g} level. Jahn-Teller theorem says that systems with degenerated orbital energy ground levels are usually unstable and there is a tendency to lower the symmetry and to remove the degeneracy. Therefore, systems with transition metals in octahedral surrounding and degenerated energy levels exhibit spontaneous distortion of octahedron and a lowering of the crystal field symmetry which is accompanied with splitting of energy levels, [Krup1969]. This effect is called Jahn-Teller effect and Jahn-Teller distortion.

Mn^{3+} is a typical example of ion with strong distortion of local surrounding caused by the Jahn-Teller effect [Mitc1997], [Rodr1998], [Ento1999]. In oxides the Mn^{3+} ion is usually surrounded by six oxygens forming an octahedron. The Mn^{3+} ion has the electron configuration $3d^4$. The $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals are oriented towards surrounding oxygen ions, xy orbital lies around the xy plane, while the $3d_{3z^2-r^2}$ orbital is aligned along the z -axis. When, for example, the $3d_{3z^2-r^2}$ orbital is unoccupied the nucleus of the transition metal is not shielded from the ions along the z -axis direction and the oxygen octahedron is distorted due to electrostatic interaction and undergoes a compression along the z -axis direction. Analogously, if the $3d_{x^2-y^2}$ electron is missing, the oxygen octahedron is elongated in the z direction.

The Jahn-Teller effect is typically an order of magnitude smaller than the crystal field splitting energy. One of possible modes of the Jahn-Teller distortion is presented in Figure 2.6. In the presence of the Jahn-Teller distortion the e_g orbitals have different energies, which leads to many interesting phenomena like orbital ordering in manganese perovskites.

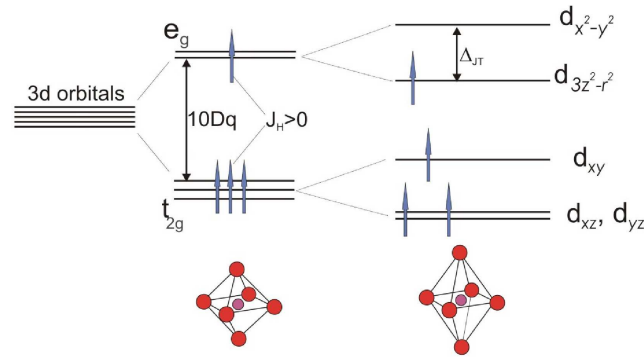


Figure 2.6: Scheme of energy levels of $3d$ ion in the crystal field, splitting of e_g and t_{2g} caused by Jahn-Teller effect.

2.4 Magnetic interactions

For understanding the physics related to manganese perovskites it is also essential to introduce possible magnetic interactions, which can occur between Mn and Co ions, i.e. the super-exchange (SE) and double exchange (DE) interactions. Both of them are indirect exchange interactions mediated by the oxygen, which is located between two Mn cations.

Superexchange interaction is an indirect magnetic coupling occurring in ionic solids between two magnetic ions of the same valence through the occupied oxygen $2p$ orbital. The distance between the magnetic ions is too large for direct exchange interaction. The SE interaction is a virtual exchange between electrons of magnetic ions with electrons from the same $2p$ orbital of oxygen, which have antiparallel spins according to Pauli's exclusion principle. Therefore the orientation of spins of magnetic ions is also antiparallel and leads to antiferromagnetic coupling. The SE interaction can lead to ferromagnetic coupling, this happens when electrons from magnetic ions interact with electrons from different oxygen orbitals [Good1955]. The superexchange mechanism is schematically shown in the Figure 2.7.

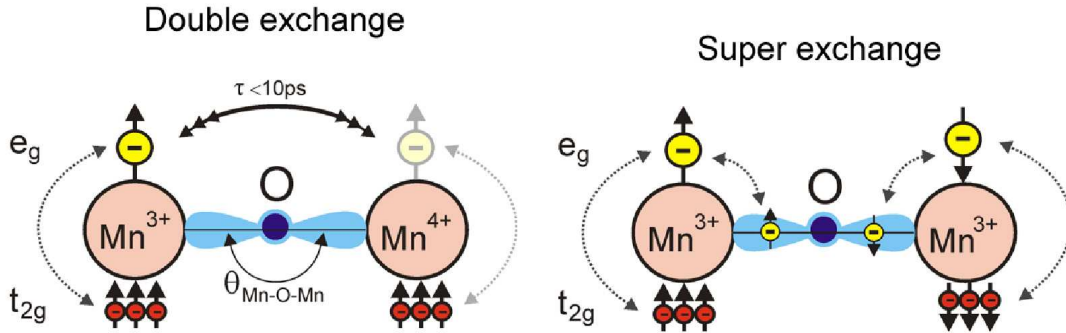


Figure 2.7: Schematic diagram of the double exchange (DE) and super exchange (SE) interactions mechanism.

Double exchange (DE) interaction is a magnetic coupling of two cations also via an oxygen orbitals, but the mechanism is different than in the case of SE interaction. The electron hops from $3d$ shell of one magnetic cation (e.g. manganese) to $2p$ orbital of oxygen from which one electron simultaneously hops to $3d$ shell of a second magnetic cation. This hopping occurs with preservation of the spin sign, therefore the DE leads to ferromagnetic order of magnetic cations [Zene1951a], [Zene1951b], [Ueha1999]. Hopping electrons are responsible for metallic properties. The mean time of hopping is around 10 ps, One electron has a nonzero probability to occur in $3d$ orbitals of both transition metal cations. The hopping is allowed only if the Hund's rules are fulfilled. This interaction is observed for example in the $LaMn_{0.8}Co_{0.2}O_3$ compound, when $Mn^{3+}-O-Mn^{4+}$ bonding angle is close to 180° . Since the hopping

is very fast it is difficult to detect electron only at one of manganese cations and for example in the NMR spectra only the averaged state is observed.

2.5 Phase separation

Strong competition between the DE, SE and electron-phonon interactions in manganites and cobaltites results in a large number of possible types of magnetic (paramagnetic, ferromagnetic, antiferromagnetic, canted antiferromagnetic) and electronic (metallic, insulating) phases which can be realized.

Ferromagnetic metallic phase can coexist with ferromagnetic insulating or antiferromagnetic insulating phases in manganese or cobalt perovskites. When we take into account possibility of charge ordering of Mn^{3+} and Mn^{4+} ions and orbital ordering of $3d$ orbitals the number of physical parameters, which have influence on the observed physical properties of manganites and cobaltites is very high.

First observations of phase coexistence in manganese perovskites date to 1950s and were concluded from neutron diffraction measurements, but nowadays imaging techniques provide much more detailed information on the nature and length scales of these phases. The first experiment with imaging technique (transmission electron microscopy) revealed coexistence of a ferromagnetic metallic phase and charge ordered insulating phase in compounds $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ [Ueha1999]. The phase separation problem has recently been studied with many other techniques.

Also NMR was used to study electronic phase separation in manganese perovskites. First such results were presented in [Allo1997], [Papa1997], [Rena1999], [Kapu2000]. Phase separation is pronounced by distinct spectral lines in the frequency swept NMR spectra. Resonances around 320 MHz or above 400 MHz are assigned to Mn^{4+} and Mn^{3+} cations in the ferromagnetic insulating phase. Signals between 250–290 MHz are assigned to the resonance of Mn^{4+} cations in the antiferromagnetic insulating phase. The resonance around 370–380 MHz belongs to manganese ions with averaged valence (between $3+$ and $4+$) resulting from the ferromagnetic coupling due to the DE interaction [Mats1970]. Observation of this resonance indicates that the characteristic time of electron hopping due to the DE interaction is shorter than the difference in precession periods of the nuclear magnetic moment in the two ionic states, i.e. it is shorter than 10^{-9}s .

2.6 Magnetic and transport properties

The compound $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ has been studied since 50s of the previous century. Magnetic, properties of the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds were described by Goodenough [Good1961], [Good1955]. They depend strongly on the cobalt content in

the compound. $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ exhibits nearly linear change of saturation magnetization for $0.2 < x < 0.7$. Authors conclude that only Mn contribute to the saturation, while the Co ions are in low spin state. According to Goodenough the ferromagnetism in the Co doped LaMnO_3 is caused by superexchange interaction of $\text{Mn}^{3+}-\text{Mn}^{3+}$.

G.H. Jonker assigned the ferromagnetic ordering to the $\text{Mn}^{4+}-\text{Co}^{2+}$ positive magnetic interaction, [Jonk1966]. Jonker also confirmed the Goodenough's results on saturation magnetization and discussed possibilities of Co^{2+} and Co^{3+} coexistence, $\text{Mn}^{4+}-\text{Co}^{2+}$ arrangement together with possibility of Co^{3+} being in HS state.

Recently the magnetic and magnetotransport properties of the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds have been systematically studied by Troyanchuk, [Troy2000]. LaMnO_3 compound is an insulator and antiferromagnet. In one plane there is ferromagnetic ordering of Mn magnetic moments, but two planes are antiferromagnetically coupled. Néel temperature of LaMnO_3 is around 140 K [Troy2000]. LaCoO_3 compound is a diamagnetic insulator. In [Troy2000] authors reported changing of the magnetic state from antiferromagnet for LaMnO_3 to ferromagnet for compounds with the $x < 0.6$ at low temperatures. The result is in agreement with [Good1961]. The highest spontaneous magnetization was found for sample with $x = 0.2$ and it decreases on both sides from $x = 0.2$. Compounds from Co rich region of the phase diagram exhibit diamagnetic properties with transition to paramagnetic state around 100 K, which is explain by change of the spin state, from LS to HS or IS state.

Co ions in diamagnetic LaCoO_3 (rhombohedral structure) are in valence state 3+ with LS state, however, at temperature close to 100 K the transition to paramagnetic state takes place with forming mixture of Co in a HS state and LS state, [Sena1995]. In recent literature the paramagnetic state is associated with an IS state of Co ions, [Koro1996], [Sait1997].

Valence of manganese in antiferromagnetic LaMnO_3 is 3+ and manganese cations are in HS state with the electron configuration $3d^4$ and $S = 2$.

The appearance of the ferromagnetic ordering in the mixture of LaMnO_3 and LaCoO_3 is frequently discussed. However the origin of the ordering was not successively explain, since the problem is rather complex. Park reports a tendency to the $\text{Co}^{2+}-\text{Mn}^{4+}$ arrangement rather than $\text{Mn}^{3+}-\text{Co}^{3+}$ distribution. The $\text{Co}^{2+}-\text{Mn}^{4+}$ charge redistribution leads to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ mixture which induced ferromagnetic coupling of Mn^{3+} , Mn^{4+} pairs by double exchange mechanism, [Park1997]. On the other hand van Elp [Elp1999] is in opposition to the Park opinion, that the Co is in rigid 2+ state. He follow Jonkers conclusion and claim the Co has mixed valency assuming the Co^{2+} and Co^{3+} states.

$\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds are insulators at low temperatures for all values of x , with transition to metallic state at higher temperatures. These compounds also exhibit magnetoresistance effect [Troy2000]. In [Troy2000] the influence of annealing process is described. Also drastic influence of oxygen non-stoichiometry on physical

properties was reported in the literature. Even a small deviation from the stoichiometry for LaMnO_3 results in presence of Mn^{4+} cations and ferromagnetic ordering of the compound.

Another important question is the magnetic state of Co^{3+} which can reach the LS, IS, HS states. The spin states of Mn and Co cations are discussed in the [Joy2000]. Author reports an existence of two different phases in the $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ compound differing by origin of magnetic coupling and temperature T_c (observed in ZFC curves). Phase with higher T_c (around 225 K) is according to [Joy2000] ferromagnetically ordered due to the positive superexchange of $\text{Mn}^{3+}(\text{HS})\text{--Co}^{3+}(\text{LS})$, while the phase with lower T_c (around 151 K) is formed by $\text{Mn}^{4+}\text{--Co}^{2+}$ coupling. Two magnetic transitions were observed in a compound with $x = 0.4$, [Autr2005], which authors assigned to two regions in the material. The single crystal investigation of magnetic properties of LaMnO_3 are presented in [Koro2004], authors measured magnetic susceptibility along different crystallographical directions, and the direction of the b -axis was found as an easy magnetization direction. The single crystals of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ were studied by Barilo, [Bari2003]. Barilo analyzed the magnetization data assuming phase separation into ferromagnetic clusters embedded into an antiferromagnetic matrix. Phase separation is mentioned also in [Dass2003].

The electronic and magnetic properties of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ have been studied by theoretical calculations based on the density functions methods [Zhon1999]. Recently, results of investigations using XANES [Siko2006] have been published which brought new information about valence states of Mn and Co cations. The authors report the mean valence state Mn and Co with respect to the Co content in the sample. The ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ was determined by using XANES and magnetic data, see Figure 2.8.

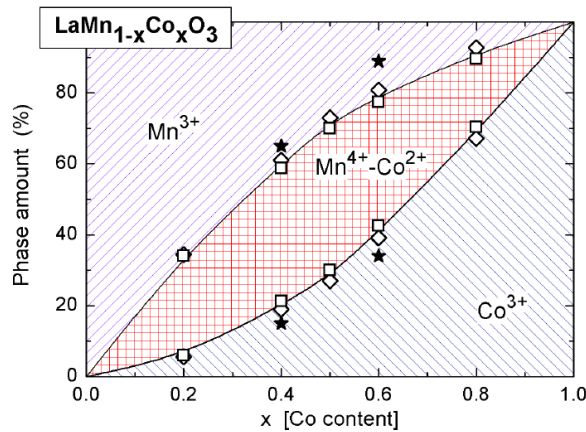


Figure 2.8: Diagram of transition metal content in the sample $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ derived from data published in [Siko2006].

Moreover, Sikora in [Siko2008] reported the average spin evolution on the basis of high resolution X-ray emission spectroscopy data concluding presence of Mn^{4+} , Mn^{3+} HS and Co^{2+} and Co^{3+} (LS).

The question about the ferromagnetic ordering and explanation of two phases arrangement in material close to 0.5–0.5 composition of Mn and Co is still open. The influence of thermal treatment during preparation process on the phase arrangement and properties of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds have been discussed in [Troy2000].

Chapter 3

EXAFS

EXAFS (Extended X-ray Absorption Fine Structure) is a spectroscopic method providing structural information about sample by means of the analysis of X-ray absorption spectrum [Theo1986]. It allows determining the chemical environment of a probe atom in terms of number and type of its neighbors, inter-atomic distance and structural disorder. The synchrotron X-rays are needed for the EXAFS experiment. Charged particle with a velocity close to the velocity of light moving on the circular trajectory emits radiation in the direction tangent to the motion. This occurs in bending magnets, undulators or wigglers in a synchrotron storage ring.

Synchrotron consists of several parts such as LINAC, BOOSTER and a storage ring. In general, a LINAC and BOOSTER accelerate particles bearing electric charge (usually electrons/positrons or protons) and then accelerated particles are delivered to the storage ring. They are kept in their trajectory in the synchrotron ring by bending magnets. In bending magnets the synchrotron radiation is emitted, however, such radiation is not very intense and it is suitable only for some experiments. For those which require high intensity of the radiation, special insertion devices such as undulators and wigglers are placed in straight sections of the storage ring. They produce very intense synchrotron radiation by multiple periodic bending of the charge particle trajectory. The electromagnetic radiation emitted by undulator or wiggler cover broad energy range, [Rohl2004], [Mulh1999].

This broad energy range and high intensity of synchrotron radiation resulted in fast development in the field of experimental methods which use electromagnetic radiation for material studies. With increasing the power and energy of the synchrotron radiation many possible applications have been found and various experimental methods which found very broad use in Biology, Chemistry, Medicine and in Physics have been developed.

Experimental methods using synchrotron radiation differ in terms of energy, polarization and brilliance of the radiation beam etc. which is required. Methods exploiting the synchrotron radiation can study phenomena related to the crystal

structure, magnetism, electronic structure and many others. In this work we use the Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The experimental details of the method are presented in this chapter.

3.1 Basic principles of EXAFS

In the absorption spectroscopy experiment the absorption of monochromatic synchrotron radiation by the system under study is measured as a function of energy. This process is described by the absorption law:

$$\mu(E) = \ln \left(\frac{I_1}{I_2} \right) \quad (3.1)$$

where I_1 is the X-ray radiation intensity of incident beam and I_2 is a radiation intensity of transmitted beam, $\mu(E)$ is an absorption coefficient. The energy dependence of the absorption $\mu(E)$ is schematically shown in Figure 3.1.

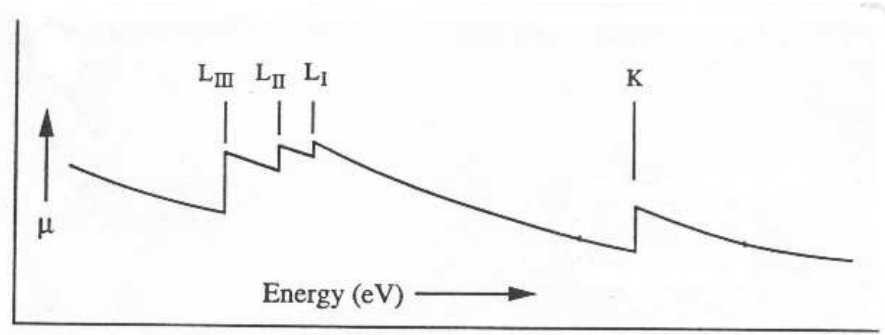


Figure 3.1: Energy dependence of the absorption coefficient. The individual absorption edges are marked.

In the energy dependence of $\mu(E)$ three main features can be observed. First, the $\mu(E)$ decrease with the energy increase. This is mainly due to the photoelectric defect. Second, in the $\mu(E)$ the step increase (absorption edge) occur at certain energies. The last, the oscillations of $\mu(E)$ (not shown in Fig. 3.1) can be observed above the absorption edge, with the amplitude of few percent of the edge step, [Zaja2007], [Siko2002]. The outstanding steps in $\mu(E)$ (absorption edge) are connected with crossing of the incoming radiation energy the difference between core level (energy of 1s (K-shell), 2s (L-shell) or 2p (M-shell) electrons) and Fermi energy. Since the energy of incident X-ray crosses the energy difference between core level and Fermi level the absorption $\mu(E)$ increase rapidly, incoming X-ray photons energy is absorbed, core electron is excited above Fermi level and reach a nonzero kinetic energy. EXAFS method is based on effect of photoelectron emission by absorption

of photon by core electrons (see Figure 3.2) Emitted photoelectron propagates in the material crystal lattice or molecule) and interacts with surrounding atoms. The forward propagating wave associated with the photoelectron scatters on surrounding atoms. The forward propagating wave and the back-scattered photoelectron wave interferes. Results in interference pattern shows up as a modulation of the measured absorption coefficient, thereby causing the oscillation of absorption coefficient called EXAFS spectra (see Figure 3.3). These oscillations are analyzed by simulations and best-fit procedures to obtain the structural parameters, i.e. distances between atoms and Debye-Waller factor.

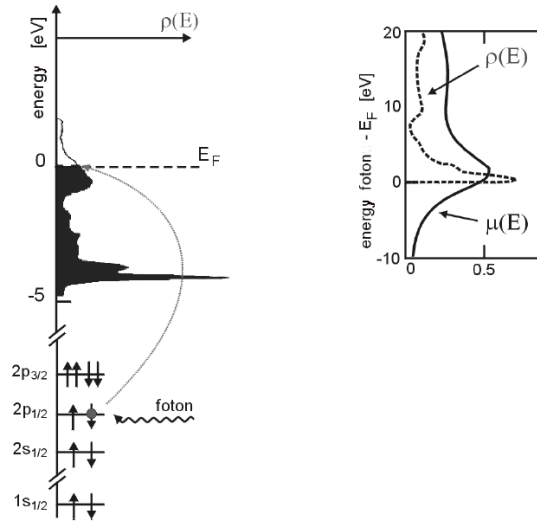


Figure 3.2: Emission of a core level electron due to absorption of the X-ray photon, $\rho(E)$ -density of states above Fermi energy.

In our analysis we are interested in the structure of oscillations above the absorption edges. Therefore, we need to find a procedure how to remove the absorption edge and possible measurement background. The EXAFS function describing the structural oscillation is defined by:

$$\chi(E) = \frac{\mu(E) - \mu_i(E)}{\Delta_{\mu_i}(E_0)}, \quad (3.2)$$

where μ is experimental absorption coefficient, E_0 is the absorption edge energy, Δ_{μ_i} is the edge step in absorption, and μ_i is a free atomic background which represents the absorption on the free ion in the same state as in the studied material but without oscillations coming from diffraction of photoelectron on the surrounding atoms. If we define photoelectron wave vector k as:

$$k = 10^{-10} \sqrt{\frac{2m_e e}{\hbar^2}} (E - E_0), \quad (3.3)$$

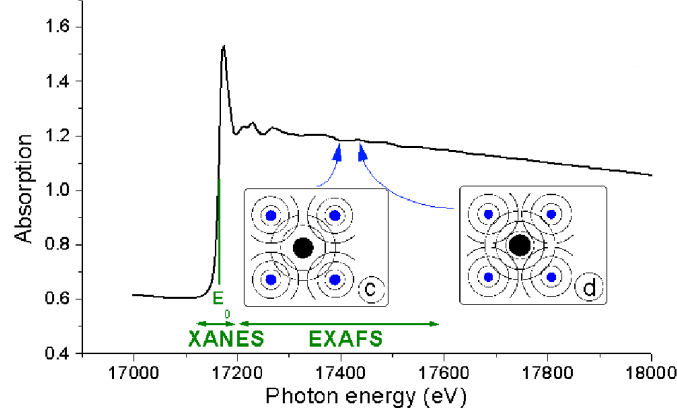


Figure 3.3: Interference of photo electrons in the crystal.

where e is the electric charge of the electron, E_0 is the absorption edge energy, E and E_0 are in eV and k is in $1/\text{\AA}^{-1}$ the function $\chi(E)$ should be written as a function of k vector i.e. $\chi(k)$. Symbol k has in our notation meaning of absolute value of photoelectron wave vector $\vec{k}$, $k = |\vec{k}|$. The $\chi(k)$ function is a sum of $\chi_i(k)$ contributions of electron waves back-scattered from each surrounding ion/atom A_i ,

$$\chi(k) = \sum \chi_i(k) \quad (3.4)$$

The EXAFS $\chi(k)$ function is Fourier transformed to obtain a radial distribution function, which provides the information on the distances and type (number of electrons) of surrounding atoms or ions. Further details on the EXAFS analysis, including Fourier Transform (FT) procedure is provided in the chapter 10. EXAFS method was successfully used for example for study of rare earth nickel perovskites [Piom2006] or CaSO_4 , [Bhat2006].

3.2 Experimental setup

The setup for EXAFS measurements can have different configurations. The first element of experimental setup is a slit which defines the beam cross-section. Then the beam is monochromatized and usually the Si single crystals are used in the monochromator. After monochromating the beam dimensions are again reduced and then the beam intensity I_1 is measured by the detector 1. Next, the beam

¹we use $\text{\AA}$ for units of length except SI units in order to follow typical convention of EXAFS literature, $1 \text{ \AA} = 0.1 \text{ nm}$

is directed to the sample which is placed on a special sample holder. The beam intensity after interaction with the sample is detected by the detector 2.

The experimental setup for a transmission mode includes one detector located in front of the sample and the second detector located behind the sample, see Figure 3.4. Another experimental setup is for a fluorescence mode, where the intensity of incident beam and fluorescent radiation emitted from the sample is measured, see Figure 3.4.

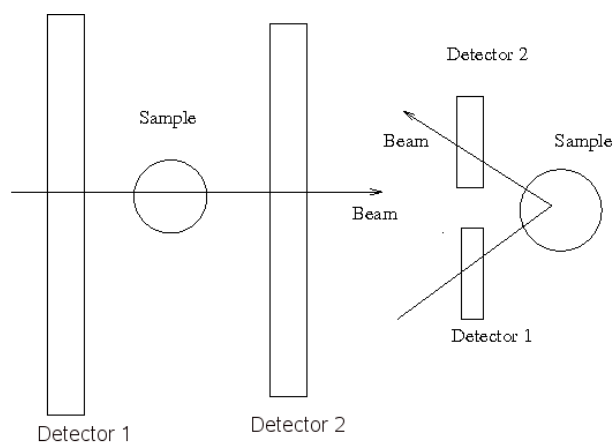


Figure 3.4: Transmission mode (left side) and fluorescence mode (right side) of EXAFS measurement.

Chapter 4

EXAFS data elaboration

X-ray absorption measurements were carried out at A1 station in DESY, Hamburg (Co:K edge measurements) and on the beamline ID26 in ESRF, Grenoble, France (Mn:K edge measurements). EXAFS spectra on the Co:K edge were measured in transmission mode and the spectra on the Mn:K edge were measured in fluorescence mode. The samples $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8$ and 1 prepared by solid state reaction method were measured. All measurements were carried out at room temperature. Obtained EXAFS spectra were analyzed using FEFF tools, [Rave2000], [Rave2001], [Newv2004], [Feff2002], [Newv1997], [Newv1998], [Newv2001], [Zabi1995].

Double Si(111) single crystal monochromator with energy resolution of order of 2 eV was used and absorption spectra μ were measured in the energy range from 7500 eV to 8700 eV for Co:K edge measurements and in the energy range from 6300 eV to 7500 eV for Mn:K edge measurements.

The information about the local environment is in the post edge absorption region where the oscillations occur as it was described in chapter 3. Detailed analysis has to be performed in order to obtain a precise and reliable information from measurements. The analysis procedure is based on fitting a theoretical function to experimental data. We use a software package called FEFF which is a set of programs for processing the EXAFS data; this package was developed by Bruce Ravel and his colleagues at the Washington University [Anku2002]. It consists of several procedures which have different purpose and all of them cover the area of operations necessary in order to obtain a final result.

In the following paragraphs parameters and variables used during analysis with the FEFF package are typed with a **type writer** font to make the reading clear and more informative.

4.1 Pre-edge subtraction

The pre-edge part of the absorption spectrum is fitted with a linear function within the range which is chosen by user defined variables `pre1` and `pre2` (see Figure 4.1). If `pre1` and `pre2` parameters are not set by the user then values of these parameters are set as defaults by the software.

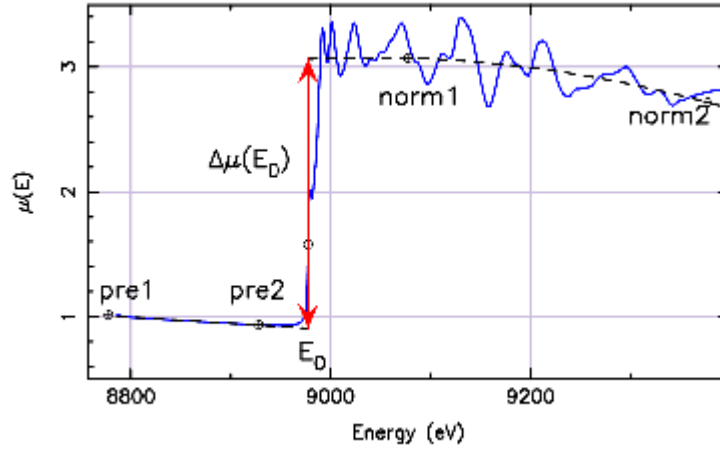


Figure 4.1: Pre-edge subtraction,

4.2 Edge step

Next step in the analysis is to find the edge energy E_0 (in software the edge energy is represented by `E0`) which is defined as a maximum of derivative $\partial\mu(E)/\partial E$. Option for manual setting of `E0` is also available in the software. The quadratic function is fitted to the post-edge region which is determined by parameters `norm1` and `norm2` (default values are: `norm1`=100 eV and `norm2`=300 eV). The difference between the quadratic function (fitted to post edge region) and the linear function (fitted to the pre edge region) at E_0 is taken as the edge step (denoted as `edge_step` or $\Delta_{\mu(E_0)}$)

Spectrum is normalized to the unity edge step according to formula

$$\mu_n = \mu - f_l\Psi(E_0) - (1 - f_q\Theta(E_0)), \quad (4.1)$$

where f_l is the pre-edge line, f_q is the post edge quadratic function, $\Psi(E_0)$ is equal to 1 for $E < E_0$ and to 0 for $E > E_0$, $\Theta(E_0)$ is equal to 1 for $E > E_0$ and to 0 for $E < E_0$. The result of this normalization is stored in an array `$group.norm`

where `$group.` is a user defined name (label) of a given analysis. This step is done in order to compare the absorption spectra of different samples. The example of normalized EXAFS spectra is shown in Figure 4.2.

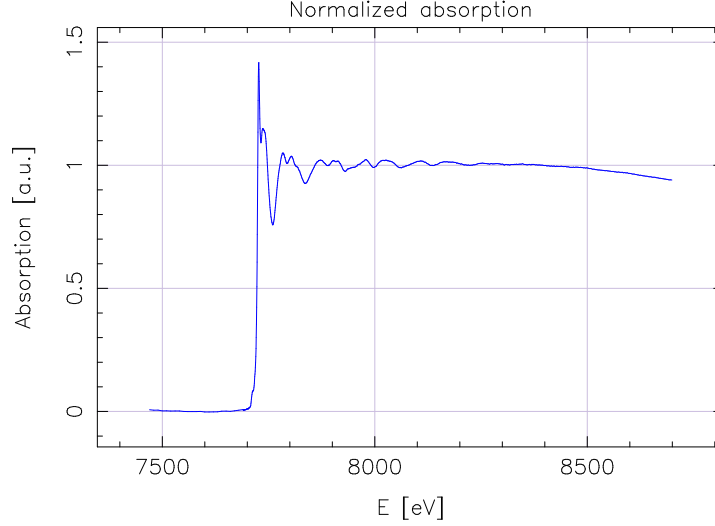


Figure 4.2: Example of normalized absorption spectrum.

4.3 Free atom background removal

A correct free atomic background removing is an essential step in the analysis of EXAFS measurement. The FEFFIT application contains a procedure called `spline` which finds optimal free atom absorption $\mu_0(E)$. Procedure `spline` also contains the pre-edge and post-edge background removing. It is based on minimizing of $FT(\chi)$ in the range from 0 to `rbkg`, which is an input parameter for the spline procedure. There are also other parameters which have to be given by the user in order to remove the free atomic background, they include: Fourier transform window, k range, r range, k -weigh and others. Varying these parameters does not have a big influence on the result if the background is removed properly with the exception of the `rbkg` parameter which has a meaning of the size of the central atom.

The EXAFS function $\chi(k)$ is calculated according to the formula:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta_{\mu(E_0)}}, \quad (4.2)$$

where the E is transformed to k domain according to formula (3.3). This means that χ is always normalized to a unit edge step. The beginning of k vector is set to E_0 , electron kinetic energy E_e is given as $E_e = E - E_0$ where E is the energy of the incoming radiation. By applying the `spline` function to the experimental data we obtain the EXAFS function $\chi(k)$ in which the information about the structure is encoded. An example of the $\chi(k)$ function is shown in Figure 4.3

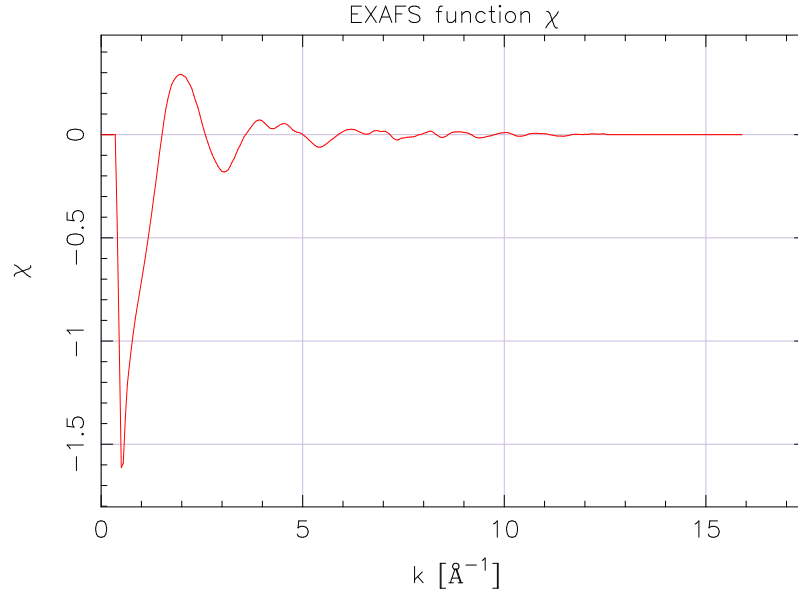
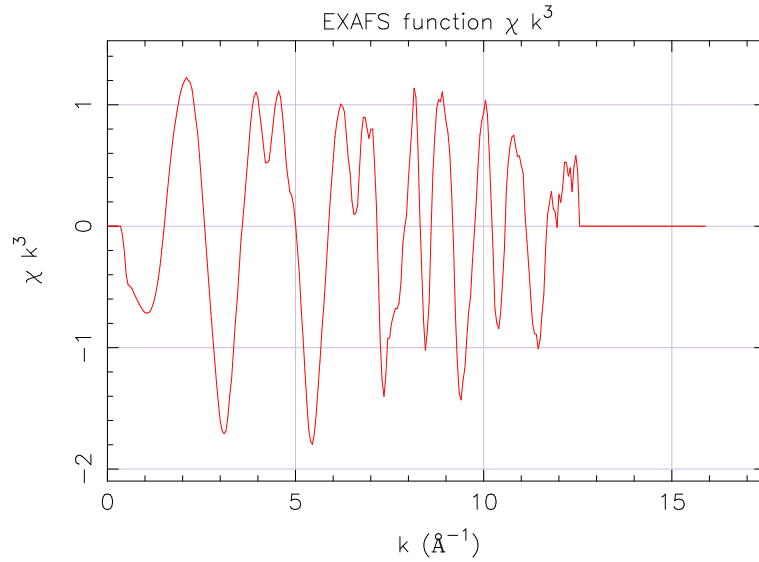


Figure 4.3: Example of the $\chi(k)$ function

Usually the $\chi(k)$ function is weighted by a factor of k^p , where p is 1, 2 or 3 depending on the measurement. The factor k^p is applied in order to treat the data points at high k values which are strongly damped as compared with those at low k , and in order to obtain more suitable function for the Fourier transformation. The $\chi(k)k^p$ function is plotted in the Figure 4.4. Making a Fourier transform of weighted $\chi(k)$ function we obtain radial distribution function (EXAFS function in R -space) which is related to the charge density around central atom. From the $\chi(R)$ function (see Figure 4.5) we can already make a qualitative conclusions without further analysis. The EXAFS function in the R -space has peaks at R values considerably lower than the neighbor atom distances. The difference between the peak in R and the neighbor atom distance is typically around 0.5. This effect is understood to be due to the scattering phase shift $\phi_{eff} + \phi_c$ in the sinus function in the EXAFS equation (4.3). Extraction of the structural details from x -ray absorption spectra is described

Figure 4.4: Example of the $\chi(k)k^3$ function

also in [Vaic2004], [Klem2001].

4.4 FEFF calculations

FEFF program calculates functions $\chi(k)$ and $\mu(E)$ for a given crystal structure. Calculation is based on an all-electrons, real space relativistic Green's functions formalism with no symmetry requirements. Scattering potentials are calculated by overlapping the free atom densities within the muffin tin approximation, [Rave2000].

When the photoelectron is emitted from the central atom it propagates in the matter and the wave associated with this electron is reflected on a neighboring atom. Then it propagates back and it can be reflected on the original central atom or another atom which is close. So the photoelectron during propagation through the material can be reflected once, twice or more times before it "returns" to the central atom. All possible traces of the photoelectron are called paths. A path can consist of several legs where the leg is a trajectory of the photoelectron from one ion to a neighboring ion. A schematic diagram of the photoelectron propagation can be seen in Figure 4.6.

Each path contribute to the total χ function and the paths are combined to the

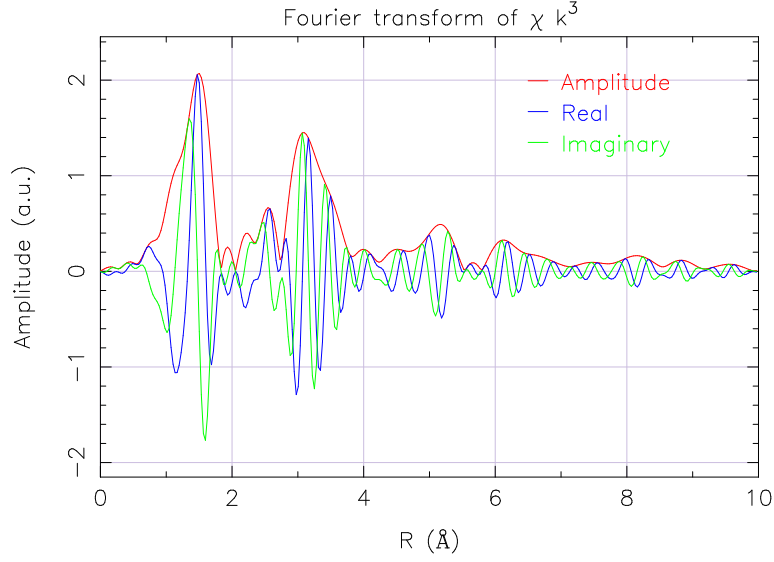
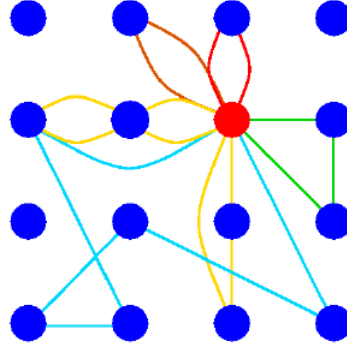
Figure 4.5: Example of the $\chi(R)$ function, $\chi(R) = \text{FT}(\chi(k)k^3)$.

Figure 4.6: Path of a photoelectron during propagation in the crystal.

total χ function according to the formula

$$\chi(k) = S_0^2 \mathcal{R} \sum_{\text{shell}} \frac{N_{\text{shell}} F_{\text{eff}}}{k R_{\text{shell}}^2} \exp(-2r/\lambda) \sin(2k R_{\text{shell}} + \phi_{\text{eff}} + \phi_c) \exp(-2k^2 \sigma^2), \quad (4.3)$$

where N is a number of atoms in each shell, S_0^2 is the amplitude of χ function, R_{shell} is the distance between central and surrounding atom, σ is the Debye-Waller factor, λ is the mean free path, ρ is the total central atom loss factor, F_{eff} is the effective

backscattering amplitude, ϕ_{eff} is the phase correction, ϕ_c is the total central atom phase shift and $\mathcal{R}$ is the total central atom loss factor.

A path with one reflection is called a single path, a path with more reflections is called a multiple path. Paths do not have the same weight (importance) and the contribution of each path to the χ function depends on the path length, number of reflections and angle between legs. For example if we consider photoelectron which moves from the central ion and it is reflected back on a neighboring ion to direction of the central ion, there are two legs and the angle between them is 180 degrees. Paths with the angle between legs equal to 180 degrees are more important than paths for which this angle is much different from 180 degrees.

The input of FEFF calculation are positions of all surrounding atoms up to the defined distance limit (usually around 10 Å). User has to define also conditions for calculation and the form of output of calculated data.

FEFF programs work only with integer numbers of atoms. In the case of a doped compound the central atom can have in average non integer number of neighbors of the same type. It means that in this case a systematic error is present in calculations. If this fact is crucial for obtaining satisfactory results, this systematic error should be fixed during the fitting procedure.

FEFF program assumes the atoms are neutral. Valence state could be added to calculations, but usually it leads to non-physical results. FEFF calculates χ and μ together with parameters $F_{\text{eff}}(k)$ and phase shift $\alpha(k)$ which are necessary inputs for fitting procedure.

4.5 Fitting procedure

The whole fitting procedure is done by program module called FEFFIT. In FEFFIT input file `feff.inp` it is defined which paths will be loaded and then used to calculate the χ function and which path parameters of the function (4.3) are fitted. Experimental data are loaded from a data file and initial values for fitting procedure are set. For fitting procedure also interactive program called IFEFFIT can be used, it is a command-line based interactive program for fitting. The IFEFFIT program includes procedures and functions for fitting together with AUTOBK functions for removing the free atomic background. Additionally it is possible to write script files for the IFEFFIT program, which is very useful and significantly reduces time needed for starting calculations of the EXAFS data.

As the first step for the fitting procedure we have to "build" a "physical model" for the measured compound. Each path has up to five parameters which can be varied during the fitting procedure. Therefore, we have to simplify the situation and make some constraints between parameters which reduces the number of fitted parameter. The physical model is based on known or anticipated physical properties

of the material studied.

During the fitting procedure we should control the goodness of the fit. The first important parameter of the fit quality is a χ^2 error (do not confuse it with the EXAFS χ function) which is a sum of squares of differences between experimental and theoretical $\chi(k)$ function,

$$\chi^2 = \sum_{i=1}^N \left(\frac{f_i}{\epsilon_i} \right)^2, \quad (4.4)$$

where N is a number of experimental points, f_i is the difference between experiment and fitted function and ϵ_i is an error of i -th point in $\chi(k)$.

Because the output of EXAFS measurement is spectral data, the measured points are not independent. According to the information theory the number of independent points is given by a formula

$$N_{idp} = \frac{2(k_{max} - k_{min})(R_{max} - R_{min})}{\pi} + 2. \quad (4.5)$$

The number of independent points in measurement is only given by the range of values of k and R , where we make the analysis, [Ster1997]. From equation (4.5) we see that the number of independent points is not an integer number. Usually we have $k = \{1 - 12\}$ and $R = \{1 - 4\}$ which give $N_{idp} \sim 17$

Goodness of the fit is controlled by the reduced χ^2 denoted as χ_ν^2 which is given by equation 4.6 rather than by χ^2 .

$$\chi_\nu^2 = \frac{\chi^2}{\nu}, \quad (4.6)$$

where

$$\nu = N_{idp} - N_{vary}. \quad (4.7)$$

Another parameter which informs about the quality of the fit is R -factor defined as

$$R = \frac{\sum_{i=1}^N \{[\text{Re}(f_i)]^2 + [\text{Im}(f_i)]^2\}}{\sum_{i=1}^N \{[\text{Re}(\chi_{\text{data}_i})]^2 + [\text{Im}(\chi_{\text{data}_i})]^2\}}. \quad (4.8)$$

This number is directly proportional to χ^2 , and gives a sum-of-squares measure of fractional misfit. For good fits of carefully measured data $R \lesssim 0.02$ and $\chi_\nu > 10$ are common. Such fits are very good as the theory and measured data do not differ more than by one percent.

4.6 Path parameters

For each path generated by FEFF there are seven parameters important for calculating the $\chi(k)$ function. Let's describe briefly all path parameters.

The first parameter is called **e0**. This parameter does not have the same meaning as E_0 , however, it is directly related to that. **e0** is a difference between theoretically calculated E_0 and E_0 obtained from the measurement. This parameter couples the theoretical and measured energy absorption edge together. Usually the **e0** parameter is the same for all paths in the fit and it is varied during the fitting process. Parameter **e0** shifts the energy origin

$$k \rightarrow \sqrt{k^2 - \mathbf{e0}(2m_e/\hbar^2)} \quad (4.9)$$

Next parameter is called **S02** which according to the formula (4.11) has a meaning of the amplitude of the χ function. This parameter is also often the same for all path. This parameter usually introduces the damping to the analysis in the case if it is necessary.

One of the most important parameters is a parameter called **delR**. which is given by

$$R_{\text{eff}} = R_0 + \mathbf{delR}, \quad (4.10)$$

R_{eff} is a half of the real (calculated by FEFF) path length and R_0 is a half of the path length calculated from lattice parameters and crystal structure given as an input.

Debye-Waller factor usually denoted as σ^2 , here as a fitting parameter **sigma2**, is a mean square deviation from the equilibrium position in the crystal structure. This deviation can be caused by a thermal motion of atoms/ions (time mean value) and also by a static disorder (space mean value).

Other parameters are less important. **ei** is the imaginary energy shift, **third** and **fourth** are 3rd and 4th cumulants from anharmonicity.

All paths are combined according to the equation, [Rave2001]

$$\chi_{\text{path}}(k) = \text{Im}\left(\frac{F_{\text{eff}}(k) \times N_{\text{degen}} \times \mathbf{S02}}{kR_{\text{eff}} + \mathbf{delR}^2} e^{-2p''R_{\text{eff}} - 2p^2\mathbf{sigma2} + \frac{2}{3}p^4\mathbf{fourth}} \times e^{i[2kR_{\text{eff}} + \text{Phase}(k) + 2p(\mathbf{delR} - 2\frac{\mathbf{sigma2}}{R_{\text{eff}}}) - \frac{4}{3}p^3\mathbf{third}]}\right), \quad (4.11)$$

where

$$\chi(k) = \sum \chi(k)_{\text{path}}. \quad (4.12)$$

The parameter $\text{Phase}(k)$ is given by $\text{Phase}(k) = \phi_{\text{eff}} + \phi_c$ (see chapter 4.4), where both terms are calculated by FEFF, $F_{\text{eff}}(k)$ is the effective backscattering amplitude for specific path calculated, p' and p'' are real and imaginary components of the complex momentum with respect to E_0 and N_{degen} is multiplicity of the path.

Chapter 5

Nuclear magnetic resonance

Nuclear Magnetic Resonance (NMR) is a powerful scientific research tool which has been used since the second half of a previous century. NMR is a non-invasive, non-destructive atom/isotope selective method which provides information on a microscopic scale. NMR has been used in a several scientific disciplines i.e. chemistry, biology, medicine, physics and material research. NMR technique is suitable for studying electronic and magnetic properties of materials, it can also provide information about spin state of measured element. It has been successfully employed to probe hyperfine magnetic field of magnetically ordered materials. NMR is extremely useful experimental method for observation of sublattices magnetization and their temperature dependences and it is often employed to study impurities and defects in condensed matter.

5.1 Basic principle

Energy of a single gyromagnetic particle with magnetic moment $\vec{\mu}$ in a static magnetic field $\vec{B}_0$ is given by Hamiltonian H ,

$$H = -\vec{\mu} \cdot \vec{B}_0. \quad (5.1)$$

Expression (5.1) can be written as

$$H = -\gamma \hbar \vec{I} \cdot \vec{B}_0, \quad (5.2)$$

where γ is a gyromagnetic ratio, $\hbar$ is a Planck constant and $\vec{I}$ is an angular momentum spin operator. If we choose a coordination system in which magnetic field $\vec{B}_0$ has only a z -component, i.e. $\vec{B}_0 = (0, 0, B_0)$, the expression (5.2) could be simplified to

$$H = -\gamma \hbar I_z B_0, \quad (5.3)$$

where I_z is a z -component of the momentum operator.

Solutions of stationary Schrödinger equation

$$H\psi = E\psi \quad (5.4)$$

are equidistant energy levels E_m , which are called the Zeeman multiplet (see Figure 5.1)

$$E_m = -\gamma\hbar B_0 m. \quad (5.5)$$

The quantity m is called magnetic quantum number with $2I + 1$ allowed values from I to $-I$, where I is a spin of particle. Transitions between energy levels of Zeeman multiplet can be induced by radio frequency (rf) magnetic field $\vec{B}_1$, which is perpendicular to the static magnetic field $\vec{B}_0$. When the rf magnetic field is applied Hamiltonian of the system is given by

$$H = -\vec{\mu} \cdot \vec{B}_0 - \vec{\mu} \cdot \vec{B}_1. \quad (5.6)$$

Let's consider a rf field $\vec{B}_1$ much weaker than the static magnetic field $\vec{B}_0$, therefore the second term in (5.6) can be considered as a small perturbation to the total Hamiltonian H . Then the transition probability $P_{mm'}$ between Zeeman energy levels $|m\rangle$ a $|m'\rangle$ according golden rule [Klim1998] is proportional to the square of the perturbed Hamiltonian H_1 ($H_1 \sim I^+ + I^-$) matrix elements

$$P_{mm'} \sim |\langle m | H_1 | m' \rangle|^2. \quad (5.7)$$

The transition is allowed i.e. transition probability is non zero only when the condition

$$\langle m | H_1 | m \rangle \neq 0 \quad (5.8)$$

is fulfilled which is true for $m' = m \pm 1$. Transitions between energy levels are accompanied by absorption or emission of energy quantum ΔE , see Figure (5.1):

$$\Delta E = |\gamma|\hbar B_0 = \hbar\omega_0. \quad (5.9)$$

Magnetic field $\vec{B}_1$ causes a transition between energy levels of Zeeman multiplet when the frequency ω_1 of the high frequency field B_1 is equal or close to the ω_0 where ω_0 is given by:

$$\omega_0 = |\gamma \cdot B_0|. \quad (5.10)$$

Transitions between Zeeman energy levels of nucleus induced by a rf magnetic field are called nuclear magnetic resonance (NMR) and the quantity ω_0 is called the Larmor frequency.

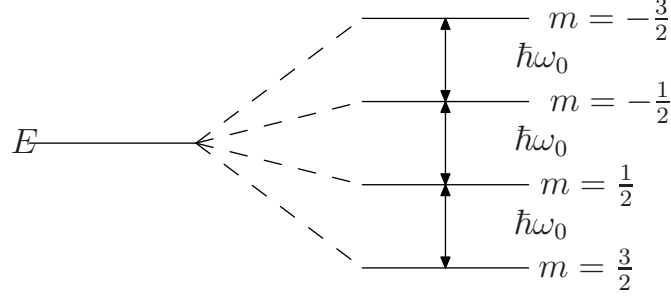


Figure 5.1: Zeeman multiplet. Splitting of energy levels of nucleus with spin $I = \frac{3}{2}$ in the magnetic field B_0 for positive gyromagnetic ratio.

5.2 Electric quadrupolar resonance

Atom nucleus is composed of protons and neutrons and therefore it has the inner structure which can be described by the electric charge density distribution $\rho_N(\vec{r})$. The energy E of a particle with the electric charge density $\rho_N(\vec{r})$ in the electric field with potential $\varphi(\vec{r})$ is given by expression

$$E = \int_V \varphi(\vec{r}) \rho_N(\vec{r}) dV. \quad (5.11)$$

Potential $\varphi(\vec{r})$ can be written as:

$$\varphi(\vec{r}) = \varphi(0) + \sum_{j=1}^3 x_j V_j + \frac{1}{2!} \sum_{i \geq j=1}^3 x_i x_j V_{ij} + \dots, \quad (5.12)$$

where V_{ij} and V_j are given by:

$$V_j = \frac{\partial \varphi}{\partial x_j}, \quad (5.13)$$

$$V_{ij} = \frac{\partial^2 \varphi}{\partial x_i \partial x_j}. \quad (5.14)$$

If we use (5.12) and apply it to equation (5.11) we obtain:

$$E = \varphi(0) \int \rho(\vec{r}) dV + \sum_{j=1}^3 V_j \int x_j \rho_N(\vec{r}) dV + \frac{1}{2!} \sum_{i \geq j=1}^3 V_{ij} \int x_i x_j \rho_N(\vec{r}) dV + \dots. \quad (5.15)$$

The first term is the electrostatic energy of nucleus in the approximation of point charge,

$$q = \int_V \rho_N(\vec{r}) dV = Ze, \quad (5.16)$$

where Z is a number of protons in a nucleus.

The second term is equal to zero (nuclear dipole moment is zero for nuclei in stationary state)

$$p = \int_V \vec{r} \rho_N(\vec{r}) dV, \quad (5.17)$$

where $\rho_N(\vec{r})$ is given by

$$\rho_N(\vec{r}) = e|\psi_N|^2. \quad (5.18)$$

If the nucleus wave function ψ_N parity is given by expression $\psi_N(-\vec{r}) = -\psi_N(\vec{r})$ the function $|\psi_N|^2$ is even. The integral of product of even and odd function is equal to zero, therefore

$$\int_V \vec{r} \rho_N(\vec{r}) dV = 0. \quad (5.19)$$

Quadrupole moment Q_{ij} is given by expression

$$Q_{ij} = \int_V (3x_i x_j - \delta_{ij} r^2) \cdot \rho_N(r) dV, \quad (5.20)$$

Q_{ij} is a symmetric tensor of second order with zero trace. The third term of equation (5.15) can be written as:

$$E_{III} = \frac{1}{6} \sum_{j=1}^3 V_{jj} \int r^2 \rho_N(\vec{r}) dV + \frac{1}{6} \sum_{i \geq j=1}^3 V_{ij} Q_{ij}, \quad (5.21)$$

$$\int x_i x_j \rho_N dV = \frac{1}{3} (Q_{ij} + \int \delta_{ij} r^2 \rho_N dV). \quad (5.22)$$

The first term in (5.21) can be simplified by defining a mean quadratic radius $\langle r^2 \rangle$ of nucleus

$$\langle r^2 \rangle = \frac{\int r^2 \rho_N(\vec{r}) dV}{\int \rho_N(\vec{r}) dV} = \frac{\int r^2 \rho_N(\vec{r}) dV}{Ze} \quad (5.23)$$

and using the Poisson equation

$$\Delta \varphi = \sum_{j=1}^3 V_{jj} = \frac{\rho_N(0)}{\varepsilon_0} = \frac{e|\psi(0)|^2}{\varepsilon_0} \quad (5.24)$$

to

$$E_I = \frac{Ze^2}{6\varepsilon_0} |\psi(0)|^2 \langle r^2 \rangle, \quad (5.25)$$

where ψ is electron wave function, $\rho(r)$ is charge density generating electric field at the nucleus position, $|\psi(0)|^2$ is a probability of electron presence at the nucleus

position. This term (called isomer shift), is constant if there are no changes of the mean square radius.

The second term in (5.21) describes interaction between nuclear quadrupole moment and internal electric field. If we rewrite Q_{ij} using spin operators the Hamiltonian of quadrupole interaction H_Q is given by expression, [Slic1990]:

$$H_Q = \frac{eQ}{6I(2I-1)} \sum_{i,j} V_{ij} \left[\frac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I^2 \right]. \quad (5.26)$$

Assuming the coordination system connected to main axes of a tensor V_{ij} the Hamiltonian can be simplified to

$$H_Q = \frac{eQ}{6I(2I-1)} (V_{xx}(3I_x^2 - I^2) + V_{yy}(3I_y^2 - I^2) + V_{zz}(3I_z^2 - I^2)). \quad (5.27)$$

Instead of definition 5.14 it is appropriate to use a modified expression in the following analysis:

$$V_{ij} = \frac{\partial^2 \varphi}{\partial x_i \partial x_j} - \delta_{ij} \cdot \frac{1}{3} \text{Tr} \frac{\partial^2 \varphi}{\partial x_i \partial x_j}. \quad (5.28)$$

Then we obtain traceless tensor and the expression for the Hamiltonian 5.27 is not changed.

Supposing axial symmetry of the electric field ($V_{xx} = V_{yy}$ and $\sum_{i=1}^3 V_{ii} = 0$) the Hamiltonian H_Q (5.26) transforms into:

$$H_Q = \frac{eQV_{zz}}{4I(2I-1)} (3I_z^2 - I^2). \quad (5.29)$$

Eigenvalues of energy are given by:

$$E_m = \frac{eQV_{zz}}{4I(2I-1)} (3m^2 - I^2). \quad (5.30)$$

Transitions between energy levels can be induced by alternating magnetic field $\vec{B}_1$ and the probability of these transitions is proportional to the square of H_1 matrix elements $P_{m'm}$.

$$P_{m'm} \sim |\langle m \pm 1 | H_1(t) | m \rangle|^2. \quad (5.31)$$

As the condition $\langle m \pm 1 | H_1(t) | m \rangle \neq 0$ is fulfilled for $m' = m \pm 1$, only transitions between neighboring levels are allowed. The difference between neighboring energy levels $\Delta E_{m \pm 1, m}$ amounts to:

$$\Delta E_{m \pm 1, m} = \frac{eQV_{zz}}{4I(2I-1)} 3|1 \pm 2m|. \quad (5.32)$$

Frequency of the magnetic field is given by equation:

$$\omega_{m\pm 1,m} = \frac{3eQV_{zz}}{4I(2I-1)\hbar} |1 \pm 2m|. \quad (5.33)$$

Effect of inducing transitions between energy levels E_m by radiofrequency magnetic field with frequency $\omega_{m\pm 1,m}$ is called Nuclear Quadrupole Resonance (NQR), Figure (5.2).

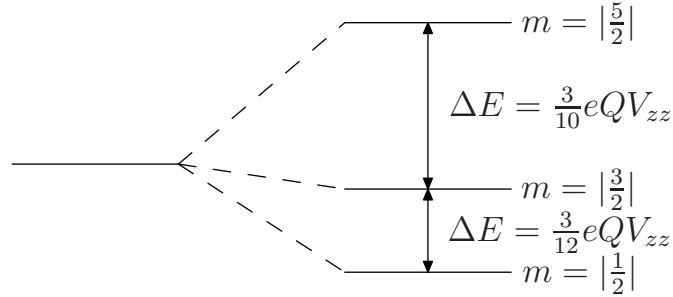


Figure 5.2: Quadrupolar splitting in electrical field of axial symmetry. Splitting of energy levels for nucleus with spin $I = \frac{5}{2}$.

5.3 Interaction of nucleus with electric and magnetic field

The nucleus with a non-zero magnetic moment can interact with the magnetic and electric field.

Hamiltonian of interaction with the electric and magnetic field is given by:

$$H = -\gamma h \sum_{i=1}^3 B_{ef,i} I_i + \frac{eQ}{6I(2I-1)} \sum_{i,j}^3 V_{ij} \left[\frac{3}{2} (I_i I_j + I_j I_i) - \delta_{ij} I^2 \right]. \quad (5.34)$$

Effective field $\vec{B}_{ef}$ can be expressed by:

$$B_{ef,i} = A_0 n_i + \sum_{j=1}^3 A_{ij} n_j, \quad (5.35)$$

where the term A_0 describes isotropic part and A_{ij} anisotropic part of the effective magnetic field, n_i are components of unit vector in the direction of magnetization.

There can be three different situations depending on the relative strengths of the magnetic and electric interaction. First, magnetic interaction is much weaker than

electric interaction. In this case the magnetic interaction is treated as a perturbation and for calculation of eigenvalues we can use the perturbation theory [Sed1977].

In the second case the electric interaction is much weaker than magnetic interaction and also in this case for solving the problem one can use the perturbation theory where the electric field is treated as a small perturbation. In this case the structure of the Zeeman multiplet changes and in the NMR spectra the line splitting can be observed.

The third case takes place when both interactions, magnetic and electric are comparable. Energy levels are given by the stationary Schrödinger equation

$$H\psi = E\psi. \quad (5.36)$$

We express Hamiltonian H in a matrix representation in base of eigenvector of I_z (z -component of operator I)

$$H_{mn} = \langle m | H | n \rangle, \quad (5.37)$$

$$H = H_m + H_e, \quad (5.38)$$

where $|m\rangle$ is an eigenfunction of operator I_z and m is an eigenvalue of operator I_z . We now introduce creation and annihilation operators I^+ and I^- and Hamiltonian H_m can be rewritten using relations:

$$\begin{aligned} I_x &= \frac{I^+ + I^-}{2}, \\ I_y &= \frac{I^+ - I^-}{2i} \end{aligned} \quad (5.39)$$

to form:

$$H_m = -\gamma\hbar[(A_0 + A_{zz})I_z + A_{xz}I_x + A_{yz}I_y] = -\gamma\hbar[A_I I_z + A_{-1}I^+ + A_1I^-], \quad (5.40)$$

where $A_I = A_0 + A_{zz}$ and $A_{\pm 1} = \frac{1}{2}(A_{xz} \pm iA_{yz})$. Because $\langle m | I_z | m \rangle = m$ and $\langle m \pm 1 | I^\pm | m \rangle = \sqrt{(I \mp 1)(I \pm m + 1)} H_m$ matrix, e.g. for nucleus with the spin $\frac{3}{2}$, equals to:

$$H_m = \begin{pmatrix} -\gamma\hbar\frac{3}{2}A_I & -\gamma\hbar\frac{\sqrt{3}}{2}A_{-1} & 0 & 0 \\ -\gamma\hbar\frac{\sqrt{3}}{2}A_1 & -\gamma\hbar\frac{1}{2}A_I & -\gamma\hbar A_{-1} & 0 \\ 0 & -\gamma\hbar A_1 & -\gamma\hbar - \frac{1}{2}A_I & -\gamma\hbar\frac{\sqrt{3}}{2}A_{-1} \\ 0 & 0 & -\gamma\hbar\frac{\sqrt{3}}{2}A_1 & -\gamma\hbar\frac{-3}{2}A_I \end{pmatrix}. \quad (5.41)$$

Hamiltonian H_e using operators I^+ and I^- and (5.39) can be written as:

$$\begin{aligned} H_e &= \frac{eQ}{4I(2I-1)}[(3I_z^2 - I^2)V_0 + (I^+I_z + I_zI^+)V_{-1} + \\ &+ (I^-I_z + I_zI^-)V_1 + I^{+2}V_{-2} + I^{-2}V_2], \end{aligned} \quad (5.42)$$

where

$$\begin{aligned} V_0 &= V_{zz} \\ V_{\pm 1} &= V_{xz} \pm iV_{yz} \\ V_{\pm 2} &= \frac{V_{xx} - V_{yy}}{2} \pm iV_{xy}. \end{aligned}$$

Matrix of quadrupole interaction with of the nucleus with the spin $\frac{3}{2}$ is:

$$H_e = \begin{pmatrix} \frac{eQ}{12}3V_0 & \frac{eQ}{12}V_{-1}2\sqrt{3} & \frac{eQ}{12}V_{-2}2\sqrt{3} & 0 \\ \frac{eQ}{12}V_{+1}2\sqrt{3} & -\frac{eQ}{12}3V_0 & 0 & \frac{eQ}{12}V_{-2}2\sqrt{3} \\ \frac{eQ}{12}V_{+2}2\sqrt{3} & 0 & -\frac{eQ}{12}3V_0 & -\frac{eQ}{12}V_{-1}2\sqrt{3} \\ 0 & \frac{eQ}{12}V_{+2}2\sqrt{3} & -\frac{eQ}{12}V_{+1}2\sqrt{3} & \frac{eQ}{12}3V_0 \end{pmatrix} \quad (5.43)$$

We can find eigenvalues and eigenvectors of matrix H_{mn} by diagonalizing and we can calculate the energy of transition and frequency of transitions.

For the case of comparable magnetic and electric interactions selection rules are no longer valid. For example in the case of nucleus with the spin $\frac{3}{2}$ we can have six spectral lines , see Figure (5.3)

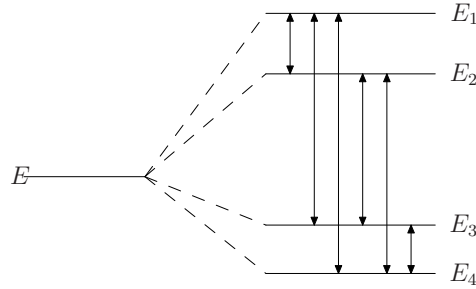


Figure 5.3: Splitting of energy levels by electric and magnetic field for nucleus with spin $I = \frac{3}{2}$.

5.4 Formulation of Bloch equations

Classical motion equation of a magnetic moment in the external magnetic field has a form (5.44) and is the same as quantum mechanical description of a mean value of magnetic moment motion in the magnetic field.

$$\frac{d\vec{\mu}}{dt} = \gamma(\vec{\mu} \times \vec{B}). \quad (5.44)$$

For description of a solid state material which has a large number of nuclei it is useful to introduce the quantity called nuclear magnetization, i.e. $\vec{M}$ which is

defined as the total magnetic moment of nuclei per a unit volume. $\vec{M}$ is given by expression:

$$\vec{M} = \frac{1}{V} \sum_i \vec{\mu}_i. \quad (5.45)$$

In a solid state material we have to take into account also interactions of nuclei with surrounding ions and the lattice. The transition to thermodynamic equilibrium state has a relaxation character.

The relaxation process of in-plane magnetization components M_x and M_y is called the transverse or spin-spin relaxation and it is usually characterized by spin-spin relaxation time T_2 . The spin-spin relaxation is a process in which the spin system does not change its energy.

Relaxation of a longitudinal magnetization component M_z is called the spin-lattice relaxation and the relaxation time is written as T_1 . This relaxation process is responsible for establishing the equilibrium state between the spin system and the lattice.

These relaxation processes are described by following equations:

$$\begin{aligned} \frac{dM_x}{dt} &= -\frac{M_x}{T_2}, \\ \frac{dM_y}{dt} &= -\frac{M_y}{T_2}, \\ \frac{dM_z}{dt} &= -\frac{M_z - M_0}{T_1}. \end{aligned} \quad (5.46)$$

Using equations (5.44), (5.45) and (5.46) we obtain phenomenological Bloch equations:

$$\begin{aligned} \frac{dM_x}{dt} &= \gamma(\vec{M} \times \vec{B})_x - \frac{M_x}{T_2}, \\ \frac{dM_y}{dt} &= \gamma(\vec{M} \times \vec{B})_y - \frac{M_y}{T_2}, \\ \frac{dM_z}{dt} &= \gamma(\vec{M} \times \vec{B})_z - \frac{M_z - M_0}{T_1}, \end{aligned} \quad (5.47)$$

which describe the movement of the nuclear magnetization with slightly interacting nuclei in external magnetic field.

5.5 Pulse solution of Bloch equations

The solution of Bloch equations can be divided into several regions which are shown in the Figure (5.4). Coordination system is chosen such that the static magnetic field $\vec{B}_0$ has only one nonzero component $\vec{B}_0 = (0, 0, B_0)$.

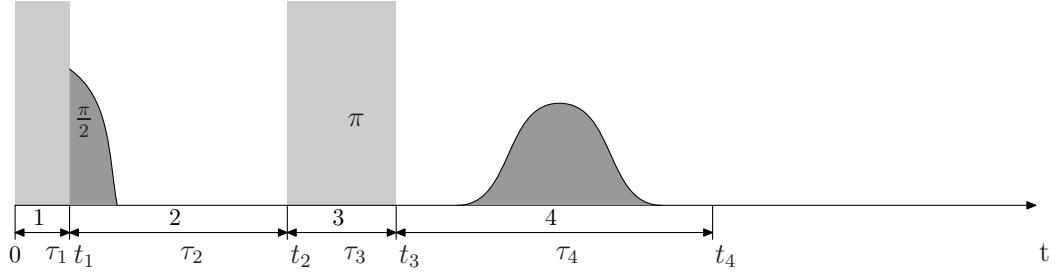


Figure 5.4: Schematic diagram of regions for solution of Bloch equations.

1. In the first region the alternating magnetic field $\vec{B}_1 = (2B_1 \cos \omega t, 0, 0)$ is applied to the sample during time τ_1 . We suppose that time $\tau_1 \ll T_1, T_2$, so the relaxation processes can be neglected.

In a coordinate system which rotates with a frequency ω which is the same as the frequency of the magnetic field $\vec{B}_1$ and using notation $\omega_0 = \gamma B_0$ and $\omega_1 = \gamma B_1$ Bloch equations can be rewritten as:

$$\begin{aligned} \frac{dM_x}{dt} &= (\omega - \omega_0)M_y, \\ \frac{dM_y}{dt} &= \omega_1 M_z - (\omega - \omega_0)M_x, \\ \frac{dM_z}{dt} &= \omega_1 M_y, \end{aligned} \quad (5.48)$$

which then can be written as a differential equation

$$\frac{d^2 M_y}{dt^2} = -((\omega - \omega_0)^2 + \omega_1^2)M_y, \quad (5.49)$$

The solution of equation (5.49) is in the form

$$M_y = c \sin \alpha t + d \cos \alpha t, \quad (5.50)$$

where α is given by expression

$$\alpha^2 = (\omega - \omega_0)^2 + \omega_1^2. \quad (5.51)$$

Solutions for components M_x and M_z have form

$$\begin{aligned} M_x &= -\frac{\omega - \omega_0}{\alpha} (c \cos \alpha t - d \sin \alpha t) + E, \\ M_z &= \frac{\omega_1}{\alpha} (c \cos \alpha t - d \sin \alpha t) + E. \end{aligned} \quad (5.52)$$

Constants c , d and E can be found by knowing initial conditions. If magnetization at time $t = 0$ amounts to $\vec{M} = (0, 0, M_0)$ the final solution is

$$\begin{aligned} M_x &= M_0 \frac{\omega - \omega_0}{\omega_1 + \omega - \omega_0} (1 - \cos \alpha t), \\ M_y &= M_0 \frac{\alpha}{\omega_1 + \omega - \omega_0} \sin \alpha t, \\ M_z &= M_0 \frac{\omega_1}{\omega_1 + \omega - \omega_0} \left(\frac{\omega - \omega_0}{\omega_1} + \cos \alpha t \right). \end{aligned} \quad (5.53)$$

In the case of a resonance, i.e. $\omega = \omega_0$, if we applied so called $\frac{\pi}{2}$ pulse for which $\omega_1 \tau_1 = \frac{\pi}{2}$, the magnetization rotates from the initial state along z axis towards direction of y axis.

2. There is no applied magnetic field $\vec{B}_1$ any longer, but the relaxation processes have to be taken into account when using equations (5.47). We are looking for a solution of differential equations (5.47) in the rotating coordination system

$$\begin{aligned} \frac{dM_x}{dt} &= -(\omega - \omega_0)M_y - \frac{M_x}{T_2}, \\ \frac{dM_y}{dt} &= (\omega - \omega_0)M_x - \frac{M_y}{T_2}, \\ \frac{dM_z}{dt} &= \frac{M_z - M_0}{T_1}. \end{aligned} \quad (5.54)$$

The M_z component can be directly calculated by integration. Concerning initial condition $t_1 = 0, M_z = 0$ it has a form

$$M_z = M_0 \left(1 - \exp \frac{t}{T_1} \right). \quad (5.55)$$

For the other two components it is satisfactory to use their sum in complex number notation:

$$M_{\perp} = M_x + iM_y, \quad (5.56)$$

$$\frac{dM_{\perp}}{dt} = \left(\frac{1}{T_2} + i(\omega - \omega_0) \right) M_{\perp}. \quad (5.57)$$

The in-plane component of magnetization has a form

$$M_{\perp}(t) = M_{\perp}(0) e^{-(\frac{1}{T_2} + i(\omega - \omega_0))t}. \quad (5.58)$$

Nuclei with resonance frequency slightly different from frequency ω are also excited. Expression in exponent in the equation (5.58) can be rewritten by

defining the mean value $\bar{\omega}_0$ of the distribution function g . Distribution function $g(\omega_0 - \bar{\omega}_0)$ describes the amount of nuclei with frequency ω_0 in a unit volume.

$$\frac{1}{T_2} + i(\omega - \omega_0) = \frac{1}{T_2} + i(\omega - \bar{\omega}_0 + \bar{\omega}_0 - \omega_0). \quad (5.59)$$

$x = \omega_0 - \bar{\omega}_0$ is a small deviation from the mean value of the distribution function. Now we can proceed integration to obtain contribution from all excited nuclei.

$$M_{\perp}(t) = \int_{-\infty}^{\infty} M_{\perp}(0) e^{-(\frac{1}{T_2} + i(\omega - \bar{\omega}_0 - x))t} g(x) dx \quad (5.60)$$

Function $g(\omega_0)$ is schematically shown in the Figure (5.5).

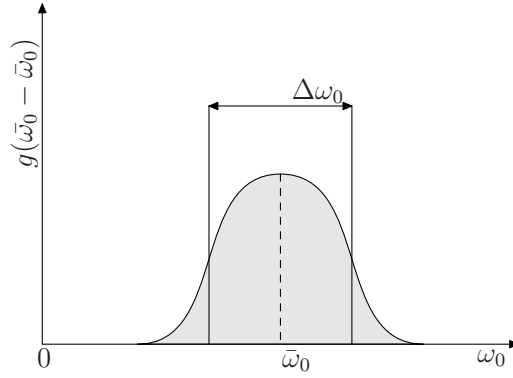


Figure 5.5: Distribution function $g(\omega_0 - \bar{\omega}_0)$, $\Delta\omega_0$ is a width in half of maximum of the distribution function.

The Expression (5.60) can be rewritten to

$$M_{\perp}(t) = M_{\perp}(0) e^{-(\frac{1}{T_2} + i(\omega - \bar{\omega}_0))t} \int_{-\infty}^{\infty} e^{ixt} g(x) dx = M_{\perp}(0) e^{-(\frac{1}{T_2} + i(\omega - \bar{\omega}_0))t} G(t), \quad (5.61)$$

where

$$G(t) = \int_{-\infty}^{\infty} e^{ixt} g(x) dx. \quad (5.62)$$

Function $G(t)$ is a Fourier transform of the distribution function $g(\omega_0)$. NMR spectrometer detects the signal which is proportional to the $G(t)$ function. After excitation with a $\frac{\pi}{2}$ pulse spins are dephased and the signal called Free Induction Decay (FID) occurs.

3. In the third region there is again the alternating field $\vec{B}_1$ during time $\tau_3 \ll T_1, T_2$. The solution of Bloch equations has same the form as in the first region

only the initial conditions are different. If $\tau_3\omega_1 = \pi$ the pulse is called a π pulse. Nuclear spins in resonance are rotated by 180° around x axis during this pulse, see [Slic1990].

4. In the last region there is no magnetic field $\vec{B}_1$ applied and solution is similar to solution in the second region. For the in-plane components of magnetization the following expression is valid:

$$M_{\perp}(t) = -iM_0 e^{-(\frac{t}{T_2} + i(\omega - \omega_0))t} \int_{-\infty}^{\infty} \exp^{-ix(t-2t_2)} g(x) dx. \quad (5.63)$$

Nuclear spins are coherent at time $t_e = 2t_2$, see Figure (5.6), and one can detect the spin echo signal. Using the spin-echo technique one can detect signal in cases when the FID signal is lost due to recovery time of the receiver (detector) after the first pulse (Figure 5.7). Disadvantage of the spin echo method is that the signal amplitude decreases with time due to transverse relaxation, i.e. $Ampl. \sim e^{\frac{2t_2}{T_2}}$. In the case of sufficiently long T_2 , multipulse sequences generating large number of echoes (Carr-Purcell series) can be used. Usage of such a pulse sequence significantly decreases the time of measurement.

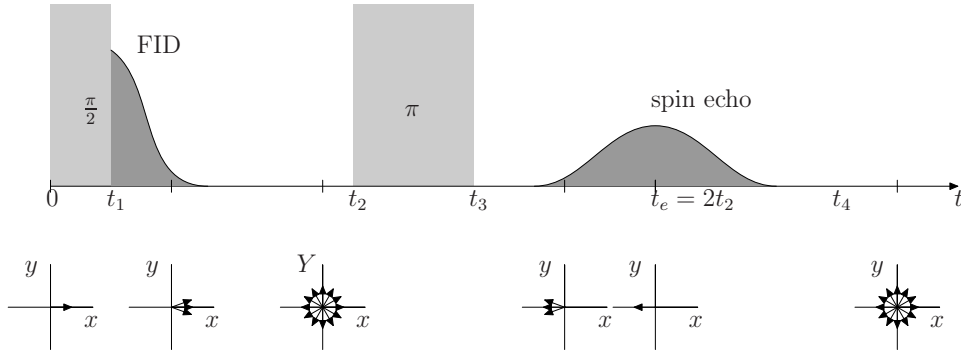


Figure 5.6: Spin-echo sequence.

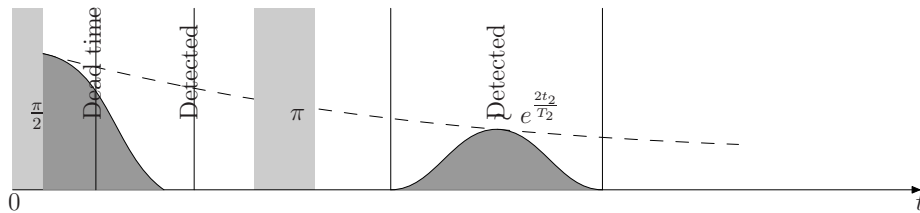


Figure 5.7: Illustration of truncated FID detection limited by the dead time of the receiver.

Spin-echo pulse sequence (described above) is the simplest one and there are many other sequences with different number and lengths of pulses which can be used by researcher. Few other pulse sequences are described in [Sedl1977], [Slic1990]. However, the spin-echo pulse sequence is the most frequently used and is a very important in material research mainly in magnetically ordered materials, which can have very short decay of FID signal.

In liquids all nuclei can be excited by a single pulse, because spectral lines are relatively narrow and the condition $\Delta\omega_0 \ll \gamma B_1$ is fulfilled for all nuclei.

Different situation occurs for magnetically ordered solid state materials which usually have very broad spectral lines and a single pulse can not excite all nuclei. Therefore, broad spectral lines are measured usually by sweeping the frequency in the whole measured range. The frequency swept spectrum is being measured point by point (it will be explained in more details in chapter 7).

5.6 NMR in magnetically ordered materials

NMR spectroscopy in magnetically ordered materials has a few characteristic features. Nuclei are influenced by the effective magnetic field $\vec{B}_{ef}$, which consist of several contributions. Usually the biggest contribution is the hyperfine field $\vec{B}_{hf}$.

Next contribution is the dipolar field $\vec{B}_{dip}$, which is an interaction with surrounding magnetic ions. The total effective field $\vec{B}_{ef}$ contains also external magnetic field $\vec{B}_0$. Effective magnetic field $\vec{B}_{ef}$ can be expressed as:

$$\vec{B}_{ef} = \vec{B}_{hf} + \vec{B}_{dip} + \vec{B}_0. \quad (5.64)$$

Due to spontaneous magnetic ordering in magnetic materials the effective magnetic field $\vec{B}_{ef}$ is non-zero even if the external magnetic field is zero, i.e. the NMR signal can be detected also without external magnetic field and the magnetic hyperfine field at the nuclei can be studied by NMR.

Another characteristic feature is the enhancement effect. Electron shell is influenced by the B_1 field and magnetic moments of electrons quasistatically follow B_1 . The induced electronic field B_2 is much higher than B_1 . This effect is described by enhancement factor η

$$\eta = \frac{B_2}{B_1}, \quad (5.65)$$

where B_2 is the amplitude of total radiofrequency (rf) field acting on nucleus and B_1 is the amplitude of external rf field, see [Sedl1977]. Condition

$$\frac{\pi}{2} = \gamma B_2 \tau = \gamma B_1 \tau \eta. \quad (5.66)$$

has to be fulfilled for the excitation $\frac{\pi}{2}$ pulse (τ is the pulse length) . The enhancement factor for nuclei in domains is given by expression, [Sed1977]:

$$\eta = \frac{B_{ef}}{B_0 + B_A}, \quad (5.67)$$

where B_A is the effective anisotropy field and B_0 is the external magnetic field. The enhancement factor for nuclei in magnetic domain walls is given by expression:

$$\eta = \pi c \frac{M_\alpha B_{ef}}{\delta} \cdot \frac{1}{\nu[(\Omega^2 - \omega^2) + (\frac{\beta}{\nu}\omega)^2]^{\frac{1}{2}}}, \quad (5.68)$$

where ν , β and Ω are parameters describing the the domain wall dynamics, M_α is the magnetization in neighboring domain, δ is the wall thickness and c is the domain wall type constant. From expression (5.68) one can conclude that the enhancement factor for nuclei in domain walls has strong frequency dependence.

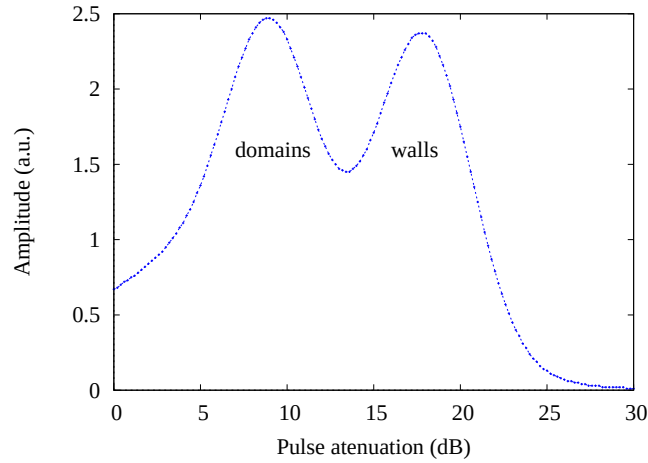


Figure 5.8: Illustration of signals from nuclei in domains and from domain walls measured with different excitation conditions.

The enhancement factor is usually different for nuclei in domains and in domain walls which gives us an opportunity to separate signal of nuclei in the domains from signal of nuclei in domain walls. According to formula (5.66) the amplitude of a high frequency magnetic field $\vec{B}_1$ could be chosen to excite only nuclei in domains or in domain walls (see Figure 5.8).

More details about NMR in magnetic materials could be find in [Wink1981], [Guim1998].

Chapter 6

NMR spectrometer

The spectrometer used in this work is a system based on a commercial BRUKER AVANCE high-resolution console with special customer configuration. The original apparatus was adapted to cover broad frequency range needed e.g. for experiments in magnetically ordered materials. With the present configuration, suitable for NMR in magnetically ordered materials, the spectrometer is used as a single channel device in both transmitter and receiver sections and it covers frequency range of 6–600 MHz, with rf power of 500 W up to 365 MHz, and 300 W for higher frequencies.

The spectrometer performs a coherent summation (averaging) of NMR signals in the time domain for preset number of scans which enables to have a high sensitivity and to detect signals of very low intensity. Minimal time delay between end of a radio-frequency pulse and the start of data acquisition (detection) is about 5 μ s, which allows to carry out measurements of samples with correspondingly short spin-spin relaxation time T_2 . Effective values of the minimal delays may be increased depending on the pulse decay time in the resonant circuit/coil and on NMR signal intensity and used configuration.

An integral part of the spectrometer is a spectrum analyzer (wobbler) unit with tuning and matching display which serves mostly for measurements of low frequency NMR spectra (up to 200 MHz) where the NMR probe with a tunable resonant circuit can be easily used. For the higher frequencies and broad spectra, the untuned probe heads are commonly used.

6.1 Description of spectrometer construction

Main components of the spectrometer are presented in a scheme given in Figure 6.1. The transmitter line consists of two synthesizers - Signal Generation Units (SGU units) with frequency range of 6–1000 MHz each. The phase, amplitude and frequency are generated by Direct Digital Synthesis (DDS). SGU provides $< 0.05^\circ$

phase resolution, < 0.05 Hz frequency resolution and include a wave form memory of frequency, amplitude and phase of the pulse. As a result, SGU generates rf voltages with all desired characteristics for excitation pulse sequence so that the output of the SGU produces a miniature pattern of the final transmitted signal.

The low level high frequency pulses from the SGU unit are amplified in the rf power amplifier. Two linear power amplifiers (transmitters) are implemented in the spectrometer: BLAX 500 (500 Watt) which works in a frequency range of 6–365 MHz, and BLAH 300 (300 Watt) in a frequency range of 200–600 MHz. Blanking pulses are used to close the amplifier during times when no rf pulses are transmitted.

rf pulses of appropriate power are transmitted from the power amplifier via transmitter-receiver (T/R) switch (integrated in a multilink HPPR/2 unit) to the probe coil. The switch protects the receiver input during excitation pulses and disconnects the transmitter line during data acquisition to decrease a noise from the transmitter line. The probe coil serves as an excitation coil and a pick-up (detection) coil.

SGU generates also the Local Oscillator (LO) frequency for mixing procedure in the receiver line. In a configuration when acquisition is performed during only one time interval during a scan (e.g. in the case of a simple spin-echo sequence) only one SGU unit may be used both for excitation and LO frequencies. When the signal is acquired during more time intervals within one scan (e.g. monitoring of many spin echoes in the case of the Carr-Purcell multi-pulse series and their coherent summation) both SGU units are employed to reach the necessary rapid flexibility.

The NMR signal detected by the probe coil is processed in the receiver line. The signal proceeds to the multilink HPPR/2 unit with the above mentioned T/R switch and a broadband low noise HP-preamplifier. For measurements of magnetically ordered materials such as in this thesis a receiver (RXBB) with extended band width of 5 MHz is used. The signal is mixed with a Local Oscillator (LO) frequency (LO is by high intermediate frequency IF of 720 MHz above the excitation frequency).

The output signal, i.e. an NMR signal converted close to the Intermediate Frequency (IF) 720 MHz, is filtered by the IF filter and amplified with an adjustable gain. The amplified signal is then quadrature detected. Digital quadrature detection (DQD) using Slow AD Converter SADC and oversampling option is limited to 25 kHz band. Therefore analogous quadrature detection mode is typically used for broad spectral lines, in connection with the fast digitizer (FADC, 12 bit digitizer, 10 MHz sampling rate). Before digitizing of the signals from the two quadrature detection channels I, Q, analog bandwidth is reduced with a low pass filter system ('anti-aliasing' filter, adjustable bandwidth 0.125–4 MHz). The digitized data (after a coherent summation) is transferred to the NMR PC workstation and stored there.

The computer controlling the spectrometer includes a complete acquisition computer system (communication control unit (CCU) and the spectrometer specific function boards TCU (Timing Control Unit), FCU (Frequency Control Unit) and

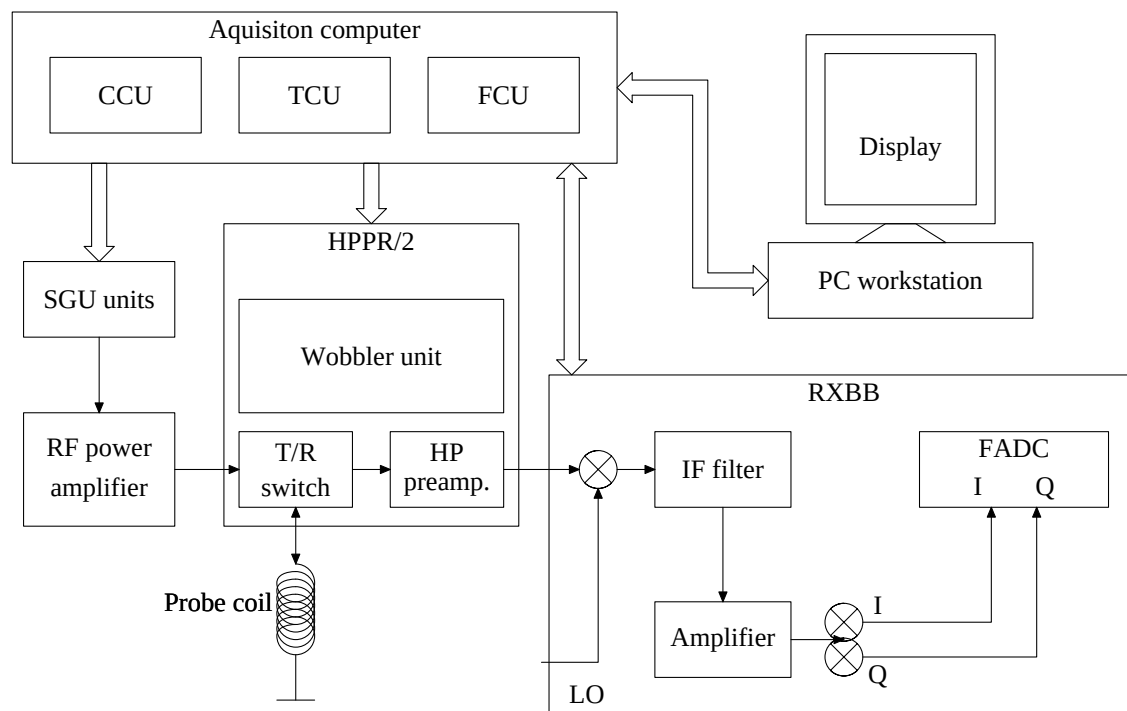


Figure 6.1: Concept diagram of Bruker AVANCE spectrometer used for NMR measurements. For details and abbreviations – see the text.

Receiver Control Unit (RCU)).

Timing control unit (TCU) is a pulse programmer which provides the exact timing and flexibility in data acquisition with 12.5 ns timing resolution, controlled by a fast RISC processor. The TCU generates real time clock pulses for the spectrometer. Based on this clock, the FCU and the RCU real time system runs synchronously, so the time synchronization between the transmitter system (TCU, FCU) and the receiver system (RCU) is maintained.

Communication Control Unit (CCU) with a high speed RISC processor, 16 MB memory, dedicated Fast Ethernet and RS-232 connection ports is responsible for communication with the NMR PC workstation operated by the operator.

Pulse programs, acquisition and processing parameters are set by the operator from the PC using either directly the original XWINNMR Bruker software display, or by means of the special software, developed for measuring frequency swept spectra, see chapter 8. Excitation frequency is changed in the spectral range with a proper step and for each step the NMR signal is measured, accumulated and stored. Evaluating of frequency swept spectra is based either on the Fast Fourier Transformation (FFT) of the time domain data for each exciting frequency by taking magnitudes of FFT at different excitation frequencies or constructing an envelope

of FFT magnitude functions obtained for individual excitation frequencies. Alternatively one can analyze the amplitude or integral of the spin echo at each excitation frequency which are plotted vs. excitation frequency.

A schematic concept diagram of the NMR spectrometer is shown in Figure 6.1.

Chapter 7

NMR technique and developed modifications for broad line measurements

During the sixty years long history of the NMR spectroscopy this technique became a very important analytical tool in physics, chemistry, biology and medicine. At the present time various very sophisticated NMR pulse spectrometers are commercially produced that can be used for some substances (diamagnetic liquids, diamagnetic solids and also some liquids with paramagnetic particles) in which NMR spectra are narrow enough to be excited at one frequency (see e.g [Abra1961]).

In the pulse NMR technique samples under investigation are exposed to rf pulses of magnetic field B_1 of several microseconds duration. The well excited spectral range is given by the Fourier transformation of the excitation pulse. The Fourier transform of a rectangular rf pulse with the length τ has a form (see Figure 7.1)

$$F(\omega) \sim \frac{\sin(\frac{\tau(\omega-\omega_{rf})}{2})}{\frac{\tau(\omega-\omega_{rf})}{2}}. \quad (7.1)$$

Nuclei are homogeneously excited only if their resonant frequencies are within the range where the amplitude of the Fourier transform of a rf pulse is close to the maximum value. For example pulse of 10 μ s duration can properly excite NMR spectrum in frequency range shorter than approximately 0.02 MHz.

In magnetically ordered materials the widths of spectral lines vary typically from 1 kHz to 100 MHz and NMR spectra can cover a very broad frequency range (from 1 MHz to 1 GHz). Therefore, NMR measurements at a zero or fixed external magnetic field must be carried out with a frequency sweep in the whole measured frequency range and the total spectrum is constructed from all measurements at particular frequencies. If the frequency step does not exceed the well excited spectral

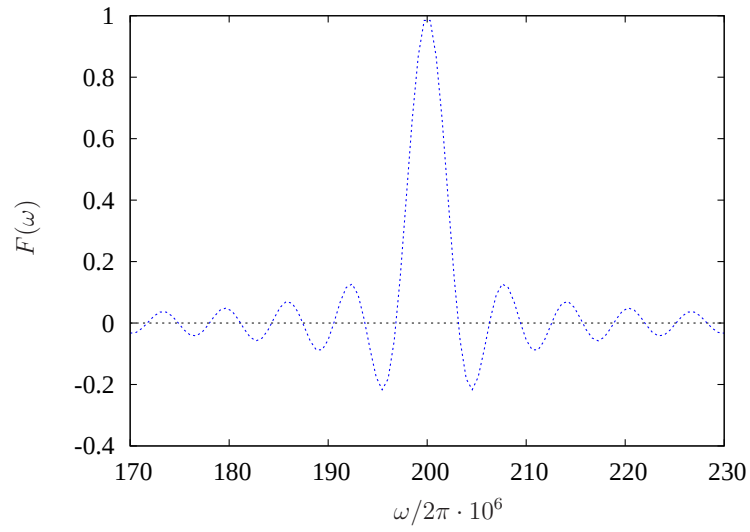


Figure 7.1: Fourier transform of a rectangular pulse at ω_{rf} . The formula is $FT(f(t)) \sim \frac{\sin(\frac{\tau(\omega - \omega_{rf})}{2})}{\frac{\tau(\omega - \omega_{rf})}{2}}$, $\tau = 1\mu s$. Only a narrow range close to pulse frequency is well excited.

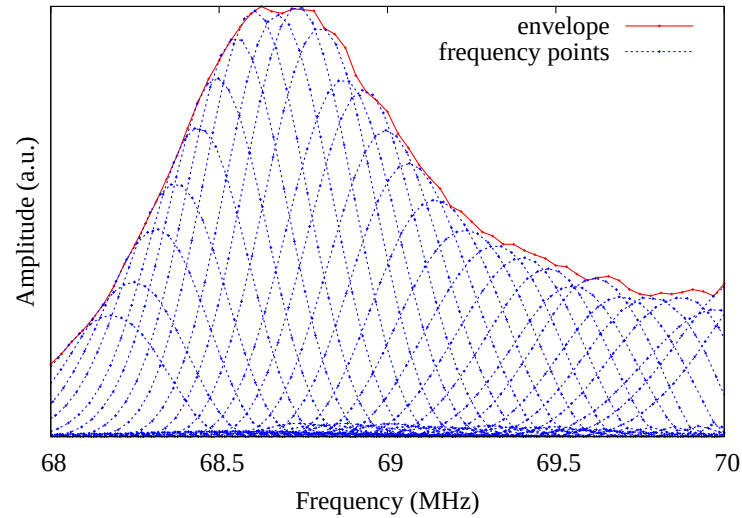


Figure 7.2: Example of a broad frequency swept spectrum measurement.

range the spectrum construction can be based on the Fourier transform (FT) performed for each measured frequency and then an envelope of obtained FT functions (in magnitude mode) is evaluated; see Figure 7.2.

The second possibility for obtaining NMR spectrum is plotting the maximum of the Fourier transform of the spin echo versus the excitation frequency. This

method is suitable for very broad spectra with very small or zero overlap of Fourier transforms for each excitation frequency (see Figure 7.3).

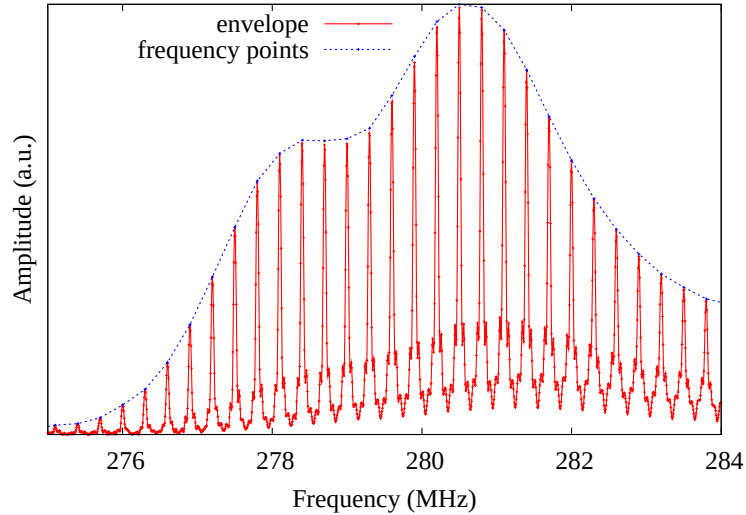


Figure 7.3: A broad frequency swept spectrum measurement measured point by point.

A wide frequency range and broad spectral lines create strong demands for frequency stability of all components of the NMR spectrometer, probe head and connecting cables.

In this chapter several important aspects of NMR measurements are analyzed and discussed. In the beginning the behavior of electromagnetic waves in coaxial lines is briefly described, this is necessary because coaxial lines are used in all NMR spectrometers and understanding their properties is crucial for NMR experimentalist. In the following paragraphs of this chapter the suggested approach to the measurements of broad spectra using broad band (untuned) probe are described and their verification is given.

7.1 Principles of NMR measurement

7.1.1 Telegraphic equation

Let us consider infinitely long coaxial line oriented in the z -axis. Its electrical properties are described by inductance per unit length L_l , capacitance per unit length C_l , transversal conductivity per unit length G_l (which includes also losses in dielectric) and resistivity per unit length R_l (which is influenced by skin effect). The relations between voltage $U = U(z, t)$ and current $I = I(z, t)$ along the line are described in

CHAPTER 7. NMR TECHNIQUE AND DEVELOPED MODIFICATIONS FOR BROAD LINE

quasistationary approximation by the equation (see e.g. [Stra1957])

$$\begin{aligned}\frac{\partial U}{\partial z} &= -L_l \frac{\partial I}{\partial t} - R_l I, \\ \frac{\partial I}{\partial z} &= -C_l \frac{\partial U}{\partial t} - G_l U.\end{aligned}\tag{7.2}$$

For harmonic wave with frequency ω follows that $U(z, t) = U_m(z)e^{i\omega t}$, $I(z, t) = I_m(z)e^{i\omega t}$. After differentiation we get so called telegraphic equation [Stra1957]

$$\begin{aligned}\frac{d^2 U_m}{dz^2} &= \vartheta^2 U_m, \\ \frac{d^2 I_m}{dz^2} &= \vartheta^2 I_m,\end{aligned}\tag{7.3}$$

where the quantity $\vartheta^2 = (i\omega L_l + R_l)(i\omega C_l + G_l)$ is the constant of propagation which in general is a complex number; therefore it can be written as $\vartheta = \alpha + i\beta$. For lossless line R_l and G_l can be neglected in comparison to $i\omega L_l$ and $i\omega C_l$ and we obtain

$$\begin{aligned}\vartheta^2 &= -\omega^2 L_l C_l, \\ \vartheta &= i\beta = i\omega \sqrt{L_l C_l}.\end{aligned}\tag{7.4}$$

For more realistic situation with low R_l and G_l the expression for ϑ can be expanded in power series. Considering only the first three terms of the expansion the expression in (7.4) yields

$$\begin{aligned}\alpha &\simeq \frac{1}{2} \left[R_l \sqrt{\frac{C_l}{L_l}} + G_l \sqrt{\frac{L_l}{C_l}} \right], \\ \beta &= \omega \sqrt{L_l C_l}.\end{aligned}\tag{7.5}$$

In several cases also G_l can be neglected because it is smaller than R_l and α and β can be expressed in the form

$$\begin{aligned}\alpha &\simeq \frac{R_l}{2} \sqrt{\frac{C_l}{L_l}} \\ \beta &= \omega \sqrt{L_l C_l}.\end{aligned}\tag{7.6}$$

General integral of telegraphic equation for coaxial line is a superposition of two attenuated linear waves with opposite direction of propagation. For harmonic wave with a frequency ω the amplitude $I_m(z)$ of current of the line can be expressed as

$$I_m(z) = C_1 e^{-\vartheta z} + C_2 e^{\vartheta z}.\tag{7.7}$$

CHAPTER 7. NMR TECHNIQUE AND DEVELOPED MODIFICATIONS FOR BROAD LINE

Using equation (7.2) we can calculate from (7.7) the amplitude $U_m(z)$ of voltage:

$$U_m(z) = Z_0(C_1 e^{-\vartheta z} - C_2 e^{\vartheta z}), \quad (7.8)$$

where the quantity

$$Z_0 = \sqrt{\left(\frac{R_l + i\omega L_l}{G_l + i\omega C_l} \right)} \quad (7.9)$$

is a characteristic impedance of the line and in general it is a complex number. For a dissipationless line the characteristic impedance is real number and is given by

$$Z_0 = \sqrt{\frac{L_l}{C_l}}. \quad (7.10)$$

Now we shall discuss situation when the probehead with impedance Z_p is connected by a coaxial line with characteristic impedance Z_0 and length d to the source of a harmonic electromotive voltage $\epsilon(t) = \epsilon_m \cos(\omega t)$ with internal impedance Z_i . The relation between the amplitude of electric current I_m and the amplitude of voltage $U_m(0)$ at the beginning of the coaxial line is given by relation

$$\epsilon_m - Z_i I_m(0) = U_m(0). \quad (7.11)$$

On the other hand the relation between the voltage $U_m(d)$ and current $I_m(d)$ at the end of the line can be written as

$$Z_p = \frac{U_m(d)}{I_m(d)} = Z_0 \frac{C_1 e^{-\vartheta d} - C_2 e^{\vartheta d}}{C_1 e^{-\vartheta d} + C_2 e^{\vartheta d}}. \quad (7.12)$$

For constants of integration C_1, C_2 , that can be determined from boundary condition at the beginning and at the end of the line, we obtain $C_1/C_2 = \Gamma_d \exp(-2\vartheta d)$, $C_1 = \epsilon_m/(Z_i + Z_0)$. Reflection coefficient Γ_d describes the ratio of a forwarded and reflected wave and is given by the relation

$$\Gamma_d = \frac{Z_0 - Z_d}{Z_0 + Z_d}. \quad (7.13)$$

When $Z_i = Z_0$ we get the result

$$I_m(d) = \frac{\epsilon_m}{2Z_d} (1 - \Gamma_d) e^{-\vartheta d}. \quad (7.14)$$

We can give a summary of the performed discussion. The electromagnetic wave generated by the source of voltage propagates forward in the line and due to inequality $Z_0 \neq Z_d$ it is partially reflected at the terminating element. The reflected

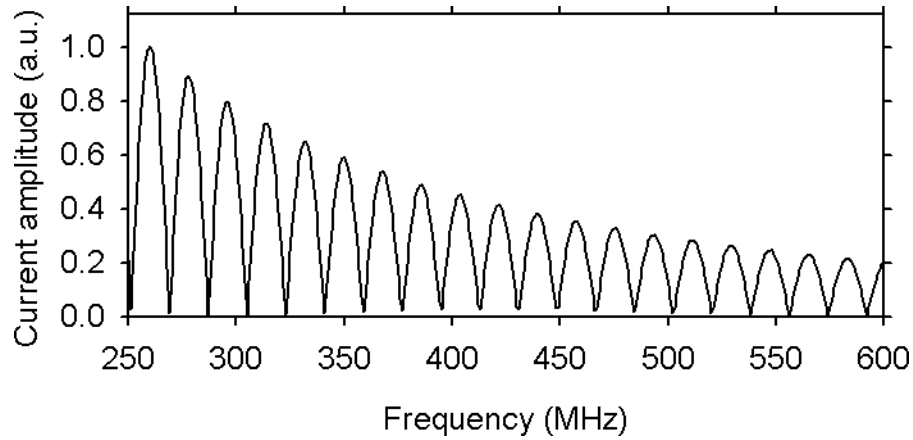


Figure 7.4: Modelled frequency dependence of probehead current.

wave propagates in the opposite direction and superposes with the wave which propagates forward. The superposed forward and reflected waves create standing waves in the cable. The amplitude of the standing wave $I_m(z, \omega)$ depends on position z and frequency ω . The current $I_m(d)$ at the end of the line is a periodic function of the frequency according to equation (7.14). An example displayed in Figure 7.4 is calculated for a line with parameters $d = 4.2$ m, $Z_0 = 50$ Ω , $L_l = 0.005$ $\mu\text{H}/\text{m}$, $C_l = 800$ pF/m, $G_l = 100$ $\mu\text{S}/\text{m}$, $R_l = 178$ $\mu\Omega/\text{m}$, connected to source with $Z_i = 50$ Ω and loaded by $Z_p = R_p + i\omega L_p$, $R_p = 16.6$ Ω and $L_p = 0.4$ μH .

From (7.14) it is very easy to calculate the period P_f of the current oscillations in Figure 7.4. We obtain

$$P_f = \frac{c}{d\sqrt{\epsilon_r}}, \quad (7.15)$$

where c is the speed of light in vacuum and ϵ_r is the relative permittivity of cable isolation.

More details about physical properties of rf electromagnetic field could be find in [Kvas1957], [Scot1966], [Vrba1958].

7.1.2 Probe head principles, impedance matching

The rf field $\vec{B}_1$ is generated by a coil, which can be a part of resonant LC circuit connected to a source of a harmonic voltage. Magnetic field B_1 is proportional to the electric current I in the coil, where I is given by the Ohm's law

$$I = \frac{U}{Z}, \quad (7.16)$$

where U is a voltage on the coil and Z is impedance of the coil.

CHAPTER 7. NMR TECHNIQUE AND DEVELOPED MODIFICATIONS FOR BROAD LINE

LC resonant circuit consists of a coil with inductance L and parallel connected capacitance C . Such a resonant circuit is characterized by resonant frequency:

$$\omega_{LC} = \frac{1}{\sqrt{LC}} \quad (7.17)$$

and by the Q factor, which is defined as:

$$Q = \frac{\omega_0}{\Delta\omega} \quad (7.18)$$

where $\Delta\omega$ is a width of the circuit resonant curve.

Now let us discuss a situation when the resonant circuit with impedance Z_{LC} and resonance frequency ω_0 is connected to the source of a harmonic voltage with frequency ω and the coaxial line has a characteristic impedance Z_0 . Impedance Z_{LC} is given by:

$$Z_{LC} = \frac{1}{i\omega L - \frac{i}{\omega C}} \quad (7.19)$$

When the impedance $Z_0 = Z_{LC}$ (the LC circuit is matched to the coaxial line) there is no reflected wave in the line. Maximal amplitude of B_1 in the coil is reached when the circuit is in resonance with the applied electromagnetic field, i.e. $\omega_0 = \omega$.

In the case when the resonant circuit is not matched, i.e. $Z_0 \neq Z_{LC}$ the standing waves are present in the line, like it is described in chapter 7.1.1. The amplitude of electric current I_m , described by equation (7.14), where quantity Z_d is now replaced by Z_{LC} , has an oscillating character, which is mainly given by the exponential term with ϑ . Supposing lossless line the constant ϑ is pure imaginary number and $\vartheta = \omega/v$, where v is a electromagnetic wave velocity in the line. The frequency difference $\Delta\omega$ at two minima of I_m is for a given length of the line d given by equation:

$$\frac{\Delta\omega d}{v} = 2\pi \quad (7.20)$$

then

$$\Delta\omega = \frac{2\pi v}{d} \quad (7.21)$$

and for ν

$$\Delta\nu = \frac{v}{d}. \quad (7.22)$$

$$\omega = 2\pi\nu \quad (7.23)$$

In the case of a commonly used coaxial line with PTFE as a dielectric material ($\varepsilon_r = 2$) and $d = 5\text{m}$, $\Delta\nu$ is around 42 MHz, therefore the amplitude of B_1 field changes from a maximal to minimal value in the frequency interval 21 MHz.

When the range of measured frequencies is comparable to $\Delta\nu/2$ the amplitude of B_1 field changes significantly and this fact has to be taken into account during analysis procedure of measured data.

7.2 Broad line measurement

The radiofrequency (rf) magnetic field $\vec{B}_1$, which excites transitions between nuclear energy levels (due to which we observe the NMR signal) is usually produced by a coil as it was mentioned in a previous chapter. The coil with the sample is fixed to the probe head, which is constructed to allow carrying out measurements in specific physical conditions (e.g. in external magnetic field, at specific temperature, pressure, etc.).

Probehead usually consists of a top part where connectors are situated together with the end of a rod for tuning capacitor of the LC circuit (in case of tuned probe head), the middle part which is made of a long stainless steel tube with leads of coaxial lines from connectors to the resonance circuit and the bottom part with the coil and the resonant circuit. A schematic diagram of the probehead can be shown in Figure 7.5.

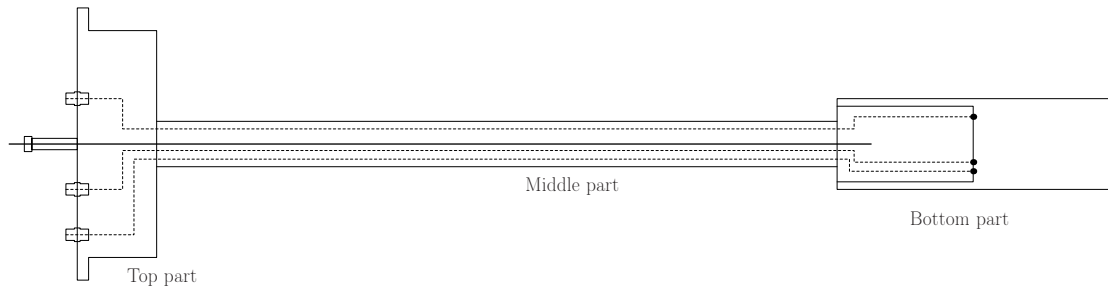


Figure 7.5: A schematic diagram of the probehead for NMR experiments. Top part - handle of connectors and a rod for tuning (in case of tune probehead), Middle part - usually stainless steel tube leading coaxial lines, Bottom part - handler for resonance circuit with sample.

Construction of the tunable resonance circuit working above 200 MHz and in wide frequency range is complicated and therefore it is necessary to find a suitable experimental approach. Sufficient solution for such experiments is to use an untuned probehead.

If we have only a coil in the probehead instead of the LC circuit, the resonant frequency of the coil is very high (GHz). Therefore, the measurement is performed on a "tail" of the resonant curve of the coil, where the curve is very flat. The impedance of the circuit is not matched to the transmitter line at the measured frequencies. A schematic diagram of the untuned probehead circuit is shown in Figure 7.6.

Situation when impedance of the circuit is not matched to the impedance of the line is described in the chapter 7.1.2. Standing wave occurs in the line and its period $\Delta\nu$ expressed by (7.22) for a coaxial line with $\varepsilon_r = 2$ (PTFE) amounts to 42.6 MHz, for a coaxial line with losses this period can be even smaller. The amplitude of the electric current in the resonant circuit is given by expression (7.14)

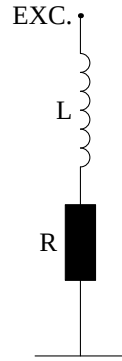


Figure 7.6: Untuned resonance circuit, suitable for measuring broad frequency swept spectra, L - resonance coil, R - resistor, EXC. point where the resonance circuit is connected to the NMR spectrometer.

and it changes from minimal to maximal value with period ranging from several MHz to tens of MHz. This effect influences the reliability of measurements, a solution of this problem is described in chapter 7.3.

The coil during detection of the NMR signal is a source of electromotive voltage ϵ_m with impedance Z_i and induction L_i which are frequency dependent this has a negative effect on the reliability of measurements. The frequency dependence of the receiver line is presented in chapter 7.3.

7.3 Procedures for broad band measurements

As mentioned above it is more convenient to use a broadband untuned probehead for measurements of very broad NMR spectra, especially at frequencies higher than ~ 200 MHz. Several aspects and measurement procedures of broad-band NMR experiments in magnetically ordered materials were reported, i.e. [Lord1995], [Darr1993], [Rosc2000], [Kubo2003]. We shall describe important experimental aspects of using such a probehead and also our experimental approach which was developed to ensure constant amplitude of rf field B_1 and frequency independent sensitivity of receiver section in the whole measured frequency range.

The basic diagram of the probehead used in our approach and its connection to spectrometer is shown in the Figure 7.7a. The probehead consists of a coil and a resistor. The coil made of copper wire is constructed so that the sample fits to it tightly to ensure high filling factor. Typically, the coil has 5–15 turns and 5 mm in diameter. The inductance of such coil is about $1 \mu\text{H}$ and the impedance at frequency 300 MHz is about $3 \text{ k}\Omega$; the role of resistor $R = 50 \Omega$ will be explained in the following text. As it is necessary to measure in cryostats and cryomagnets with rather high magnetic fields the probehead is connected to the spectrometer

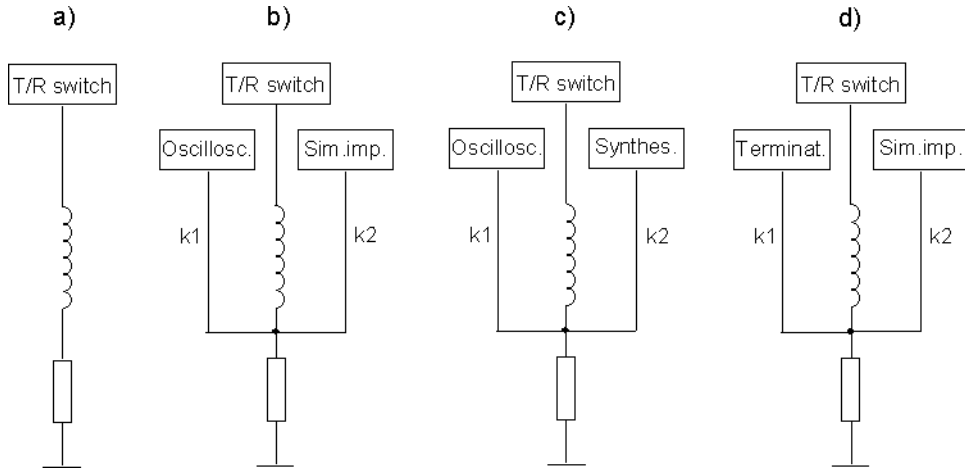


Figure 7.7: Schematic diagram of untuned probehead (a) and its connection to spectrometer. Configurations (b-d) are described in text. (T/R switch - transmitter/receiver switch, Oscillosc. - digital high frequency oscilloscope, Synthes. - input of power amplifier, see Figure 7.8, Terminat. - $50\ \Omega$ coaxial resistor, Sim. Imp. - element simulating the output impedance of synthesizer.)

by coaxial lines with impedance Z_0 . For practical purposes of calibration the basic diagram of the probehead and its functions is modified - see Figure 7.7b–7.7d.

7.3.1 Calibration and correction of transmitter section

The possibility to adjust well-defined (e.g. constant) rf field amplitude B_1 (and therefore also the electric current amplitude in the coil) is required in a whole measured frequency range. The aim of this experimental approach is to ensure this condition.

Primarily, we tested the frequency dependence of the voltage amplitude both at the input and output of the power amplifier with a constant attenuation in transmitter section, the results are given in the Figure 7.8. While the frequency dependence of the voltage at the input of power amplifier (curve a) is weak, the output voltage depends strongly on frequency (curve b). For example the amplitude at 270 MHz is higher than that at 550 MHz by factor of two.

Actual calibration process of the transmitter section begins with measurement of the current in the probe in configuration after Figure 7.7b. The probe is connected by a coaxial line with characteristic impedance Z_0 to the source of electromotive voltage represented by the power amplifier. Since the coil and the resistor are connected in series we assume that (in the quasistationary approximation) the current amplitude in the coil equals to the current amplitude in the resistor. Therefore we can measure the voltage on the resistor which is proportional to the current. The

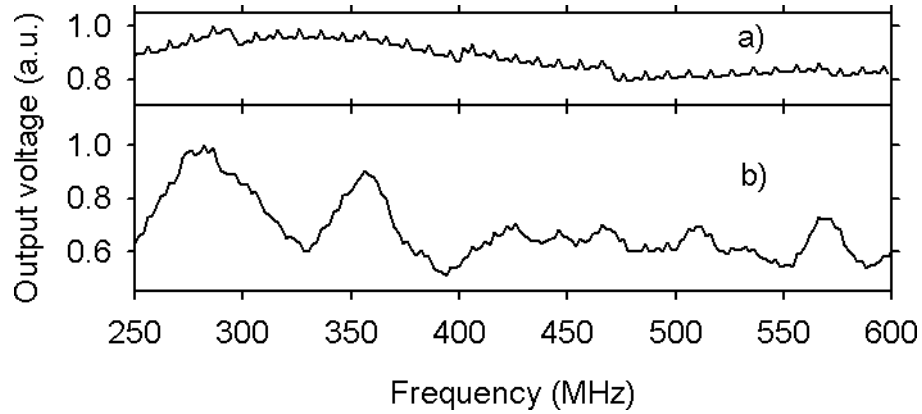


Figure 7.8: Frequency dependence of voltage; a) input voltage of power amplifier, b) output voltage of power amplifier.

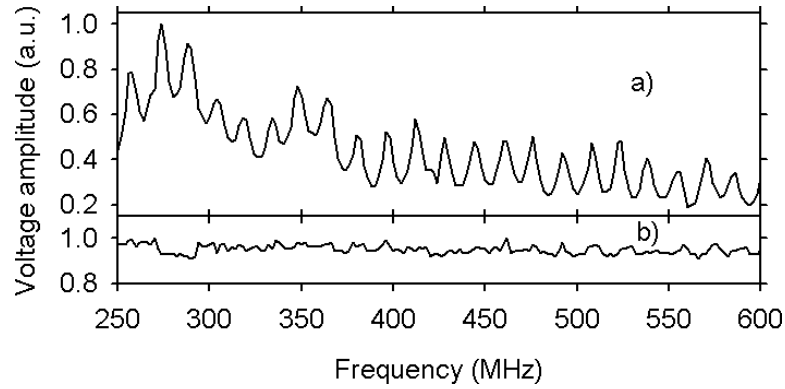


Figure 7.9: Frequency dependence of voltage on resistor in the probe (scheme on Figure 7.7b); a) before corrections, b) after corrections.

probe is fed by the power amplifier connected via transmitter/receiver (T/R) switch and the amplitude of the voltage on the resistor is detected by the line k1 using the oscilloscope. The line k2 is terminated by element "Sim. Imp." with impedance equal to that of the synthesizer in order to maintain identical conditions during calibration processes and spectrum measurement.

The results are given in the Figure 7.9a. From the dependence it follows that amplitude of rf field $\vec{B}_1$ would differ substantially for different frequencies within the spectral range. Oscillations due to standing waves appear in the frequency dependence in addition to the curve in Figure 7.8b. As the amplitude of rf pulses is controlled by adjustable attenuator in the transmitter section we can adjust the attenuator according to the dependence of the (curve a) at each frequency point.

This way we can ensure a constant level of the rf field in the coil. In Figure 7.9b the voltage amplitude on the $50\ \Omega$ resistor after such correction is shown; the voltage level is constant in the whole measured frequency range. The disadvantage of such procedure is that part of the power is "cut off" as we have to set some "base" level of the $\vec{B}_1$ field for adjusting the attenuator in the transmitter section and the base level is given by the minimum in the frequency dependence.

Now we are able to excite the whole frequency range with a constant rf field amplitude (or programmed in any demanded way) and we can also compare optimal excitation conditions found at different frequencies.

7.3.2 Calibration and correction of receiver section

The rf receiver section consists of low noise preamplifier and receiver. The preamplifier and receiver input impedances are matched to $50\ \Omega$ with precision of 5 %.

Our aim is to test the frequency sensitivity of the receiver line in order to ensure undistorted signal intensities within the measured frequency range. In order to obtain frequency dependent signal proportional to the sensitivity we simulate the detection process. We apply a frequency independent voltage to the probehead coil and measure the voltage at the output of receiver line that should be proportional to the sensitivity of the receiver section.

Application of a voltage with constant amplitude to the resonant coil can be achieved in two steps. In the first step we have to correct the frequency dependence of the voltage at the resistor when k2 is reconnected to the synthesizer via attenuator in the transmitter section. Then the amplitude of voltage in the cable k1 is measured by oscilloscope with $50\ \Omega$ input impedance (see Figure 7.7c). We obtain a curve $f(\omega)$ which describes the frequency dependence of the voltage on the probe. An example of such curve $f(\omega)$ is shown in Figure 7.10a. In the second step the attenuator of the transmitting section is adjusted according to the frequency dependence $f(\omega)$ to get constant voltage. An example of a corrected curve $f_{corr}(\omega)$ is shown in the Figure 7.10b.

Now the probehead remains in connection according to the Figure 7.10c and the attenuator of the transmitter section is controlled. The spectrometer is set to a mode that allows to measure the amplitude of continuous waves. The frequency dependence of the voltage amplitude registered by the receiver (without any external signal) characterizes the frequency dependence of the detection line. Such a curve is shown in Figure 7.10c.

Concluding, we found and tested the procedure which allows to measure very broad frequency swept spectra and control the frequency dependence of the sensitivity. For this purpose the procedure of calibrating has to be performed every time when the coil in the probehead is changed or when the sample is replaced.

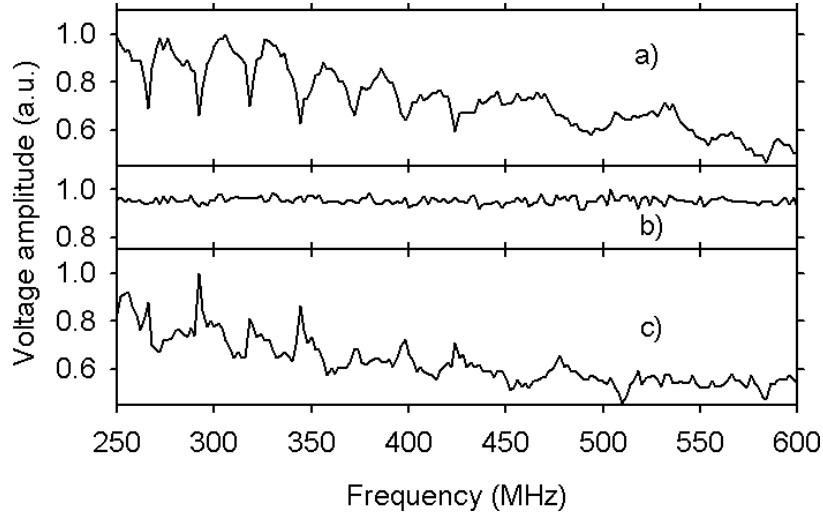


Figure 7.10: Frequency dependence of voltage on resistor (scheme on Figure 7.7c); a) before correction, b) after correction, c) detected by receiver.

7.4 Example of measured spectra

In the Figure 7.11 we illustrate the applicability of the discussed procedure on a frequency swept NMR spectrum of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ compound measured in zero external magnetic field in the frequency range 250–600 MHz. After performing the correction procedures the configuration used for spectra measurement was set according to Figure 7.7d.

As the sample is rather complex the spectrum may contain NMR signals of ^{55}Mn and ^{59}Co nuclei in Mn and Co ions of various valencies and, in addition, several crys-

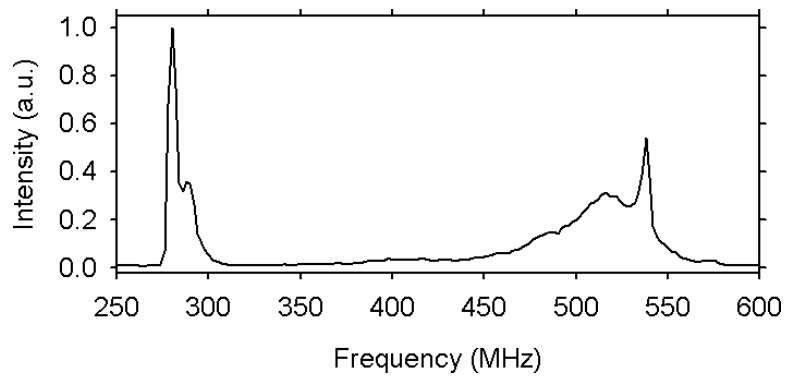


Figure 7.11: NMR spectrum of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ in zero external magnetic field at 4.2 K.

CHAPTER 7. NMR TECHNIQUE AND DEVELOPED MODIFICATIONS FOR BROAD LINE

talline phases may also be present in the sample. Consequently different spectral lines (or broader bands) need different excitation fields (see e.g [Turo1972]). Optimal excitation conditions corresponding to maximal signal were found for each resonance line. The measurement was performed repeatedly with varying the amplitude of excitation pulses. The presented spectrum was obtained as an envelope of the individual measurements.

More detailed information on the approach that we evaluated can be found in [Proc2008].

Chapter 8

Software for NMR data elaboration

There are many software programs dedicated to NMR spectra analysis in high resolution experiments. This software usually is distributed together with the measurement console (i.e. with NMR spectrometer). This software includes many useful and powerful procedures, tools and options for evaluating single and multi-domain NMR experiments, but for analysis on magnetically ordered materials such software can not be used. In order to process and analyze NMR experiments in magnetic materials we developed special software named Emil.

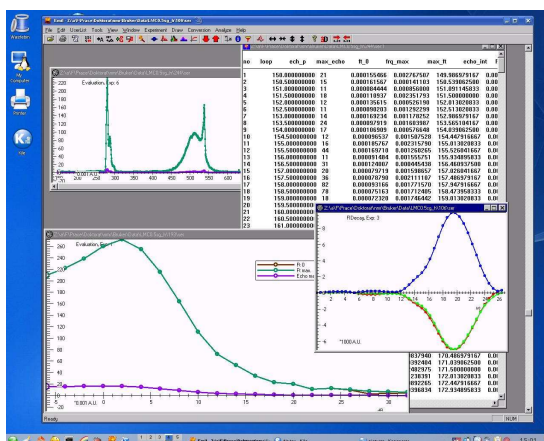


Figure 8.1: Screenshot of Emil software, software developed for NMR measurements analysis.

Emil software was developed in Microsoft Visual C++ 6.0 studio and it is based on Microsoft Foundation Classes (MFC), [Hero2000a], [Hero2000b], [Race1999], [Krug2000], [Viri1997] . Emil is able to import and read data files from the Bruker NMR spectrometer. Three experimental machines were tested, one operated with Microsoft WindowsXP operating system using XWinNMR as measurement software, and two machines operated under RedHat Linux with TopSpin as a measurement

Figure 8.3: Screenshot from Emil, setting the plot parameters

For analyzing spectral lines the fitting procedures are implemented, they allow to fit the measured spectral lines with Gaussian or Lorentzian curves, see the screenshot in Figure 8.2. Additionally it is also possible to fit and calculate relaxation times from measurements.

There is also a simple (user-controlled) phase correction option in the Emil software. The results of analysis can be exported to the ASCII files or plots which are shown on the screen can be printed with or without values of all measurement parameters. For easy manipulation and overview of the NMR results we can control several plotting parameters, see the screenshot in Figure 8.3.

Emil software also has an option to prepare the input file for spectrometer implemented. This input file has inside all necessary values to carry out a measurement using the Bruker Avance spectrometer. Emil produces a text file **userlist** which is read by the Bruker NMR spectrometer operating software which takes parameters from this file. Parameters can for example define the measurement type, number of experimental points, starting value, step of the measurement or parameters which contain information if the measurement will be tuned or untuned.

Although Emil software was designed for Microsoft Windows OS, it is fully operational also under Linux OS using "wine" Windows OS emulator. Working under Linux was tested on the RedHeat and Suse Linux distributions.

Chapter 9

Characterization of samples studied

The thesis focuses on compounds with a perovskite crystallographic structure, where A site is occupied by La and B site by Mn which is partially replaced with Co. The general formula of the compounds studied is given by $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$, where x changes from 0 to 1. Samples were prepared in group of Dr. Zdeněk Jiráček in the department of magnetism in the Physical Institute of the Czech Academy of Science, where also measurements of X-ray diffraction and magnetization measurements were done.

9.1 Sample preparation

Samples were prepared by two methods. The first method used for sample preparation is called a solid state reaction (SR). It is a standard ceramic method based on mixing of carbonates and oxides. Appropriate amounts of powders of reactants were mixed in order to obtain required ratio of La, Mn and Co elements. The mixture was calcined at 900°C in order to achieve decarbonation. The pre-reacted powder was pressed into pellets and then heated in air atmosphere up to 1500°C. Next, the samples were sintered at 1300°C during 40 hours and cooled down to room temperature. Samples with Co content $x \leq 0.4$ were subsequently annealed at 1100°C under vacuum of 10^{-3} mbar for two days in order to get rid of the cation deficiency after sintering in air.

The results of structural and electrical transport properties studies of these samples prepared using the SR method were presented in [Autr2005].

The second method used was a sol-gel preparation process (SG). The starting compounds La_2O_3 , MnCO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were separately dissolved in a nitric acid, mixed together with citric acid and ethylene glycol in the ratio of 1:1.5:2.25, respectively. The pH was adjusted to 9 by addition of NH_4OH . Further steps included evaporation of water at 90 °C, drying at 160 °C and calcination at 400 °C (4

signed by	x	method	additional treatment	comment
0.0-sr-0	0	SR	no	-
0.1-sr-0	0.1	SR	no	-
0.2-sr-0	0.2	SR	no	-
0.2-sr-1	0.2	SR	yes	-
0.2-sg-0	0.2	SG	no	-
0.2-sg-1	0.2	SG	yes	-
0.3-sg-0	0.3	SG	no	-
0.3-sg-1	0.3	SG	yes	-
0.4-sr-0	0.4	SR	no	-
0.4-sr-1	0.4	SR	yes	-
0.4-sg-2	0.4	SG	yes	-
0.5-sr-0	0.5	SR	no	-
0.5-sr-1	0.5	SR	yes	-
0.5-sg-0	0.5	SG	no	-
0.5-sg-1	0.5	SG	yes	-
0.5-sg-2	0.5	SG	yes	-
0.6-sr-0	0.6	SR	no	-
0.8-sr-0	0.8	SR	no	-
0.9-sr-0	0.9	SR	no	-
1.0-sr-0	1.0	SR	no	-
0.2-Mg-0	-	SR	no	$\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$

Table 9.1: List of studied samples. Samples are labelled $x\text{-met-}y$ where x denotes cobalt content in the sample, string met denotes the preparation method (sr- solid state reaction as a preparation method, sg- samples prepared by sol-gel method) and y means additional treatment, if any. Samples for which y amounts to 2 were not studied before an additional treatment in oxygen atmosphere. Samples labelled with 0 and 1 were prepared, measured before and after the thermal treatment.

h) and then at 600–900 °C. The pre-reacted powder was pressed into the pallets.

Then, so prepared samples were thermally treated during several hours at 1200 °C under oxygen or argon atmosphere or in the vacuum. Few samples were additionally treated in oxygen atmosphere at 750°C for two days. The effect of additional thermal treatment on the compounds was also studied. Detailed list of samples and the meaning of their labelling in a way $x\text{-met-}y$ is presented in Table 9.1. There are three possible characters: 0 means that there was no additional treatment, characters 1 and 2 mean that the sample was additionally treated in oxygen atmosphere at 750° C for two days. Two samples prepared by sol-gel method were prepared and immediately thermally treated. There were therefore no measurements carried out on these samples before the additional treatment. These two samples, for which we

do not have comparison "before" and "after" thermal treatment are labelled by 2 at the position y (i.e. samples *0.4-sg-2*, *0.5-sg-2*). Samples labelled by 1 were studied before thermal treatment, then treated in oxygen and again studied.

The compound with formula $\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$ is labelled by *0.2-Mg-0*. In this compound Co is partially substituted by magnesium ions which is preferably in 2+ valence state. Therefore we assume that manganese ions are forced to be in the 4+ valence state and Co ions are in 3+ state in order to established charge neutrality of the sample. The magnesium containing sample was studied in order to check if Mg doping will cause any redistribution of NMR spectral lines in the spectrum which can deliver new information for NMR signals interpretation.

9.2 X-ray diffraction

The standard powder diffraction was employed to characterize the samples. Diffraction patterns were analyzed using the Rietveld analysis and the crystal structure of samples was determined.

For all samples the supposed crystal structure was confirmed, i.e. for $x > 0.6$ the crystal structure is rhombohedral with space group $R\bar{3}c$ and for $x < 0.6$ the crystal structure is orthorhombic with space group $Pbnm$, for $x = 0.6$ mixture of these two structures occurs. Diffraction patterns were precisely analyzed in order to control whether the sample exhibits regions with different crystal structure or lattice parameter. We found out no additional phases in the samples. Sensitivity to different phase was estimated to be around 1%.

The diffraction patterns were analyzed also with respect to the preparation method and additional thermal treatment. No difference in diffractions experiments were observed for samples prepared by SR or SG methods and also no difference was observed for samples before and after heating.

9.3 Magnetization measurements

Magnetic properties of the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds were studied by means of magnetization measurements. The hysteresis loops, zero field cooled (ZFC) and field cooled (FC) curves were measured and analyzed in the temperature range 5–300 K.

ZFC measurements were carried out in a following way. First, the sample was cooled down at zero external magnetic field. After that the magnetic susceptibility was measured as a function of temperature in the range 5 to 300 K during heating up in the field of 0.01 T. Field cooled measurements were done in a following way. First the sample was heated to the room temperature, then the sample was cooled

down at external magnetic field of 0.01 T. After that the magnetic susceptibility was measured as a function of temperature in the range 5 to 300 K during heating up in the field of 0.01 T.

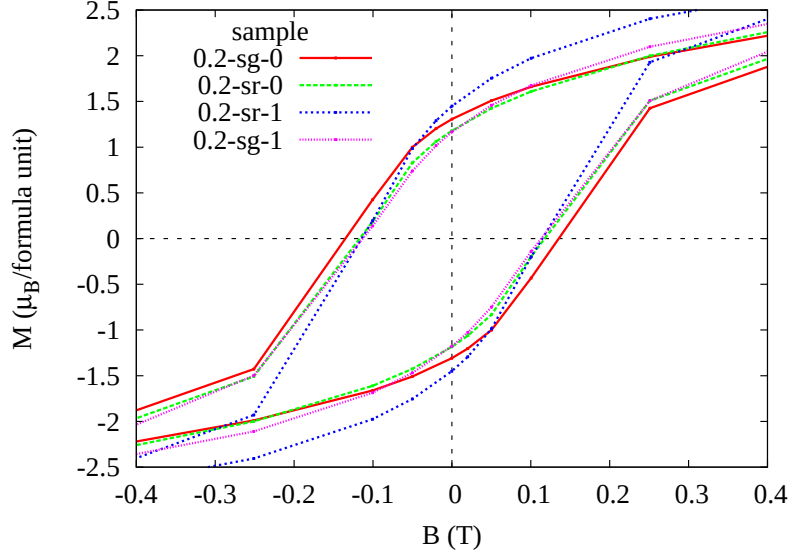
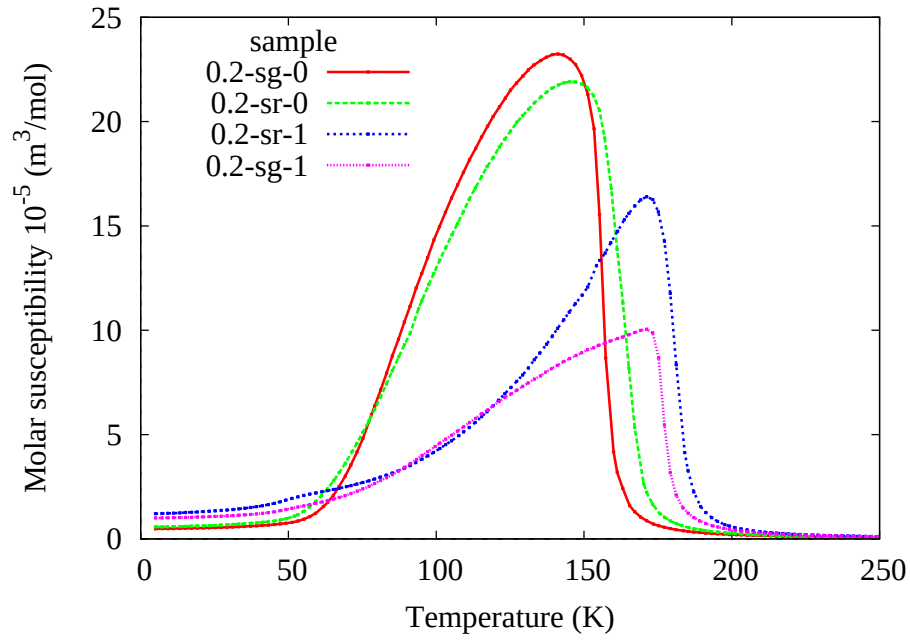
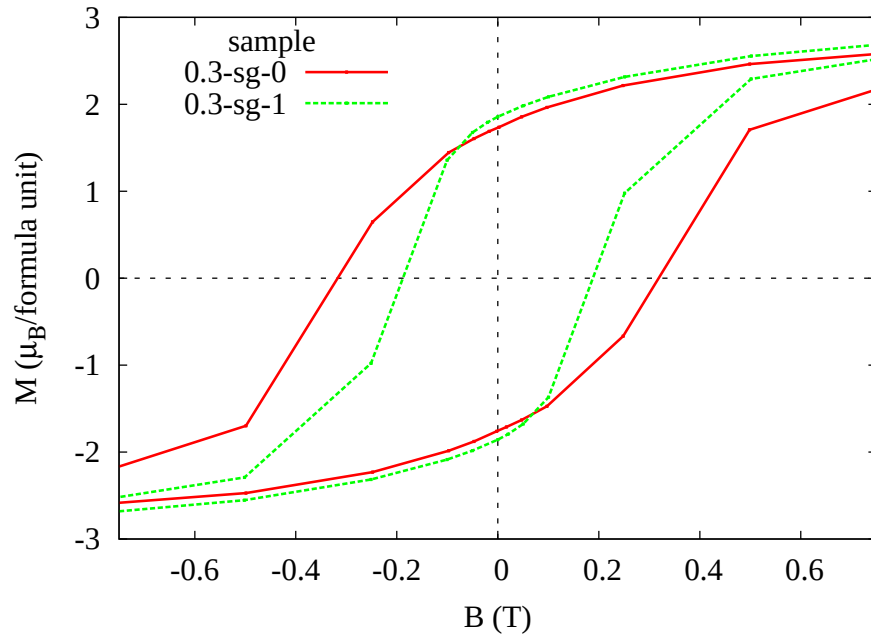


Figure 9.1: Hysteresis loops of samples with $x = 0.2$, $T = 5K$.

Hysteresis loops of samples with $x = 0.2$ prepared using the sol-gel method and using the solid state reaction methods are shown in Figure 9.1. The coercive fields H_c for samples with $x = 0.2$ prepared by SR method do not change after additional thermal treatment in oxygen atmosphere (samples *0.2-sr-0* and *0.2-sr-1*). On the other hand the coercive field of sample *0.2-sg-1* is about 18% lower than for the sample *0.2-sg-0*. The thermal treatment increase the saturation magnetization M_s , most pronouncedly (5%) for the SR method.

In ZFC curves we can observe an indication of magnetic transitions in the material. Such a transition is usually accompanied by peak or step in the ZFC curve. In Figure 9.2 we can see ZFC curves of samples *0.2-sr-0*, *0.2-sr-1*, *0.2-sg-0* and *0.2-sg-1*, where only one peak in the ZFC curve is observed for all four samples. This peak was assigned to a transition from a paramagnetic to a ferromagnetic state. The additional heating in oxygen increases the Curie temperature, T_C .

A decrease of a coercive field and a slight increase of saturation magnetization after thermal treatment can be observed also for samples *0.3-sg-0* and *0.3-sg-1*, see Figure 9.3. Additionally, while the ZFC curve of the sample *0.3-sg-0* exhibits only one peak (see Figure 9.4), two peaks are clearly present in the ZFC curve of the sample *0.3-sg-1*. The sample after thermal treatment exhibits two ordering temperatures, $T_{c1} = 148 K$ and $T_{c2} = 186K$, where the critical temperatures T_{c1} , T_{c2} can

Figure 9.2: ZFC curves of samples with $x = 0.2$.Figure 9.3: Hysteresis loops of samples with $x = 0.3$, $T = 5 \text{ K}$.

be interpreted, as in [Dass2003], [Bari2003], as ferrimagnetic ordering temperatures of two isostructural phases with different magnetic properties. This phases belongs to the ordered and disordered state, where the $\text{Mn}^{4+}\text{--Co}^{2+}$ alternating form the ordered phase with higher T_c , while small clusters of disordered $\text{Mn}^{3+}\text{--Co}^{3+}$ exhibits ferromagnetic ordering at lower temperature. Field cooled curves are presented in the Figure 9.5.

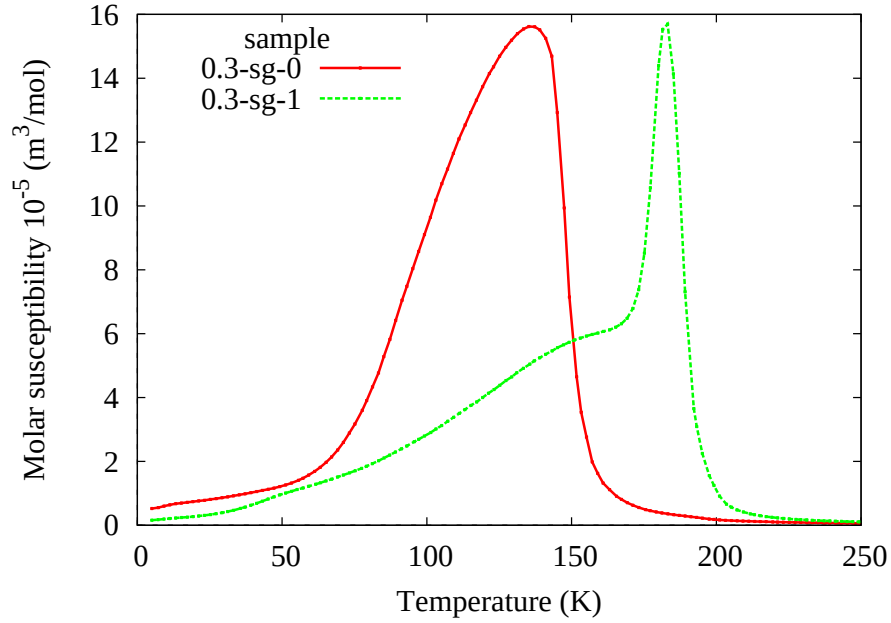


Figure 9.4: ZFC curves of samples with $x = 0.3$.

The same effect of rapid decrease of the coercive field, H_c and increase of the saturation magnetization with the thermal treatment is observed also for samples with $x = 0.4$ and $x = 0.5$ (see Figures 9.6 and 9.8). The values of coercive field and saturation magnetization are given in Table 9.2 and plotted in Figures 9.11 and 9.12. From ZFC curves of samples with $x = 0.4$ (Figure 9.7) it is evident that the sample prepared using SR method without additional treatment exhibits two magnetic ordering temperatures as well, with $T_{c1} = 153 \text{ K}$, and $T_{c2} = 224 \text{ K}$. Additional treatment (sample *0.4-sr-1* or *0.4-sg-2*) results in an increase of the temperature T_{c2} while the values of the temperature T_{c1} remains almost unchanged.

The effect of increase of critical temperature T_{c2} due to additional thermal treatment is observed also in the case of sample with $x = 0.5$. For additionally thermally treated samples the peak at T_{c2} gets narrower and more pronounced with increasing Co content, while the peak belonging to the temperature T_{c1} gets broader and less pronounced. The dependences of T_{c1} and T_{c2} values on the cobalt content, x are plotted in Figure 9.10. This behaving is probably connected with increasing

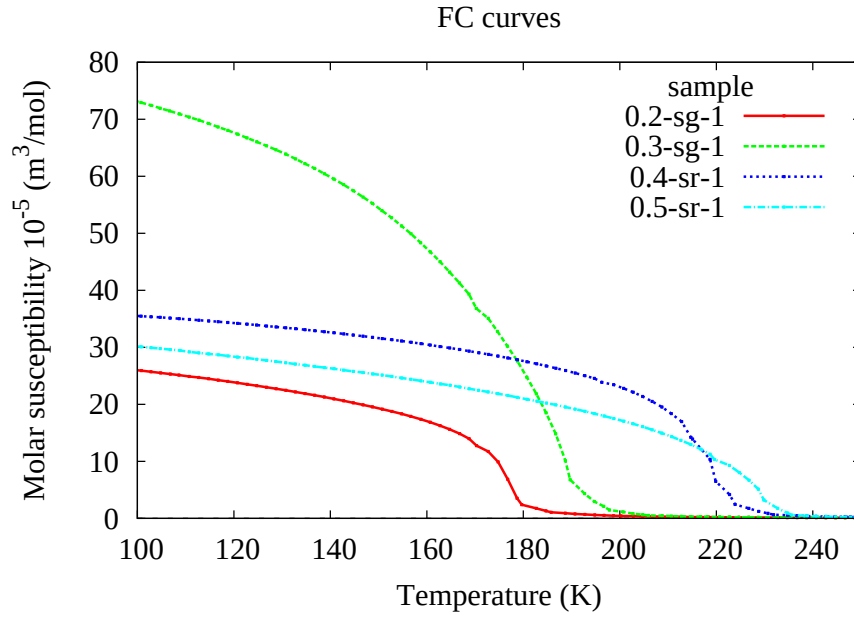


Figure 9.5: FC curves of samples additionally thermally treated, *0.2-sg-1*, *0.3-sg-1*, *0.4-sr-1*, *0.5-sr-1*.

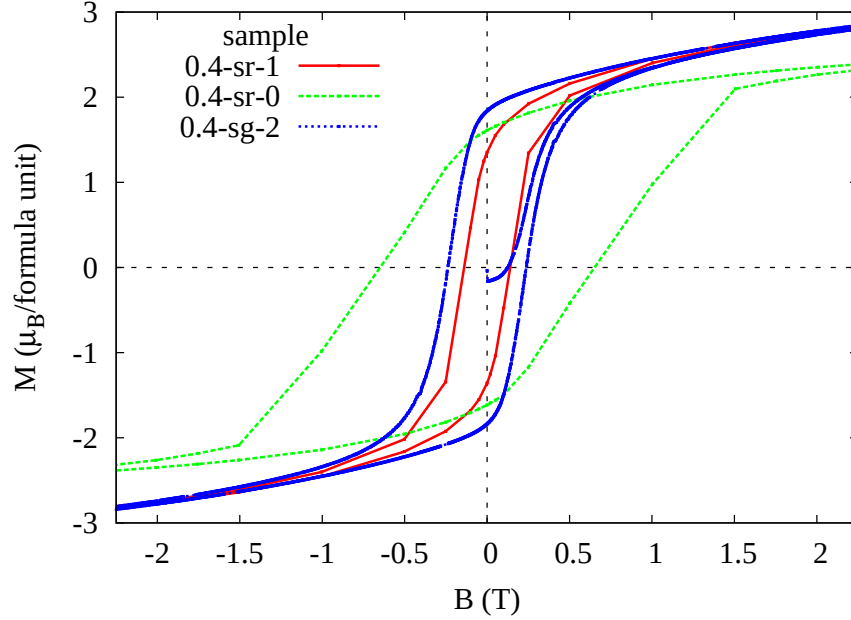
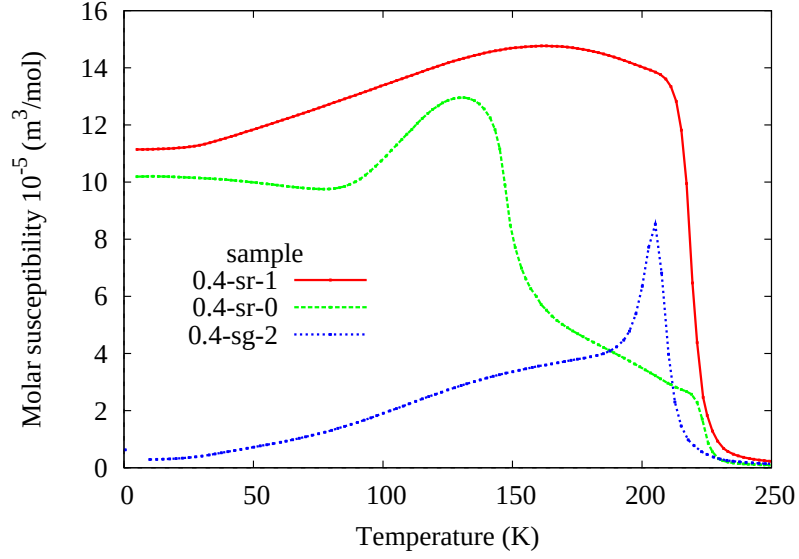
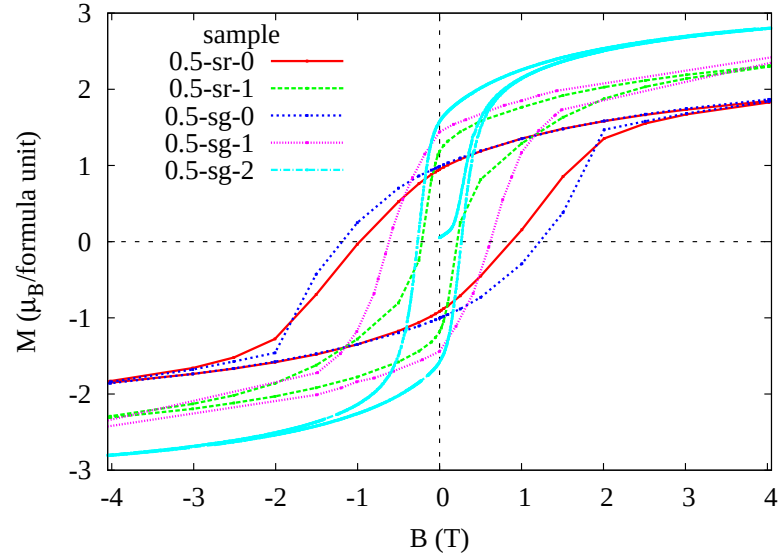


Figure 9.6: Hysteresis loops of samples with $x = 0.4$, $T = 5\text{ K}$.

Figure 9.7: ZFC curves of samples with $x = 0.4$.Figure 9.8: Hysteresis loops of samples with $x = 0.5$, $T = 5 \text{ K}$.

amount of the ordered phase in comparison to the disorder phase. While the lower T_c is nearly independent on the Co concentration, the higher T_c increases linearly with increase of Co concentration.

Now, let's discuss the difference between samples *0.5-sg-1* and *0.5-sg-2*, i.e. samples prepared using the same preparation procedure, but not in the same batch.

Sample	M_s (μ_B /formula unit)	H_c (T)	M_{s0}/M_{s1}	H_{c0}/H_{c1}
0.0-sg-0	0.35(1)	0.446(2)	-	-
0.2-sr-0	3.46(2)	0.114(1)	0.99	1
0.2-sr-1	3.5(2)	0.114(1)	-	-
0.2-sg-0	3.39(2)	0.135(1)	0.95	1.18
0.2-sg-1	3.58(2)	0.114(1)	-	-
0.3-sg-0	3.04(2)	0.318(2)	0.91	1.69
0.3-sg-1	3.36(2)	0.188(1)	-	-
0.4-sr-0	2.63(1)	0.656(3)	0.84	4.6
0.4-sr-1	3.12(2)	0.142(1)	-	-
0.5-sr-0	1.94(1)	0.913(3)	0.81	4.21
0.5-sr-1	2.41(1)	0.217(1)	-	-
0.5-sg-0	1.94(1)	1.039(2)	0.75	1.66
0.5-sg-1	2.58(1)	0.625(3)	-	-
0.6-sr-0	1.25(1)	0.747(3)	-	-
1.0-sr-0	0.041(1)	0.128(1)	-	-
0.4-sg-2	2.99(2)	0.266(1)	-	-
0.5-sg-2	2.82(1)	0.239(1)	-	-

Table 9.2: Saturation magnetization of M_s (μ_B /formula unit), coercive field H_c (Oe) for samples of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$, the ratio of saturation magnetization before and after additional thermal treatment M_{s0}/M_{s1} and the ratio of coercive field before and after additional thermal treatment H_{c0}/H_{c1} .

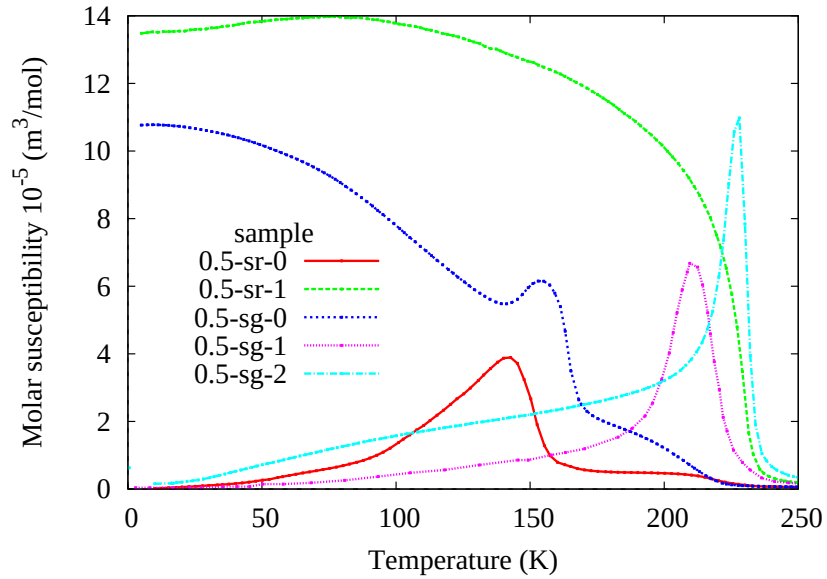


Figure 9.9: ZFC curves of samples with $x = 0.5$.

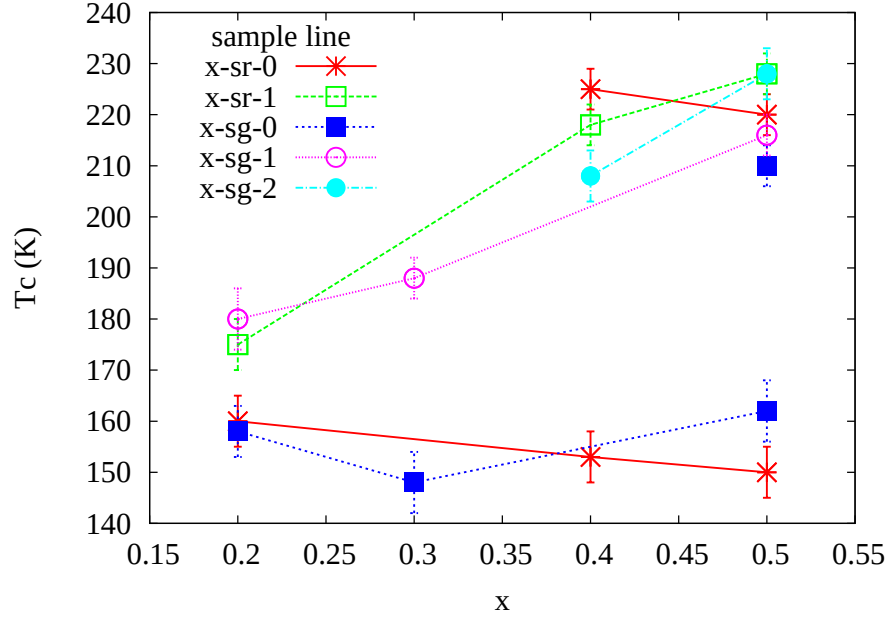


Figure 9.10: Dependence of ordering temperatures T_{c1} and T_{c2} on Co concentration in the sample. Lines connecting the experimental points are the guide eyes only.

In Figure 9.8 we can compare hysteresis loops of both samples. While the coercive field is the same for both samples, the saturation magnetization is slightly higher for the sample *0.5-sg-2*. Comparing the shape of the hysteresis loops we can conclude that the shape of loop of the sample *0.5-sg-2* is much more rectangular than for the sample *0.5-sg-1*. Moreover, in the hysteresis loop of the sample *0.5-sg-1* a two step character of magnetization reversal is evident, this could be due to a ferrimagnetic behavior of the sample.

The saturation magnetization is independent on the preparation method, but it increases if an additional thermal treatment was used and its increase depends on the Co content. The situation is different in the case of the coercive field, H_c which depends on Co content, preparation method and an additional treatment. From samples with $x = 0.5$ the highest coercive field has the sample *0.5-sg-0* and the lowest has the sample *0.5-sr-1*, see Figures 9.11 and 9.12. The decrease of the saturation magnetization with increase of Co concentration in the region of $x < 0.2$ is in agreement with result published in [Good1961], [Troy2000].

Hysteresis loops of samples prepared by the SR method before thermal treatment were also measured at the temperature $T = 77$ K and $T = 295$ K (Figures 9.13, 9.14). Samples exhibit a paramagnetic behavior at 295 K. An increase of the coercive field with increasing of Co content is observed in the Figure 9.12.

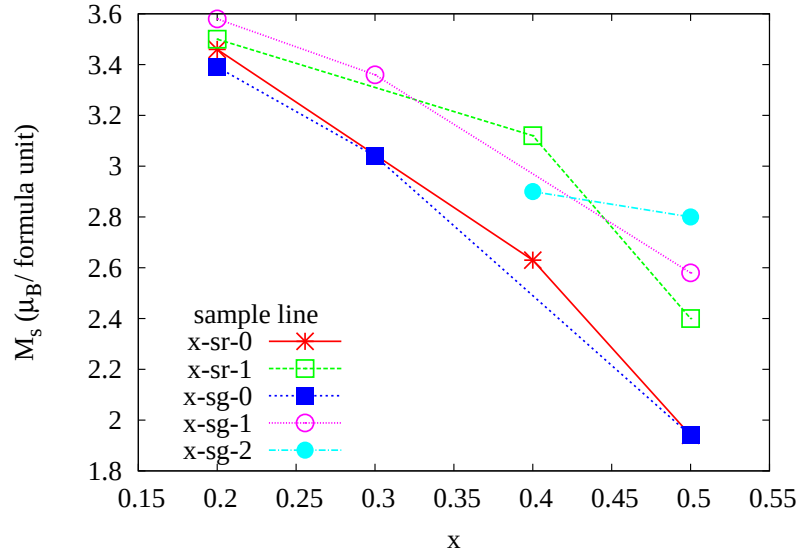


Figure 9.11: Dependence of the saturation magnetization on Co concentration. Lines connecting the experimental points are the guide eyes only. Errors do not exceed the size of point marks.

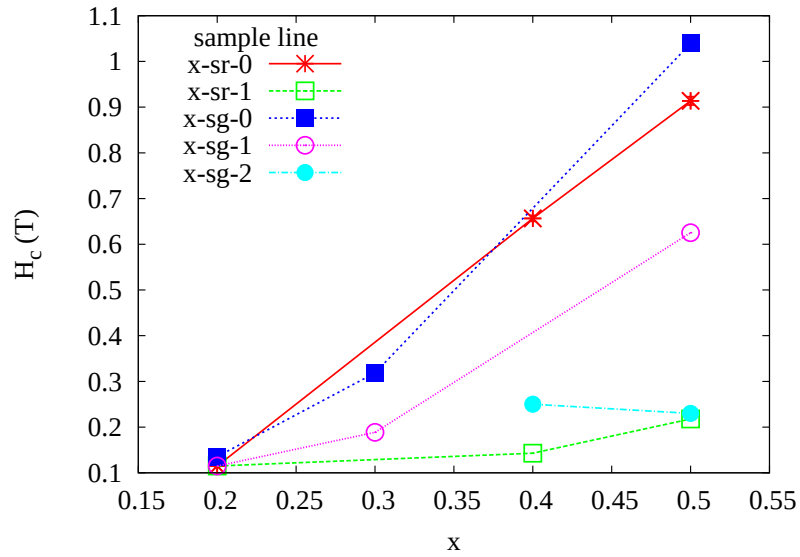


Figure 9.12: Dependence of the coercive field on Co concentration. Lines connecting the experimental points are the guide eyes only. Errors do not exceed the size of point marks.

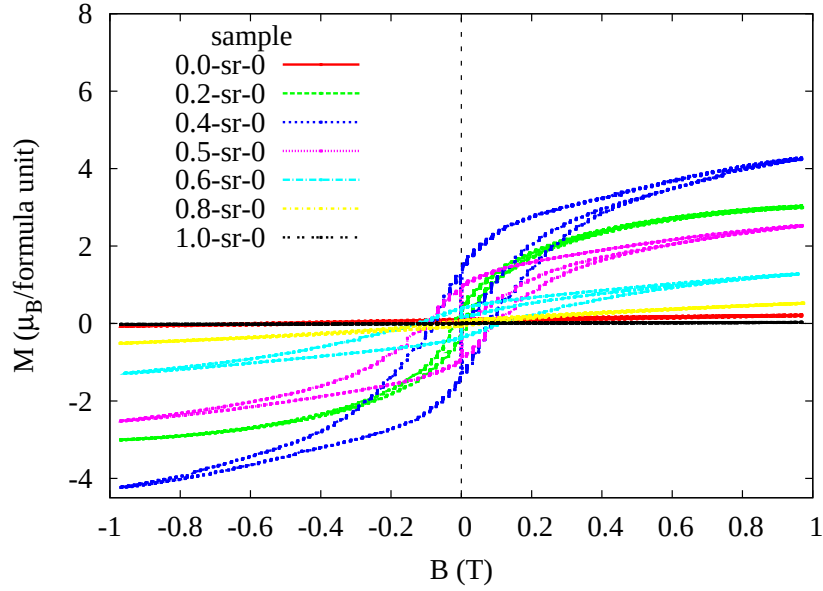


Figure 9.13: Hysteresis loops at temperature $T=77$ K of samples with x ranging from 0 to 1 prepared by the solid state reaction method.

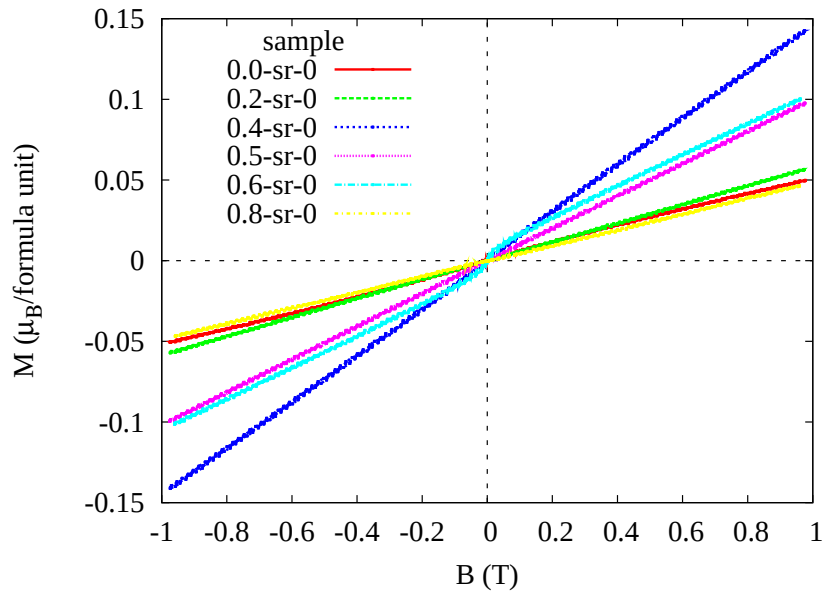


Figure 9.14: Hysteresis loops at temperature $T=300$ K of samples with x ranging from 0 to 1 prepared by the solid state reaction method.

Chapter 10

EXAFS results and discussion

10.1 Absorption spectra

The background was removed from the absorption spectra and the edge step was normalized to unity using the AUTOBK program. In Fig. 10.1, we can see the spectra at the Co K -edge of samples with $x = 0.2, 0.4, 0.5, 0.6$ which all have orthorhombic symmetry. In Figure 10.1 we can see that absorption edge of sample 0.2-sr-0 is significantly shifted towards higher energies, this is probably due to a systematic error in the energy calibration as the measurements were carried out without a reference sample. However, this does not influence our analysis because in the EXAFS experiment the absolute scaling of the energy is not crucial. The Co K -edge absorption spectra of samples with $R\text{-}3c$ structure are plotted in Fig. 10.2

In order to compare the absorption spectra of two samples with different crystal structure the absorption of samples 1.0-sr-0 (rhombohedral) and 0.2-sr-0 (orthorhombic) are presented together in Figure 10.3.

While no large differences were observed in the spectra of samples with the same crystal structure, large difference in the post edge oscillations are evident in the case of samples with different structure. The difference results from different local surrounding of the Co ion. The cobalt-oxygen distances are the same for the 1st nearest neighbor shell in the rhombohedral symmetry, while the oxygen octahedron is distorted in the orthorhombic symmetry.

Mn K :edge EXAFS spectra are shown in Figures 10.4 and 10.5 for samples with $Pbnm$ and $R\text{-}3c$ crystal structure, respectively. In the spectra of manganese K -edge we can see that the noise is bigger compared to Co K -edge measurements. Therefore, further analysis is more complicated and obtained results have larger errors. In Figure 10.6 absorption spectra of two samples with different crystal structure are presented. The effects related to differences in the local surrounding of manganese ions are evident.

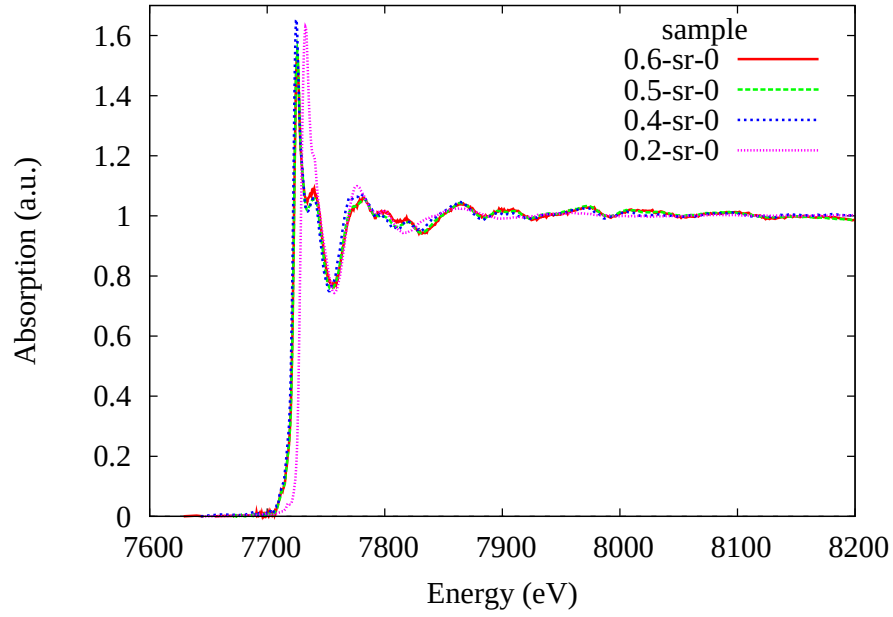


Figure 10.1: Co K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method.

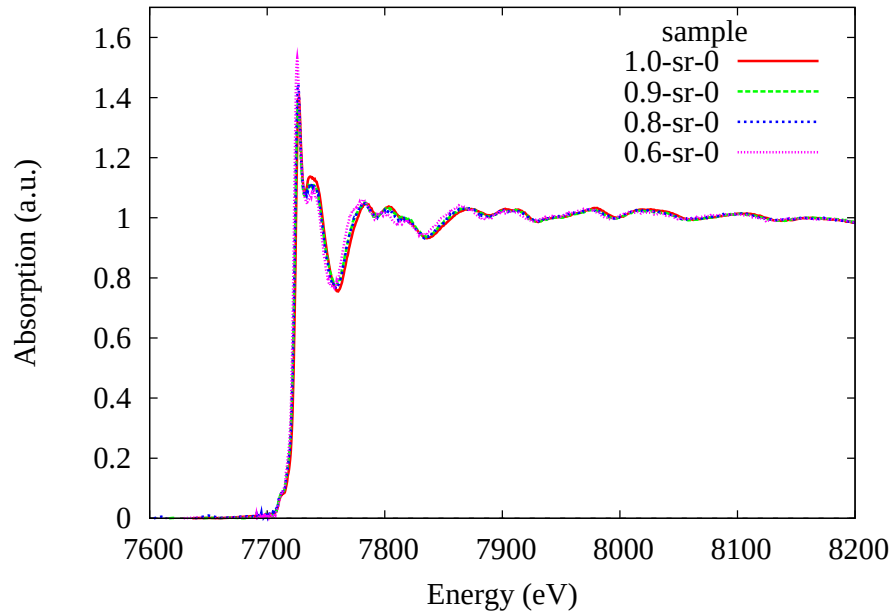


Figure 10.2: Co K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9, 1.0$ prepared by SR method.

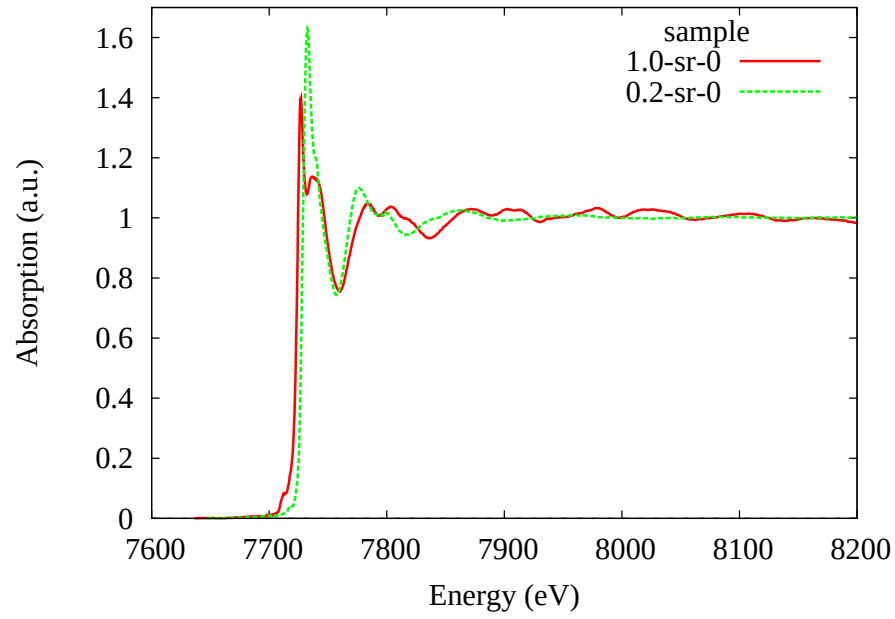


Figure 10.3: Co K -edge absorption spectra of samples 1.0-sr-0 (rhombohedral) and 0.4-sr-0 (orthorhombic) symmetry, at room temperature.

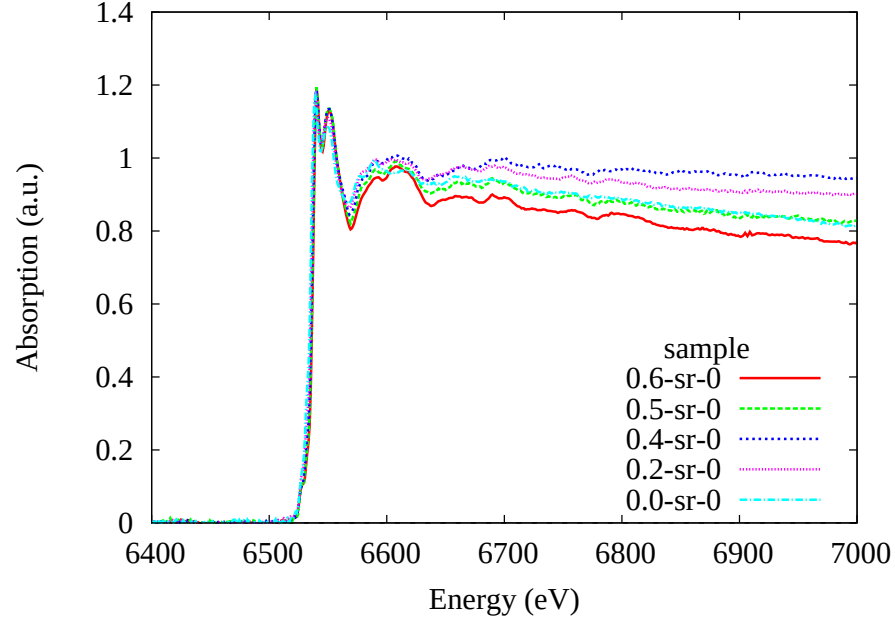


Figure 10.4: Mn K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method.

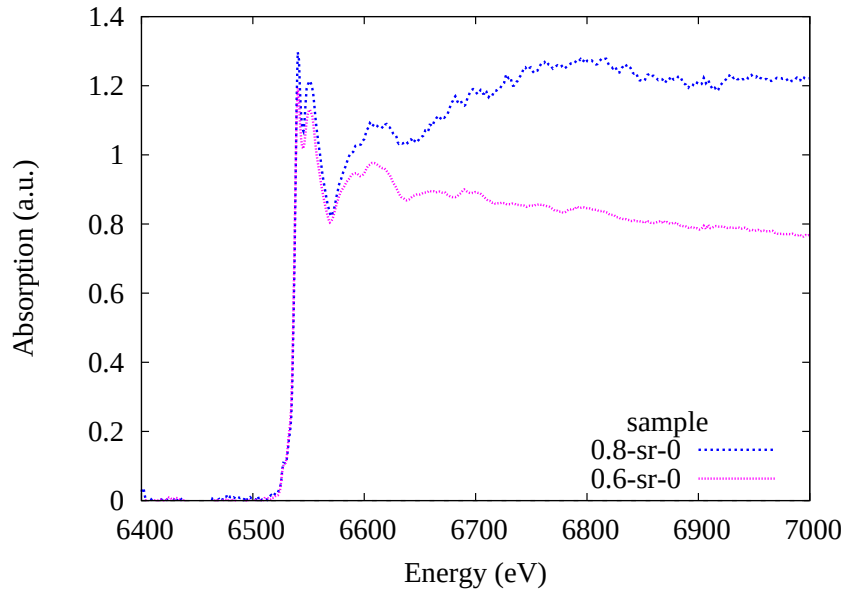


Figure 10.5: Mn K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8$ prepared by SR method.

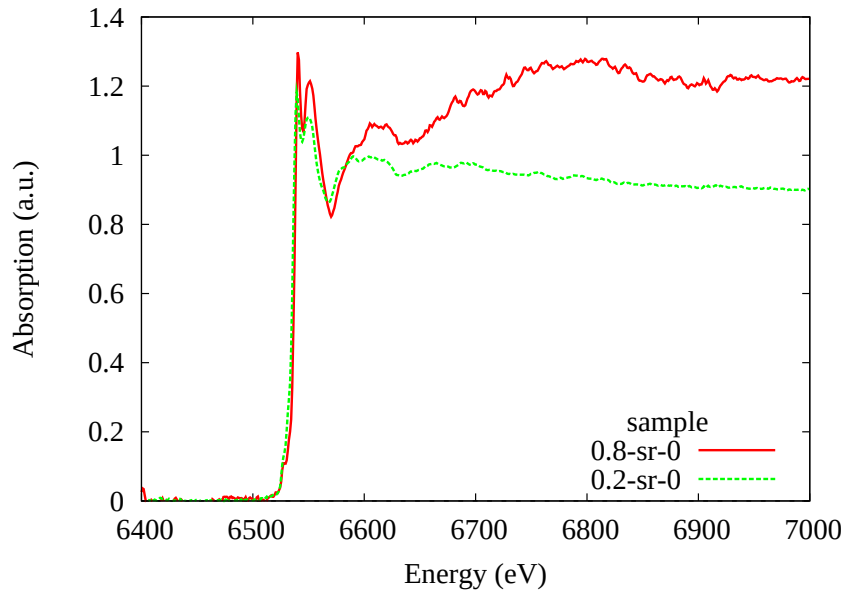


Figure 10.6: Absorption on K -edge of manganese of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.8$ and 0.2 at room temperature. Compound with $x = 0.8$ has a $R\bar{3}c$ crystal structure and compounds with $x = 0.2$ has a $Pbnm$ crystal structure.

10.2 χ functions

The μ_0 function was removed according to procedure described in 4.3 using a **spline** function in *IFEFFIT*. Also the uncertainty of background removing was estimated. The resulting EXAFS functions $\chi(k)$ obtained for the *K*-edge of Co for samples with crystal structure *Pbnm* and *R-3c*, are shown in Figures 10.7-10.8, respectively. The uncertainty of EXAFS functions due to the free atomic background removing procedure was estimated by varying background removing parameters and it amounts to around 2 % and 4 % for for all Co:K and Mn:K edges, respectively.

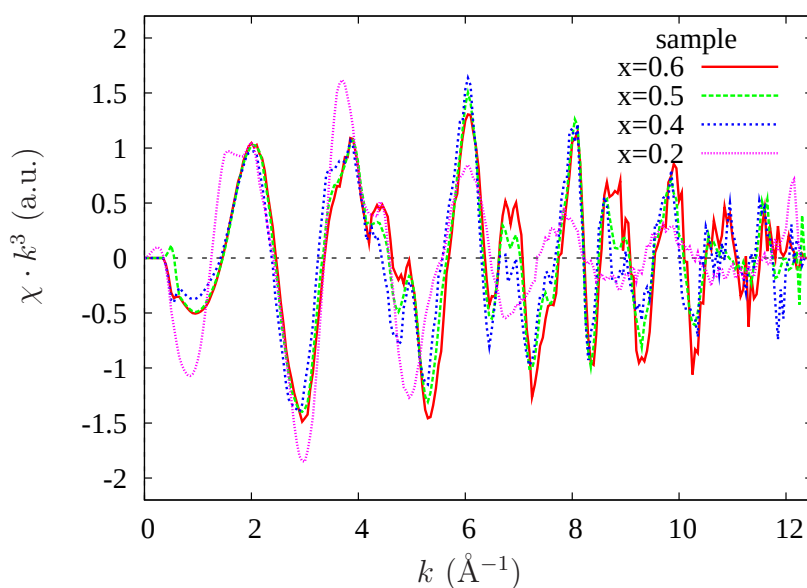


Figure 10.7: EXAFS functions $\chi(k) \cdot k^3$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method (*0.2-sr-0*, *0.4-sr-0*, *0.5-sr-0*, *0.6-sr-0*).

The $\chi(k)$ function of the measurements on the Mn:K edge are plotted in Figures 10.9 and 10.10 for samples with *Pbnm* and *R-3c* structures, respectively. It is evident that there are glitches between 7–8 $\text{\AA}^{-1}$ in Mn:K edge measurements, produced possibly by the monochromator. They can not be removed or extracted from measurements without decreasing the quality of data. These glitches in the spectrum were removed during the fitting procedure.

A more useful way of presentation of EXAFS results is the Fourier transform of $\chi(k)$ function from the reciprocal k -space to the real space R as it was described in 4.3. Such presentation provides information about the electron density around the central atom. Figures 10.11–10.14 show amplitudes of $\chi(R)$ functions for all measured compounds.

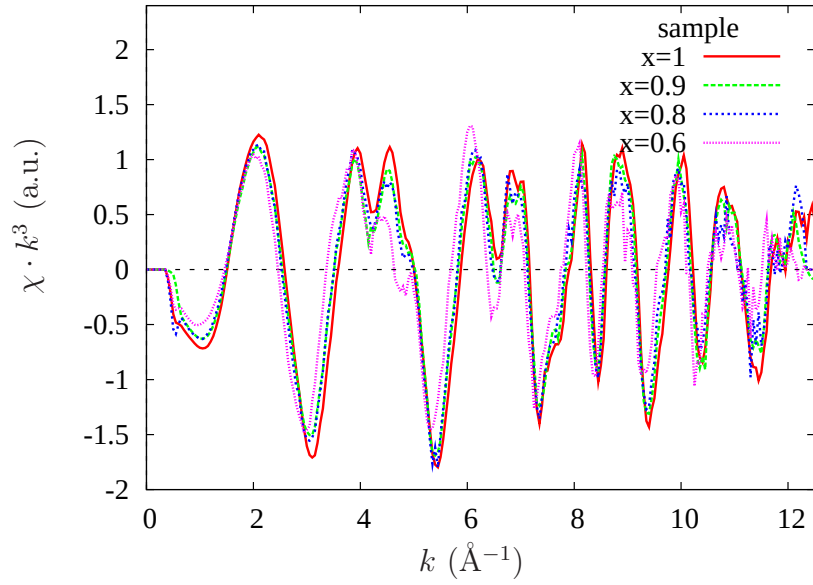


Figure 10.8: EXAFS functions $\chi(k) \cdot k^3$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9, 1.0$ prepared by SR method (*0.6-sr-0*, *0.8-sr-0*, *0.9-sr-0*, *1.0-sr-0*).

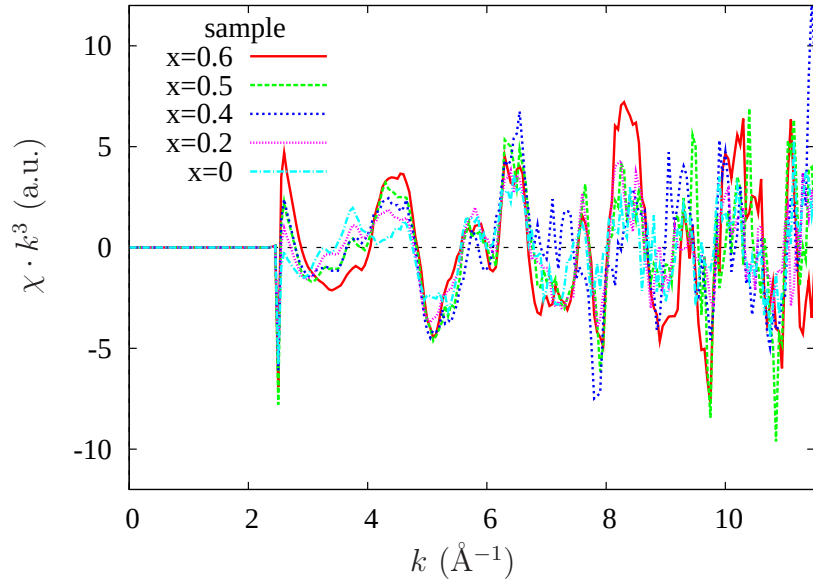


Figure 10.9: EXAFS function $\chi(k) \cdot k^3$ function measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0, 0.2, 0.4, 0.5, 0.6$ prepared by SR method (*0-sr-0*, *0.2-sr-0*, *0.4-sr-0*, *0.5-sr-0*, *0.6-sr-0*).

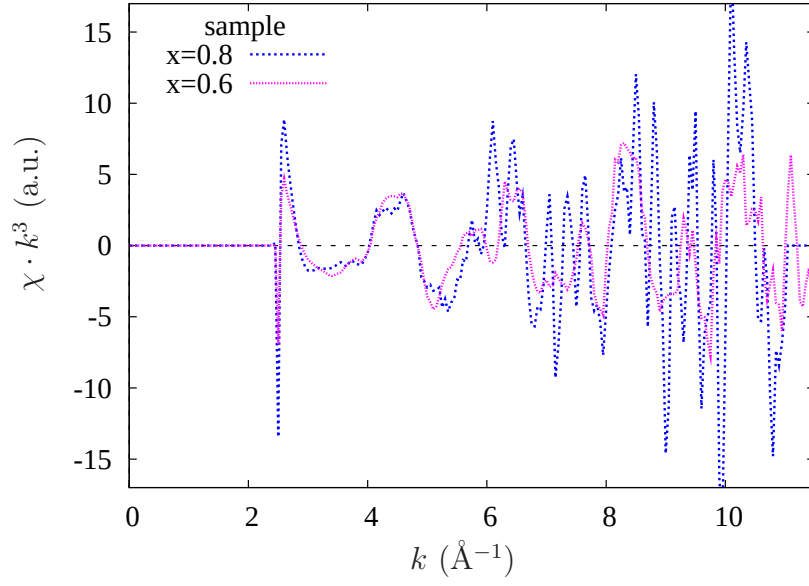


Figure 10.10: EXAFS function $\chi(k) \cdot k^3$ function measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9$ prepared by SR method (*0.6-sr-0*, *0.8-sr-0*, *0.9-sr-0*).

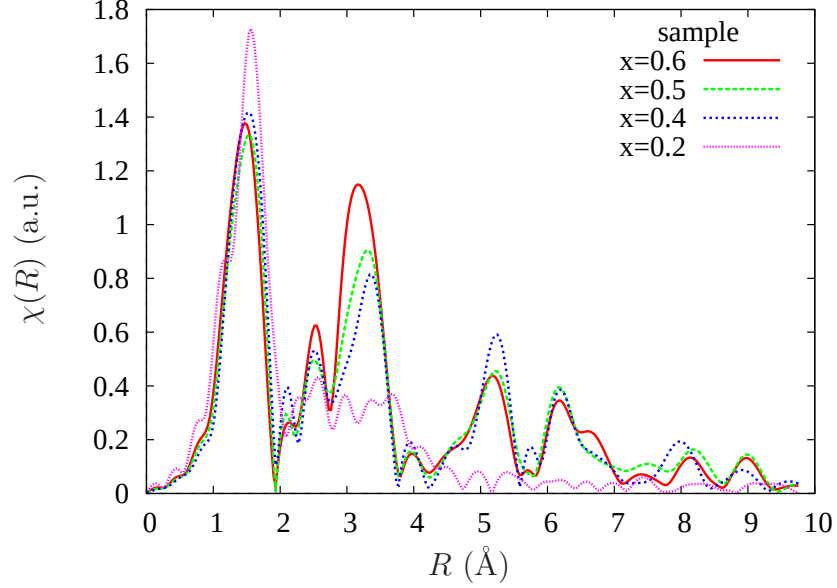


Figure 10.11: EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method (*0.2-sr-0*, *0.4-sr-0*, *0.5-sr-0*, *0.6-sr-0*).

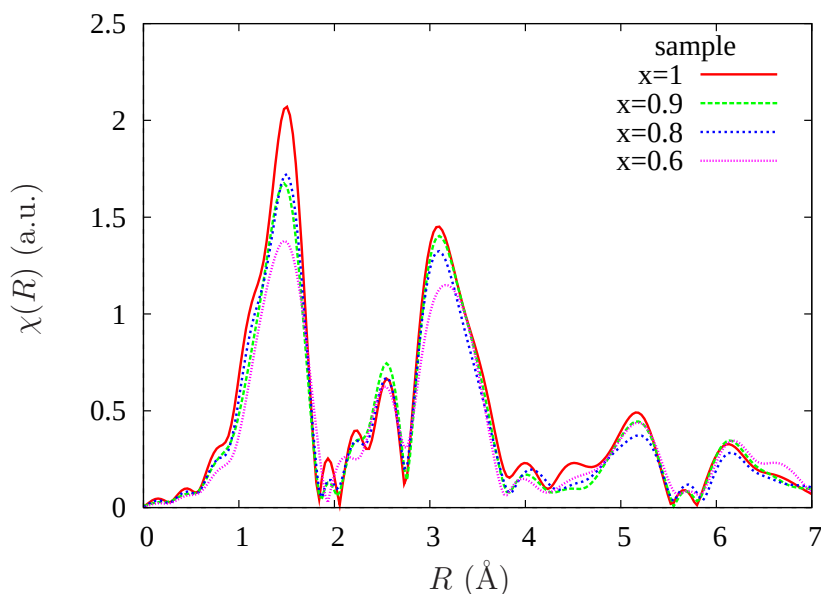


Figure 10.12: EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9, 1.0$ prepared by SR method (*0.6-sr-0*, *0.8-sr-0*, *0.9-sr-0*, *1.0-sr-0*).

The first large peak in all $\chi(R)$ functions corresponds to the nearest oxygen neighbors. Other peaks at higher values of R were assigned to lanthanum cations which are the second nearest neighbors and to the cobalt or manganese cations.

10.3 Results of the fitting procedures

The fitting is the last step in the analysis procedure. The number of fitted parameter has to be chosen carefully with respect to the number of independent points given by equation (4.5). Therefore, a proper physical model has to be constructed before fitting in order to find constraints between fitted parameters. The success of a fitting process also depends on suitably chosen initial values of fitted parameters.

The fitting process can be carried out in the k -space or in the R -space. Results of fitting in both cases should be the same. In our fitting procedures fitting in the k -space was used.

During the analysis procedure different models were tested for Mn and Co absorption edge taking the compound symmetry into consideration. In all models the edge energy shift e_0 was fitted and its value was kept the same for all paths. The same value for all paths was kept also for the second fitted parameter, S_0^2 . This parameter allows us to introduce the Co doping in the case of the second shell fitting, where transition metal is present (this was not done as the range of reliable data

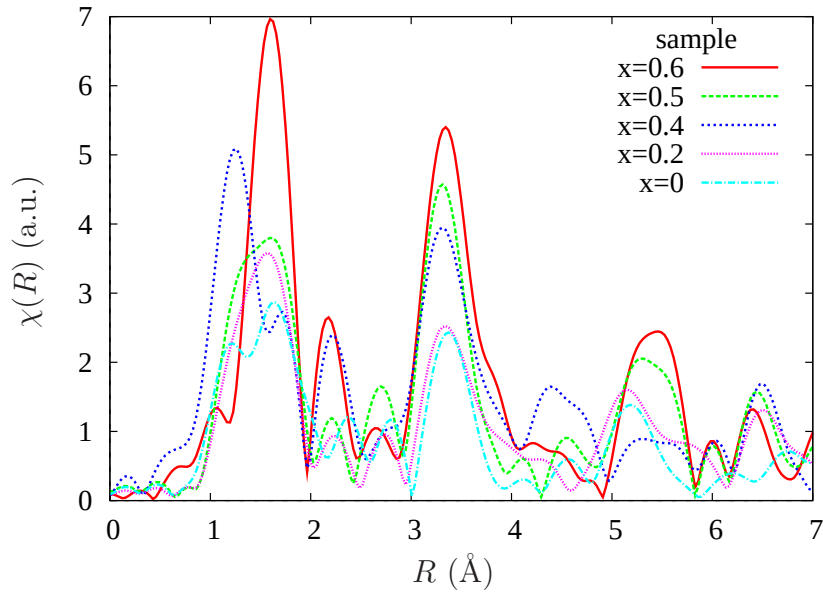


Figure 10.13: EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0, 0.2, 0.4, 0.5, 0.6$ prepared by SR method (*0-sr-0*, *0.2-sr-0*, *0.4-sr-0*, *0.5-sr-0*, *0.6-sr-0*).

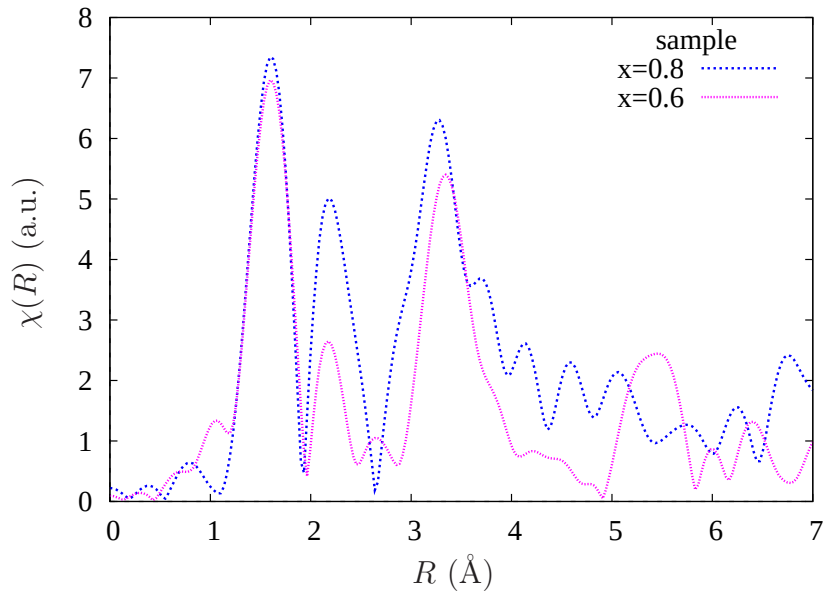


Figure 10.14: EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9$ prepared by SR method (*0.6-sr-0*, *0.8-sr-0*, *0.9-sr-0*).

was too short). In the case of the first shell fitting S_0^2 determines an amplitude of the $\chi(k)$ function. We restrict the fitting only to oxygen ions from the first shell and we take into account only single paths in the nearest oxygen shell.

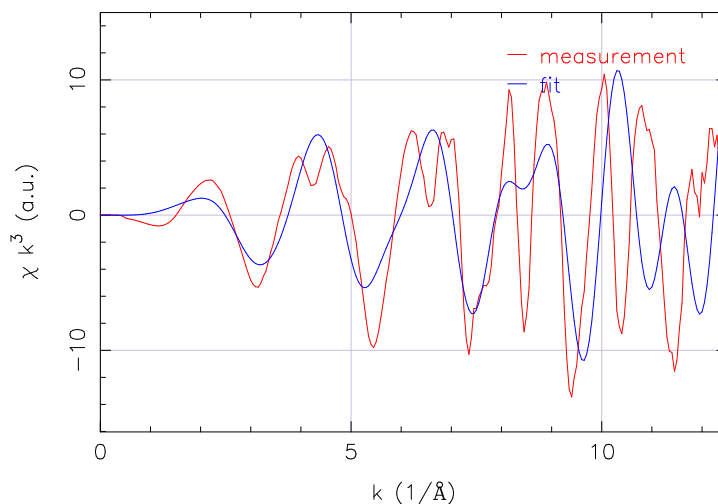


Figure 10.15: Result of the fitting procedure in the k space for cobalt K edge for LaCoO_3 . Experimental $\chi(k)$ function and the fit.

For rhombohedral samples ($R\bar{3}c$) only a single Co–O distance was fitted because all oxygen neighbors of transition metal are at equivalent distance. Co–O distance is represented during fit by parameter `delR` defined by equation 4.10. For the "rhombohedral" model also the Debye-Waller factor σ^2 was estimated by fitting. Three different Me–O distances can be found in the orthorhombic structure ($Pbnm$), therefore three Me–O distances were fitted in the "orthorhombic" model for compounds with $x \leq 0.6$. In order to decrease number of fitted parameters the Debye-Waller factor was left out of the fit. In the case of the compound with $x = 0.6$ doping i.e. where the structural change occurs, both models (orthorhombic and rhombohedral) were applied and the results are consistent. The fitting procedure was carried out in several steps. First E_0 and S_0^2 parameters were fitted, then σ^2 was included (if used in fitting) and finally all the parameters were fitted together.

An example of a fitted $\chi(k)k^3$ and $\chi(R)$ function to the Co:K edge absorption measurement is plotted in the Figure 10.15 and Figure 10.16 respectively. At first sight it seems the agreement between the experimental $\chi(k)k^3$ function with the fit is not satisfactory while the fit of $\chi(R)$ function looks better. However, the situation is more complex. If we look at the χ function in the k -space the contribution from all surrounding shells is included in the experimental curve, but only the first shell

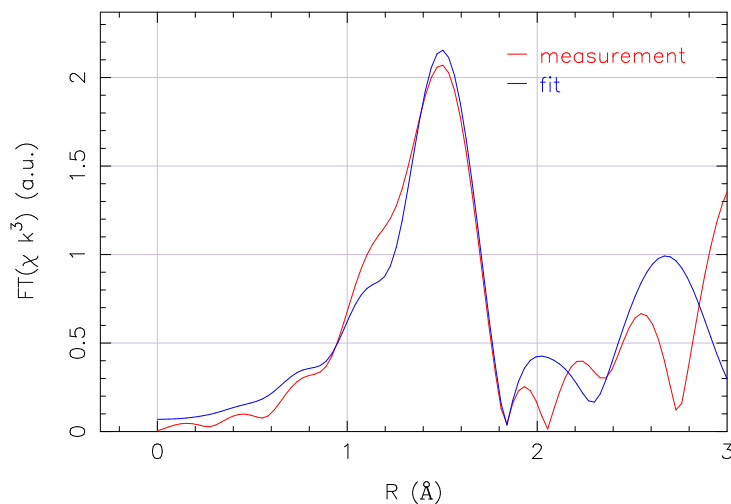


Figure 10.16: Result of the fitting procedure in the R space for cobalt K edge for LaCoO_3 . Experimental $\chi(R)$ function and the fit.

contributes to the theoretical (fitted) function and this fact results in a disagreement between experiment and fit in the k space. Therefore, it is better to check the fitting procedure in the R space (see Figure 10.16), where the contribution from different shells is separated according to their distance R .

10.3.1 Co:K edge results

Values of fitted parameters for the Co:K edge measurements are presented in Table 10.1. χ function was fitted in the k -range from 2.5 to 12.5 $\text{\AA}^{-1}$, R -range from 0.7 $\text{\AA}$ to 2 $\text{\AA}$, the Fourier transform was proceeded with using of Hanning window.

The main finding of our measurements is an increase of the Co-O distances with decreasing Co content, which can be seen in Figure (10.17). The decrease of the Co-O distance amounts to around 5% for compounds with Co doping $0.2 \leq x \leq 0.6$ and 2.5% for compounds with $x \geq 0.6$ in contrast to a much smaller decrease of the of lattice parameter which was found to be up to 1% [Autr2005].

The decrease of the Co-O distance can be attributed to a change of the mean Co valence with doping if we consider a decrease of the ionic radius with increasing Co oxidation. This result is consistent with results of XANES measurements which presented a systematic shift of the absorption edge energy with Co doping [Siko2006].

The Debye-Waller factor shows a systematic decrease with increasing Co content

sample	E_0 (eV)	S_0^2 (a.u.)	$\sigma^2(10^{-3}\text{\AA}^2)$	Model
<i>1.0-sr-0</i>	-8 (2)	0.53(4)	2 (1)	Rhomb.
<i>0.9-sr-0</i>	-9 (2)	0.44(5)	3 (1)	Rhomb.
<i>0.8-sr-0</i>	-8 (2)	0.47(5)	4 (1)	Rhomb.
<i>0.6-sr-0</i>	-8 (4)	0.41(7)	6 (2)	Rhomb.
<i>0.6-sr-0</i>	-10 (2)	0.62(7)	-	Orth.
<i>0.5-sr-0</i>	-8 (2)	0.64(6)	-	Orth.
<i>0.4-sr-0</i>	-9 (2)	0.67(8)	-	Orth.
<i>0.2-sr-0</i>	-7 (2)	0.75(8)	-	Orth.

Table 10.1: Results of fits of Co:K-edge measurements.

(Tab. 10.1), which can possibly be attributed to decreasing distortion of the oxygen octahedron around cobalt with cobalt doping. This tendency could be enhanced also by the presence of Co^{3+} in the LS state because its ionic radius is even smaller than that of Co^{3+} in the HS state, [Shan1976].

Results presented in this chapter were published in [Proc2007].

10.3.2 Mn:K edge results

The same analysis procedure with the same models like for Co:K edge measurements was used for analysis of EXAFS experimental data on the manganese *K*-edge. The values of fitted parameters are presented in Table 10.2. In Figure 10.18 we can see a plot of fitted Mn-O distances versus the Co content in the compound. Errors of fitting Mn:K absorption measurements are much bigger than in the case of fitting Co:K measurements. The higher fitting errors result mainly from the lower signal to noise ratio of measurements. χ function was fitted in the k -range from $2.5 \text{ \AA}^{-1}$ to $11.5 \text{ \AA}^{-1}$, R -range from $0.7\text{--}0.95 \text{ \AA}$ to $2 \text{ \AA}$, the Fourier transform was proceeded with using a Hanning window.

Regardless of bigger errors, it is clear from Figure 10.18 that the Mn–O distance increases slightly or remains constant with increasing Co content in the series.

10.4 Discussion of EXAFS results

Results of EXAFS analysis clearly show that in mixed valence compounds such as $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ the oxygen octahedron around the transition metal ion changes its size depending on the type of ion located in the center of the octahedron, see Figure 10.19. The decrease of cobalt–oxygen distances with increasing Co concentration, seen in Figure 10.18, is consistent with an increase of mean cobalt valence from

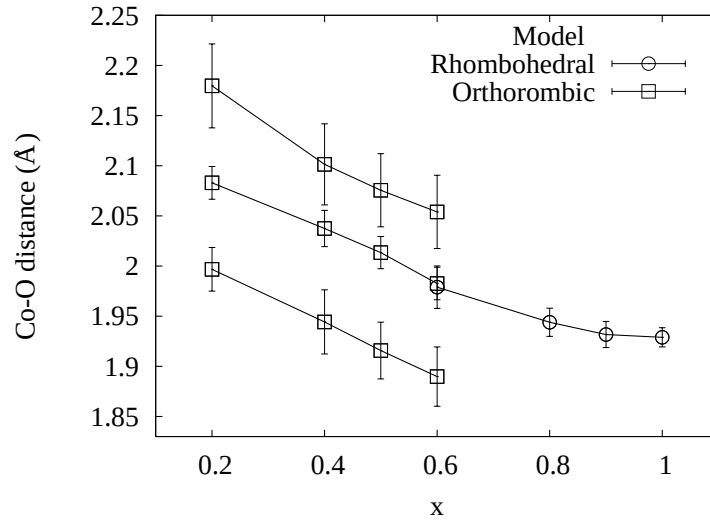


Figure 10.17: Values of cobalt-oxygen distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained from EXAFS.

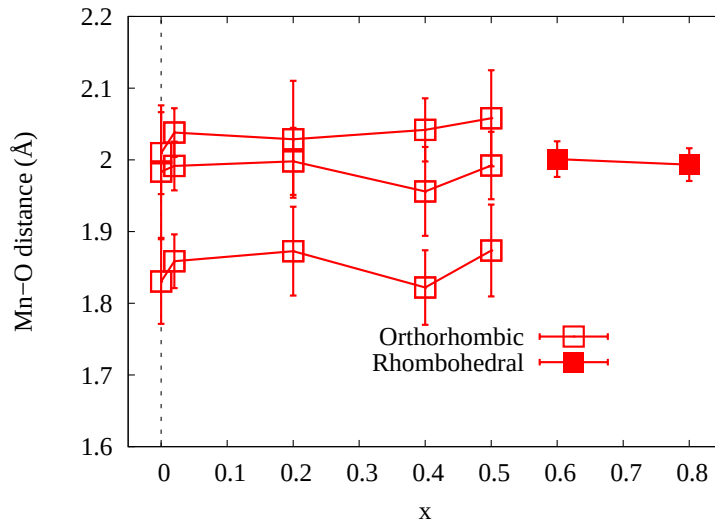
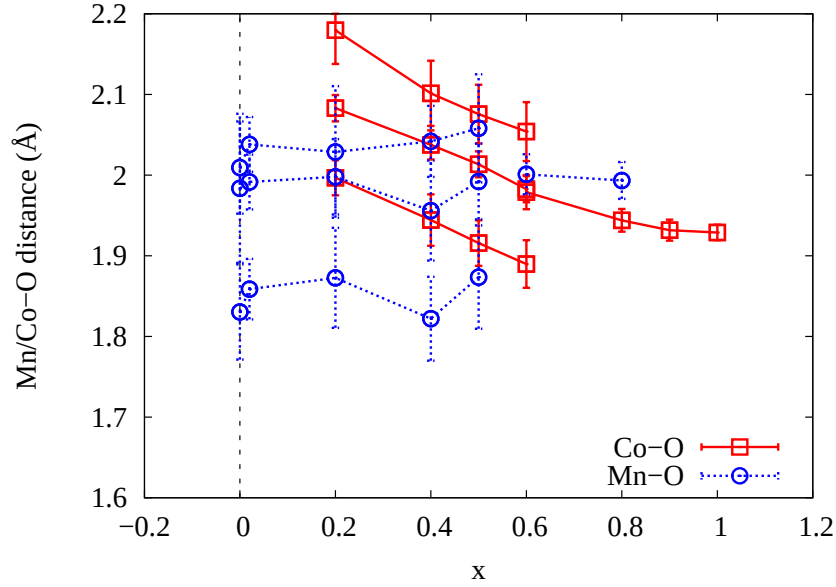


Figure 10.18: Manganese-oxygen distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained from EXAFS.

about $\text{Co}^{2.3+}$ for $x = 0.2$ to Co^{3+} for $x = 1$, determined by XANES measurements on present samples $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ [Siko2006]. This tendency might be enhanced also by the presence of Co^{3+} in the LS state, because its ionic radius is even smaller than that of Co^{3+} in the HS state [Shan1976].

To make the comparison between EXAFS and XANES data more quantitative, the dependence of mean cobalt valence in Figure 4 of Ref. [Siko2006] was first fitted

sample	E_0 (eV)	S_0^2 (a.u.)	Model
<i>0.0-sr-0</i>	-20.9 (9)	0.4 (1)	Orth.
<i>0.02-sr-0</i>	-20.49 (5)	0.4 (1)	Orth.
<i>0.2-sr-0</i>	-14.78 (7)	0.4 (1)	Orth.
<i>0.4-sg-0</i>	9.43 (6)	-0.9 (1)	Orth.
<i>0.4-sr-0</i>	26.61 (13)	0.7 (3)	Orth.
<i>0.5-sg-0</i>	-14.43 (8)	0.6 (2)	Orth.
<i>0.5-sr-0</i>	-9.7 (8)	0.4 (1)	Orth.
<i>0.6-sr-0</i>	-3.49 (6)	0.3 (1)	Orth.
<i>0.6-sr-0</i>	-6.73 (8)	0.3 (4)	Rhomb.
<i>0.8-sr-0</i>	-5.36 (5)	0.3 (1)	Rhomb.

Table 10.2: Results of fits of Mn:*K*-edge measurements.Figure 10.19: Manganese-oxygen and cobalt-oxygen distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained by EXAFS.

by quadratic polynomial, then the mean cobalt size was determined by interpolating the cobalt ionic radii in octahedral coordination according to [Shan1976], see Table 10.3. The mean Co-O distance vs. x was calculated considering separately two extreme cases: (i) a mixture of Co^{2+} in HS and Co^{3+} in LS, (ii) a mixture of Co^{2+} in HS and Co^{3+} in HS. Ionic radius $1.38 \text{ \AA}$ was taken from [Shan1976] for O^{2-} . The results are summarized in Figure 10.20. In the orthorhombic phase region ($x < 0.6$),

	Co ²⁺ HS	Co ³⁺ HS	Co ³⁺ LS	Mn ³⁺ HS	Mn ⁴⁺
RVI(Å)	0.745	0.61	0.545	0.645	0.530

Table 10.3: Effective ionic radii in octahedral coordination according to [Shan1976].

the averaged experimental Co–O distances obtained from EXAFS, and, more importantly, the slope of their dependence on x , seem to be closer to the plot calculated for the case (i), i.e. Co³⁺ in LS. The relatively less pronounced dependence of the EXAFS experimental values in the rhombohedral structure (nearly constant values found for $x > 0.6$) might be consistent with an occurrence or increasing amount of Co³⁺ in HS, which was suggested in [Siko2008] for this phase. However, to draw out reliable detailed or even quantitative conclusions for the Co spin states is hardly possible because of the experimental errors and, foremost, because of the complexity of the system. The simple approach, in which e.g. parameters of Co(HS)–O distances are considered independently on the Co(LS)–O distances, seems not to have sufficient accuracy [Kniz2009], and additionally, parameters of Mn octahedra also might play an important role.

While the monotonously decreasing Co–O distances correlate with increasing cobalt oxidation level in the LaMn_{1- x} Co _{x} O₃ series, the Mn–O distances in Fig. 10.17 display an approximately constant character and do not show the expected decrease with increasing x . This failure of simple ionic picture in the case of Mn site may point to an increasing role of Co–O covalence with x in the LaMn_{1- x} Co _{x} O₃ series.

More straightforward comparison was done between EXAFS and X-ray powder diffraction data. The X-ray powder diffraction measurements were carried out by [Autr2005] in order to confirm the crystal structure and to determine average positions of oxygen, lanthanum and transition metals. Only the average size of oxygen octahedron around transition metal can be estimated from powder diffraction, regardless of any possible differences between manganese and cobalt octahedra. Mean distances Me–O, i.e. between transition metal ions and oxygen, obtained from our EXAFS measurement and from powder diffraction presented in [Autr2005] are plotted in Figure 10.21. The distances from EXAFS experiments were averaged with weights corresponding to the ratio of cobalt and manganese contents. The values of Me–O distances are in reasonable agreement for both methods though the experimental errors of EXAFS data are higher.

We can conclude that EXAFS shows changing of oxygen octahedron size depending on the "central" atom type. In this sense the local surrounding of Co cation is different compared to the local surrounding of Mn ions.

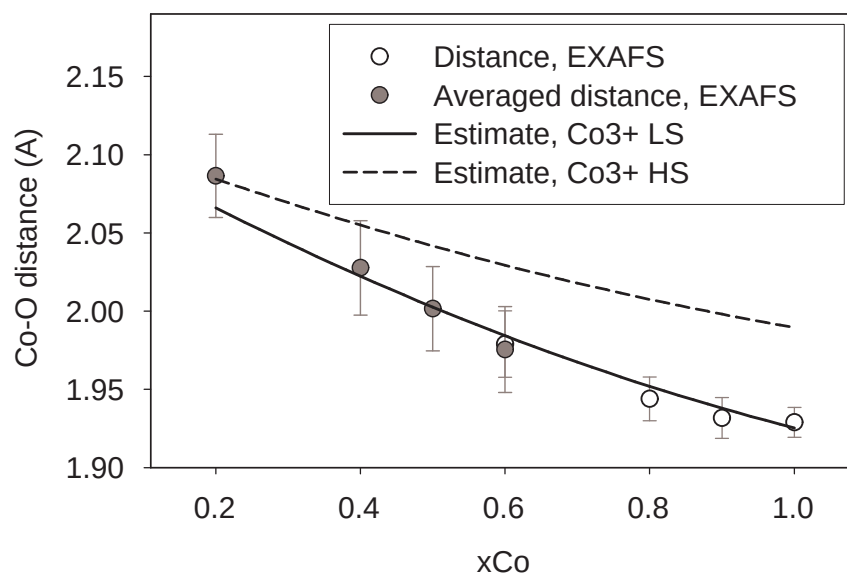


Figure 10.20: Comparison of Co-O distances evaluated from EXAFS experiments (empty circles stand for rhombohedral structure, gray circles are a simple average of the three Co-O distances obtained for orthorhombic structure) with dependences based on XANES results of [Siko2006] and calculations described in text (full line for case (i), dashed for case (ii)).

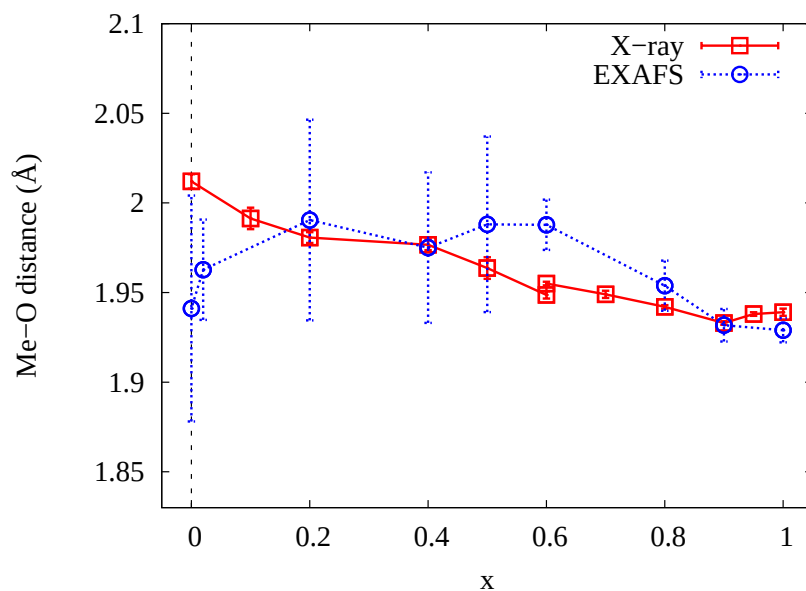


Figure 10.21: Average Me-O distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained by EXAFS and X-ray diffraction.

Chapter 11

NMR results and discussion

In order to study details of the charge and spin order in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds the NMR technique was used. Basic principles of NMR experiments were presented in chapter 5. Important experimental aspects of NMR experiments in magnetically ordered materials were discussed in chapter 7, including analysis and description of procedures we developed for control and calibration of transmission and receiver line for case of untuned probe.

To be able to observe NMR signal the nuclei of interest must have a non zero nuclear magnetic moment. In our samples all atoms have stable isotope with a non zero nuclear magnetic moment. Lanthanum has two stable isotopes, ^{138}La and ^{139}La with spin 5 and 5/2, respectively. Their magnetic and quadrupolar moments and natural abundance are listed in Table 11.1. Only one oxygen isotope, i.e. (^{17}O) is observable by NMR method, but this isotope has a very low natural abundance (0.038%), therefore, it gives very weak NMR signal. So that ^{17}O is used rarely for NMR experiment unless the sample is enriched with ^{17}O .

Manganese has one stable isotope ^{55}Mn with natural abundance 100 %. ^{55}Mn nucleus has spin 5/2, its gyromagnetic ratio is $\gamma = 1.056253 \text{ MHz/T}$ and quadrupole moment $Q = 0.33 \text{ barn}$. ^{57}Co has also natural abundance 100 % and its spin is 7/2, $\gamma = 1.007769 \text{ MHz/T}$ and quadrupole moment $Q = 0.42 \text{ barn}$ (all parameters of

isotope	spin	γ (MHz/T)	Q (barn)	natural abundance (%)
^{138}La	5	0.566152	0.45	0.902
^{139}La	5/2	0.6061148	0.2	99.098
^{17}O	5/2	0.577426	-2.558	0.038
^{55}Mn	5/2	1.0576253	0.33	100
^{57}Co	7/2	1.0077693	0.42	100

Table 11.1: NMR isotopes and their parameters,[webeleme].

nuclei are also listed in Table 11.1). The fact that gyromagnetic ratios of Mn and Co differ only by 5% has a crucial consequence for analysis of NMR experiments carried out on samples of interest. It is extremely difficult or even impossible to distinguish the shift of resonance frequency and assign it to one of these isotopes according to the shift in external magnetic field.

Hyperfine interaction is very sensitive to the electron configuration of ion and its binding. In chapter 2.2 it was already mentioned that Mn and Co can appear in different valence states. The electron shell is different for ions in the valence state $4+$ from that of ions in the $3+$ or $2+$ state. Therefore, also the hyperfine field should be different and the NMR signal should be located at different frequency. This situation takes place in the case of manganese as well as for cobalt atoms and in principle we can observe different valence states of Mn and Co, their hyperfine fields and its dependence on doping.

All measurements presented in this chapter were performed using BRUKER AVANCE NMR spectrometer described in chapter 6. Broad band NMR probehead was used and correct excitation and frequency dependence of sensitivity of the receiver line were controlled according to the procedure described in chapter 7.

Optimal excitation conditions were found for each resonance line in order to provide optimal excitation and maximum of the signal amplitude. Spectra were measured with taking into account the spin lattice relaxation characterized by the relaxation time, T_1 i.e. the repetition time was set long enough to make sure that after each scan nuclear magnetization comes back to equilibrium state.

Few samples were also measured in the external magnetic field. Field dependent measurements were performed in the cryogenic superconducting magnet JANIS with the flow cryostat insert. The superconducting solenoid can be set to produce magnetic field ranging from 0 to 5 Tesla and it allows to perform measurements at temperature ranging from 2 K to room temperature. The sample was cooled down by flowing cold helium vapors or it was immersed in the pumped liquid helium.

11.1 LaMnO_3

LaMnO_3 is an antiferromagnetic material which has already been studied using NMR, [Sido2004], [Allo2002]. In [Sido2004] authors observed one single line at 350 MHz. Our measurement on sample $0.0\text{-sr-}0$ showed one high intensity line at 350 MHz and other lines with smaller intensities at 307 MHz, 340 MHz, 370 MHz, 400 MHz (see Figure 11.1).

The spectrum of sample $0.0\text{-sr-}0$ was measured with two different excitation conditions using a single pulse sequence and the FID signal was recorded. Spectrum (a) in Figure 11.1 was measured with pulse length $100\text{ }\mu\text{s}$, which was optimal for the whole frequency range. Pulse length for spectrum (b) was $10\text{ }\mu\text{s}$, for this value the

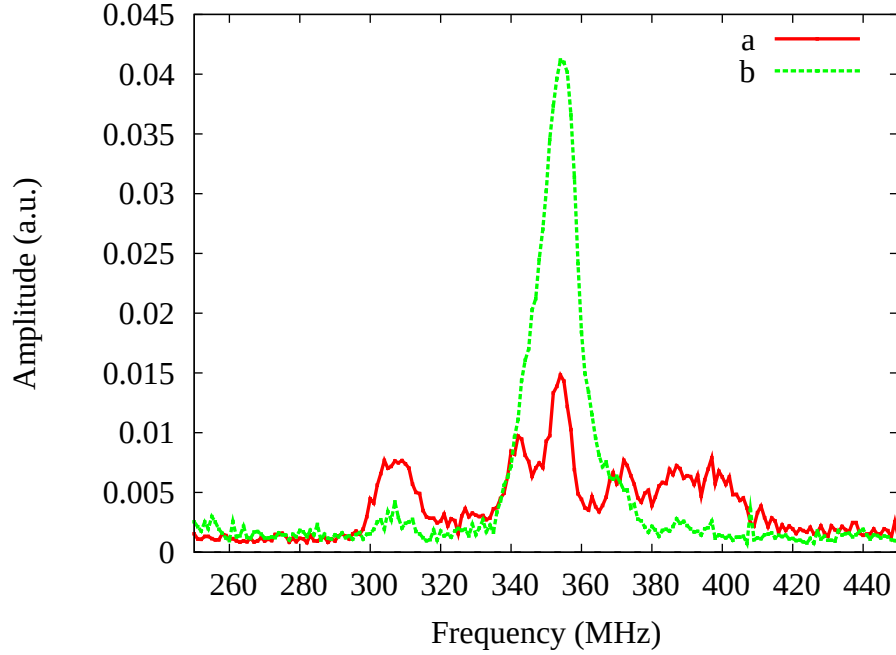


Figure 11.1: NMR spectrum of sample *0.0-sr-0*. *a*) measured with pulse length $100\ \mu\text{s}$, *b*) measured with pulse length $20\ \mu\text{s}$, spectra normalized to unity area.

ratio of intensities of lines at 350 MHz and 307 MHz was minimal. In spectrum (*b*) we can see more pronounced lines at 307 MHz, 340 MHz, 370 MHz, 400 MHz which are not evident in spectrum (*a*) due to a very strong signal of line at 350 MHz.

The line at 350 MHz is in agreement with signal observed in [Sido2004], and it is due to ^{55}Mn in Mn^{3+} state of antiferromagnetic LaMnO_3 . This assignment is supported by big length of excitation pulses which are needed for excitation. This also indicates a small enhancement factor which is typical for antiferromagnetic materials. The line at 307 MHz probably is due to the signal of Mn^{4+} which can appear in the material if there is even very small oxygen nonstoichiometry. The other lines, 340 MHz, 370 MHz, 400 MHz probably are also connected with some small ferromagnetic regions caused by oxygen nonstoichiometry.

11.2 $\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$

NMR spectra of three samples with $x = 0.2$ (*0.2-sg-0*, *0.2-sg-1*, *0.2-sr-0*) were measured at liquid helium temperature. Spectra were measured using a spin echo pulse sequence with the pulse lengths 8 and $16\ \mu\text{s}$, minimal pulse spacing $20\ \mu\text{s}$ and repetition time 25 ms. All lines observed in the spectra were properly excited.

In Figure 11.2 spectra of sample *0.2-sg-0* are plotted, they were measured with

pulse spacing varying from 20 μs to 160 μs . These spectra exhibit NMR lines in three frequency regions, which are denoted as I-III. In the first region (I) (from 270 MHz to 320 MHz) one strong and relatively narrow line is observed. The second range (signed by II) from 350 to 450 MHz contains a broad maximum around 400 MHz, and the last line with width larger than 50 MHz is located at 475 MHz, this range is denoted as III (450–600 MHz). These frequency regions denoted with symbols I, II and III are used also in the description of NMR spectra of other samples. The spectrum of sample *0.2-sg-0* exhibits another narrow line at 600 MHz of very low intensity which is marked symbol X.

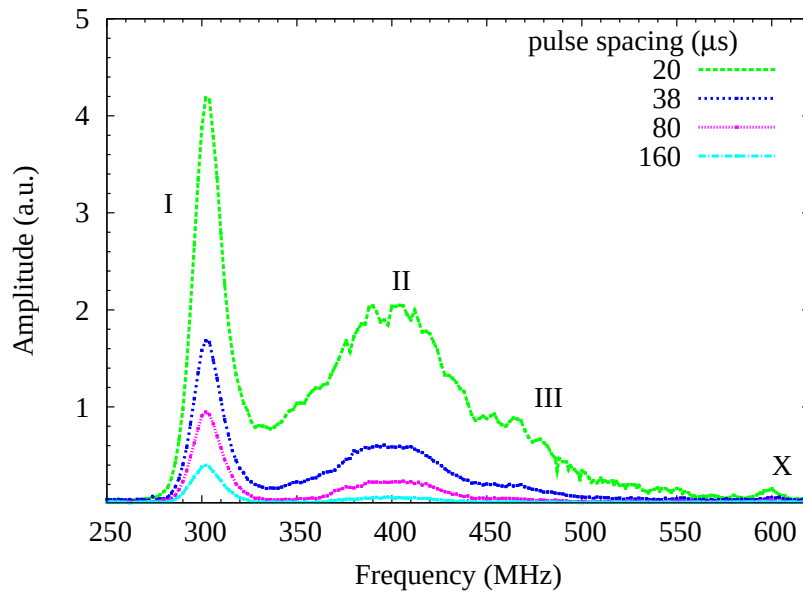


Figure 11.2: NMR spectra of sample *0.2-sg-0* measured with different pulse spacing at the temperature 4.2 K

In Figure 11.3 we can see the normalized spectra of sample *0.2-sg-0* in order to check the relative values of the spin-spin relaxation time at different frequencies. We see that spin-spin relaxation time of the line in region I is clearly longer compared to signals of the rest of the spectrum.

Spectra of all three samples (*0.2-sg-0*, *0.2-sg-1*, *0.2-sr-0*) are presented for comparison in Figure 11.4. Overall shape of spectra of all three samples exhibits the same character. In the spectra of samples *0.2-sg-0* and *0.2-sg-1* a change of line intensities in the region II and III related to thermal treatment is evident. For the sample *0.2-sr-0* we can see that the second line shifts to lower frequencies compared to the same line of samples *0.2-sg-0* and *0.2-sg-1*.

Line I following the literature was assigned to Mn^{4+} ions which have the lower magnetic moment than Mn^{3+} or Mn^{2+} , therefore, the hyperfine field is lower and

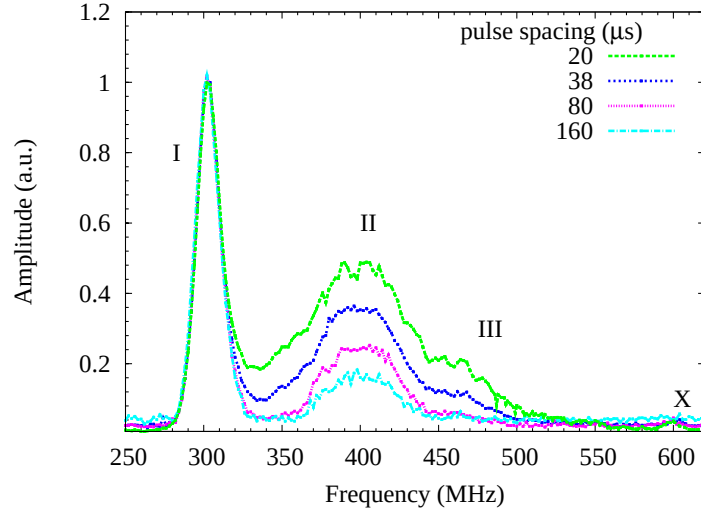


Figure 11.3: Normalized NMR spectra of sample *0.2-sg-0* measured with different pulse spacing at temperature 4.2 K.

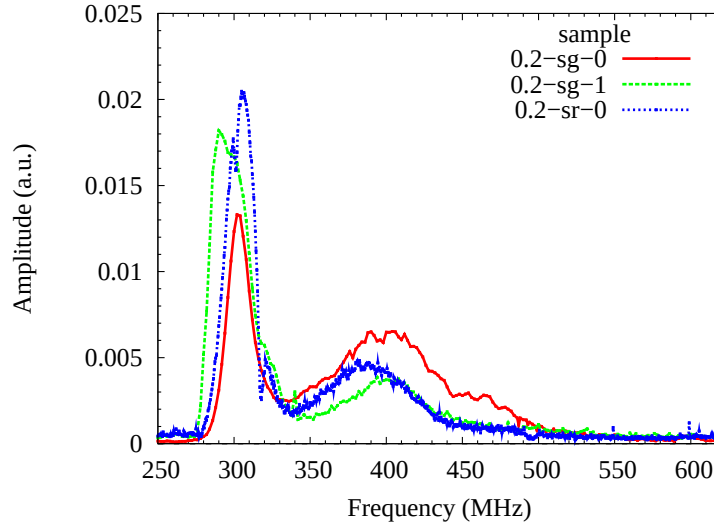


Figure 11.4: NMR spectra of samples *0.2-sg-0*, *0.2-sg-1*, *0.2-sr-0* at temperature 4.2 K, spectra normalized to unity area.

the frequency of NMR signal is lower as well.

In Figure 11.5 details of Mn^{4+} line can be seen. While the Mn^{4+} line of samples *0.2-sg-0*, *0.2-sr-0* is more or less at the same frequency (with approximately the same line width), the Mn^{4+} line of sample *0.2-sg-1* is shifted by 8 MHz to higher frequencies. This is accompanied by a rapid increase of the line width and evident splitting of the line.

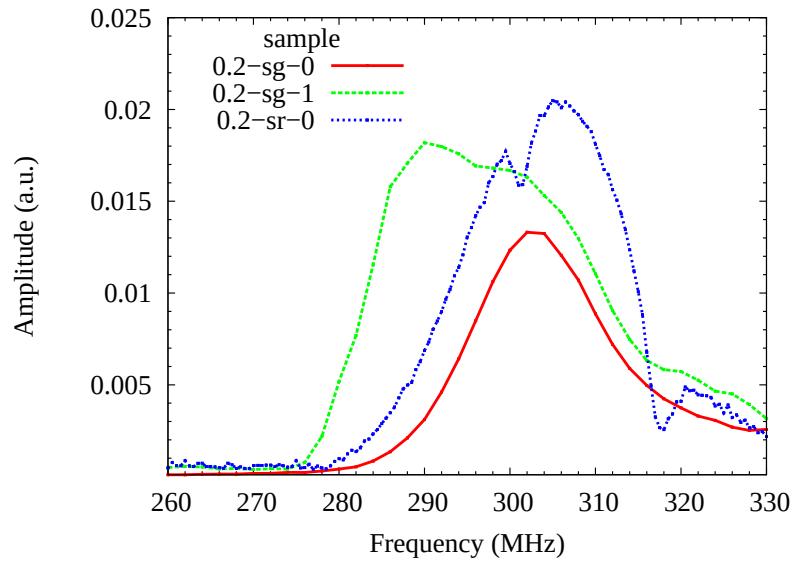


Figure 11.5: NMR spectra of samples *0.2-sg-0*, *0.2-sg-1*, *0.2-sr-0* at temperature 4.2 K, detail of Mn^{4+} line, spectra normalized to unity area.

Sample *0.2-sg-0* was measured in external magnetic field of 5 T. The spectrum measured at 5 T is presented in Figure 11.6 together with spectrum obtained at 0 T. In the spectrum measured at 5 T one can see four lines with maxima located at 255 MHz, 342 MHz, 530 MHz and 642 MHz. The Mn^{4+} line (I) shifts to lower frequency with increase of the external magnetic field. The hyperfine field of Mn^{4+} ions is known to be antiparallel to their magnetic moments and consequently Mn^{4+} magnetic moments are parallel to the direction of magnetization, hence the line shifts towards lower frequencies if the magnetic field is applied. The weak line at 600 MHz in external magnetic field shifts to higher frequencies, which means that the hyperfine field of ions resonating at 600 MHz is parallel to the spontaneous magnetization. This line was measured in more detail in three different applied magnetic fields (see Figure 11.7).

Now let us discuss the central part of spectra. It consists of two lines (region II and III). The signal II shifts to lower frequencies and the signal III shifts to higher frequencies, which indicates that the hyperfine field is antiparallel and parallel to the direction of spontaneous magnetization, respectively.

We conclude that the spectrum consists of four lines, two lines with hyperfine field antiparallel to the spontaneous magnetization and two lines with hyperfine field parallel to it.

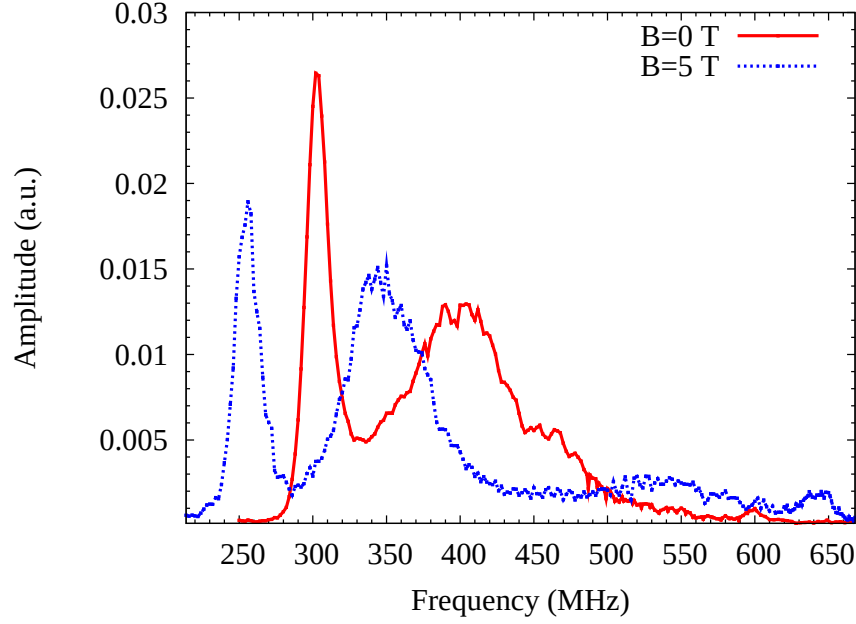


Figure 11.6: NMR spectrum of sample $\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$ prepared by SG method (*0.2-sg-0*) measured at external field of 0 and 5 Tesla.

11.3 $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$

NMR spectrum of sample $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ (*0.3-sg-0*) consists of three regions similarly to spectra of samples with $x = 0.2$, see Figure 11.8, therefore we signed these regions like in case of samples with $x = 0.2$ by I, II and III. Signal at 305 MHz (I) was assigned to the Mn^{4+} , next line has maximum at 400 MHz (II) and very broad (the half width is around 90 MHz) line has the maximum at 500 MHz (III). No NMR signal was observed at 600 MHz. The spectra measured in external magnetic field of 3.5 Tesla and 5 Tesla are plotted together with zero field spectra in Figure 11.8.

We can see that the spectral lines in external magnetic field behave similarly to spectra of $\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$, i.e. two lines at lower frequencies shift towards lower frequencies and line III shifts to higher frequencies.

11.4 $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$.

The NMR spectra of the sample *0.4-sg-2* measured with different pulse spacing are shown in Figure 11.9. The spectra consist of four lines. First three signal regions are the same as in previous samples (i.e. with $x = 0.2$ and 0.3) and they are denoted with symbols I, II, and III. The first line (I) (around 300 MHz) is assigned to Mn^{4+} ,

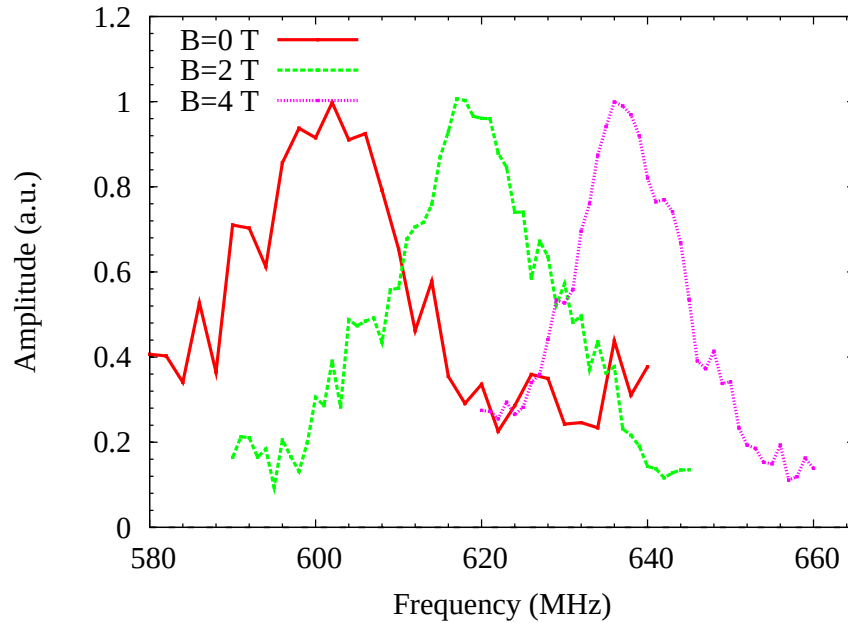


Figure 11.7: LaMn_{0.8}Co_{0.2}O₃ sol-gel (0.2-sg-0) measured at external field ranging from 0 to 5 Tesla, the upper line is located at 600 MHz in 0 Tesla, at 619 MHz in 2 Tesla and at 637 MHz in 4 Tesla

this line exhibits additional structure which will be discussed later. Next line (II), with full width at half maximum of 60 MHz is located at 410 MHz. A broad plateau is observed in region III and finally a relatively narrow line (with full width at half maximum of 5 MHz) was found at 540 MHz, this line is denoted as IV.

Spectra were normalized to unit maximal amplitude (see Figure 11.10). From Figure 11.10 it is evident that the spin-spin relaxation for signals I and IV is similar while the other two signals (II, and III) relax faster.

Again, an important information for interpretation of the NMR spectrum comes from measurements in the external magnetic field which are presented in Figure 11.11. Signals I, II and IV shift to lower frequencies while the line III (broad plateau) shifts to higher frequencies. We conclude that the three lines which shift to the lower frequencies origin from ferromagnetically ordered ions with magnetic moments parallel to the direction of magnetization while the plateau origins from ions ordered antiferromagnetically. Similar spin-spin relaxation time of the line at the lowest and at the highest frequency can indicate a very strong coupling. However, it is not possible to distinguish whether in magnetic field the line shifts with the gyromagnetic ratio of manganese or cobalt because their gyromagnetic ratios differ only by 5% and the observed lines are too broad.

Let us focus on the splitting of Mn⁴⁺ line (I). In Figure 11.12 the detail of

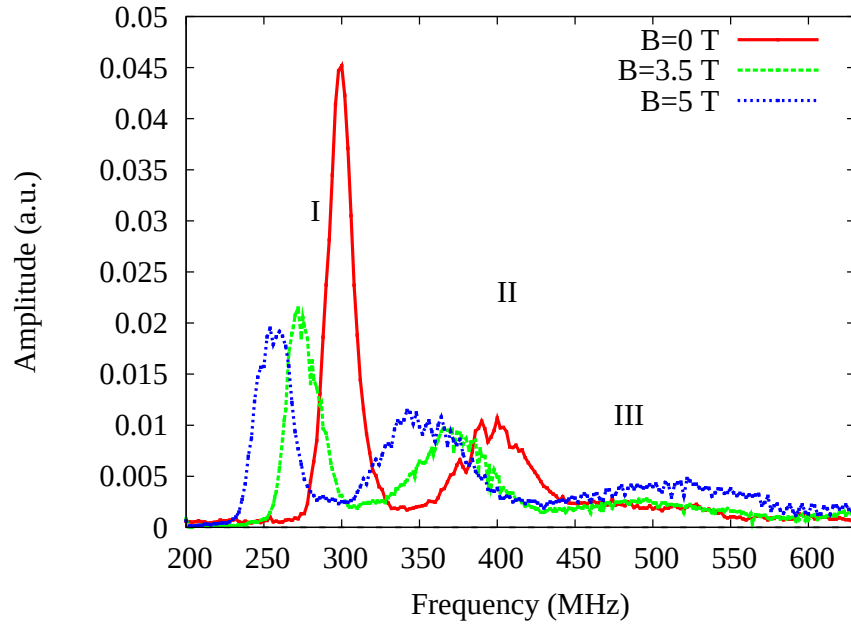


Figure 11.8: NMR spectrum of LaMn_{0.7}Co_{0.3}O₃ sol-gel (0.3-sg-0) in dependence on magnetic field 0–5 T.

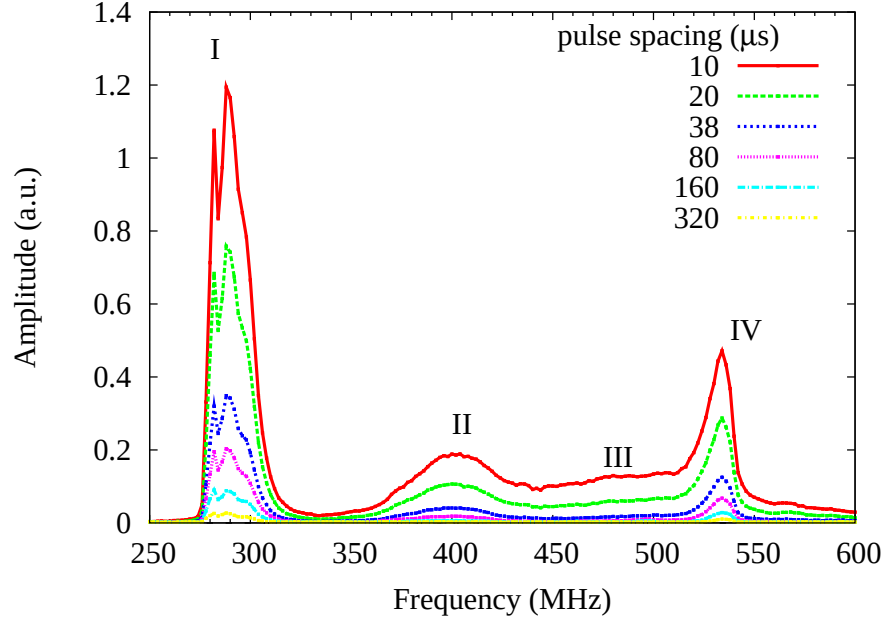


Figure 11.9: NMR spectra of sample 0.4-sg-2 measured with different pulse spacing, at 4.2 K

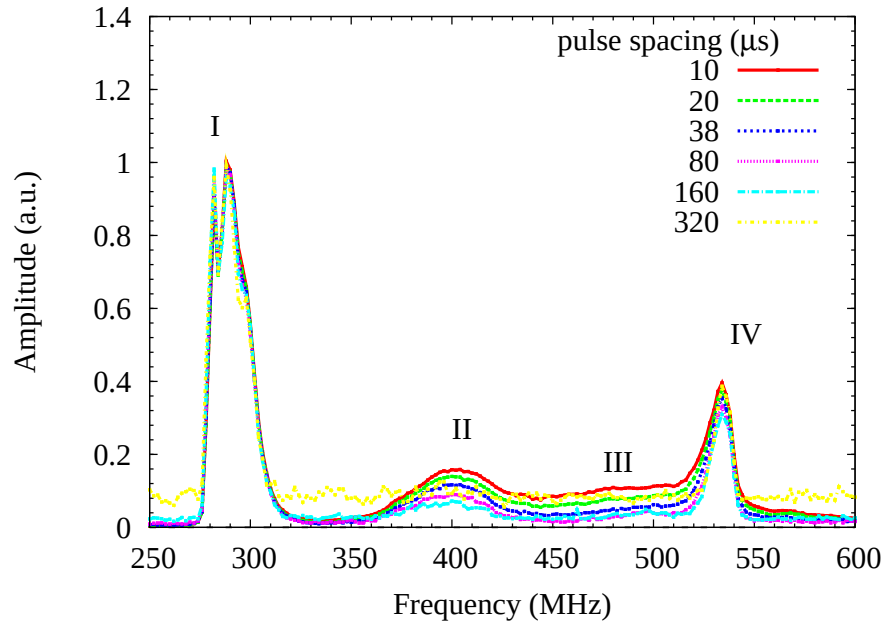


Figure 11.10: Spectra of sample $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$ (0.4-sg-2), normalized to unit maximal amplitude and measured with different pulse spacing, at 4.2 K

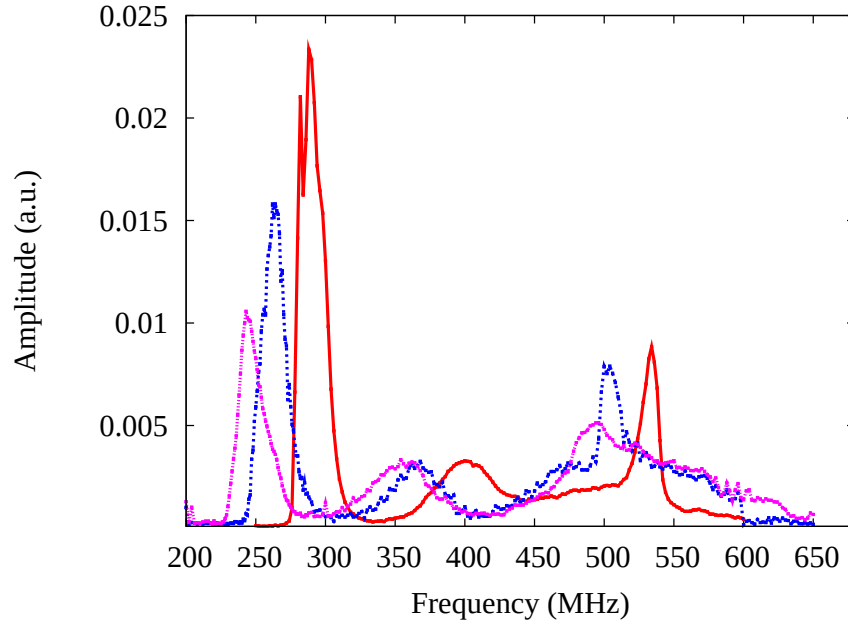


Figure 11.11: Field dependence of NMR spectra of sample 0.4-sg-2 , at 3 K.

Mn^{4+} line is presented. The line is split into peaks with different intensities with approximately equidistant positions. Manganese atom in the $Pbnm$ crystal structure is situated in the center of oxygen octahedron and it is surrounded by six nearest neighbors $3d$ transition metals. For random distribution of Mn and Co ions on the B-site the probability that the manganese atom is surrounded by 0, 1, ... 6 manganese neighbors is given by the binomial distribution.

We tested three possibilities of arrangement in the Mn surrounding. The first was alternating Mn and Co ions, the second was a random distribution and the third, mixture of preferable ordering and random distribution. However, none of tested arrangements can describe in a simple way the Mn^{4+} line splitting.

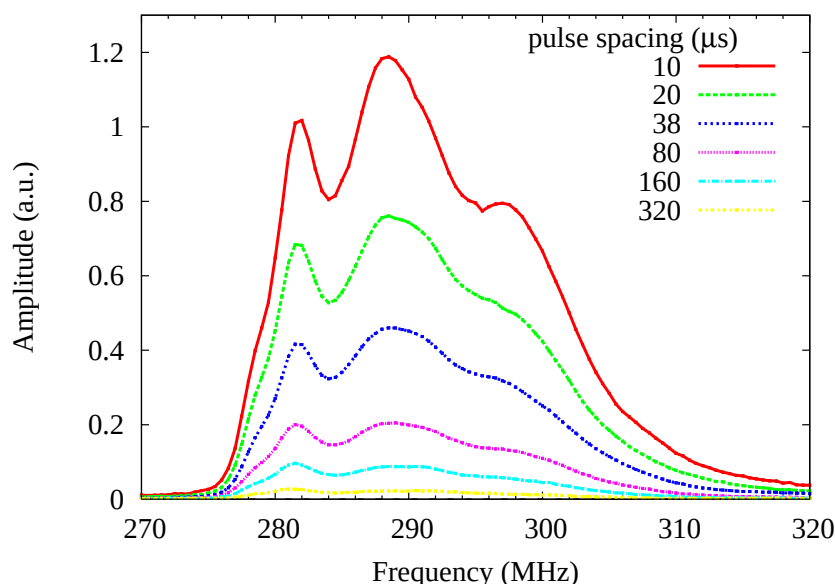


Figure 11.12: Spectra of $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$ (*0.4-sg-2*), details of Mn^{4+} line.

The relaxation time T_2 was found to be the same for all components of the Mn^{4+} line, see Figure 11.13. In Figure 11.13 NMR spectra of sample *0.4-sg-2* measured with different pulse spacing T_2 are shown to compare the spin-spin relaxation time. The relaxation times T_1 and T_2 were measured and their values are listed in Table 11.2.

NMR spectra of samples with $x = 0.4$ prepared using the solid state reaction method were measured before (sample *0.4-sr-0*) and after (sample *0.4-sr-1*) the additional treatment at 750°C in the oxygen atmosphere. The spectra are plotted in Figure 11.14 and the detail of the Mn^{4+} line is plotted in Figure 11.15. No significant effect of the thermal treatment on the NMR spectrum is observed in the case of samples *0.4-sr-0* and *0.4-sr-1*. Moreover, almost the same shape of Mn^{4+} line is observed for all three samples with $x = 0.4$ doping.

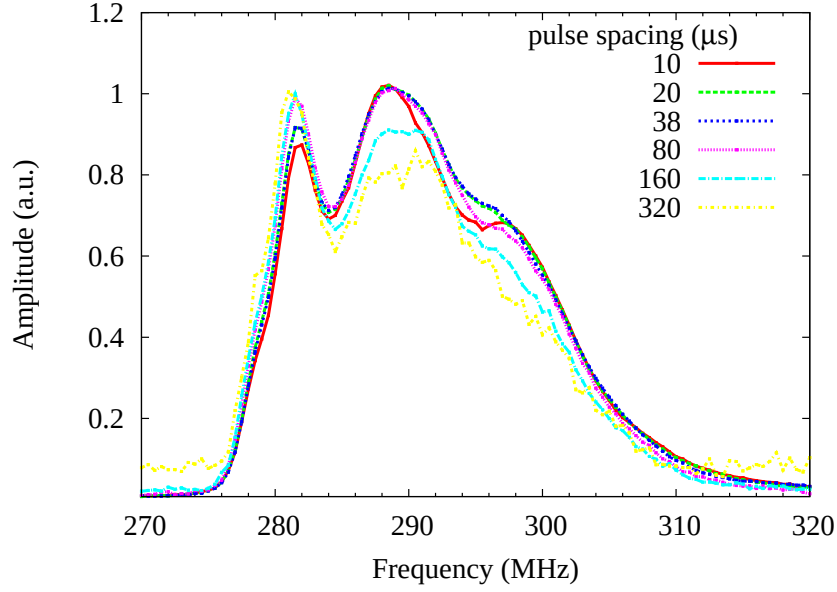


Figure 11.13: Spectra of $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$ (*0.4-sg-2*), details of Mn^{4+} line, normalized to maximal amplitude.

11.5 $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$

NMR spectra of samples with $x = 0.5$, one prepared using the SR method *0.5-sr-0* and three using the SG method (*0.5-sg-0*, *0.5-sg-1*, *0.5-sg-2*) were measured at 4.2 K. Samples *0.5-sr-0*, *0.5-sg-0*, *0.5-sg-1* exhibit similar spectral pattern like samples with lower cobalt content. Spectra are plotted in Figure 11.16 and details of Mn^{4+} line are shown in Figure 11.17.

Samples with $x = 0.5$ prepared using SG or SR method without thermal treatment exhibit similar spectral pattern. This allows us to make a conclusion that the type of the preparation method (SR or SG) has only small influence on the order-

Frequency (MHz)	T_1 (ms)	T_2 (μs)
288	1.19(6)	72(4)
396	1.32(7)	44(2)
510	1.89(9)	29(1)
534	1.13(6)	59(3)
440	1.00(5)	21(1)
496	0.86(4)	31(2)

Table 11.2: Relaxation times of sample *0.4-sg-2*.

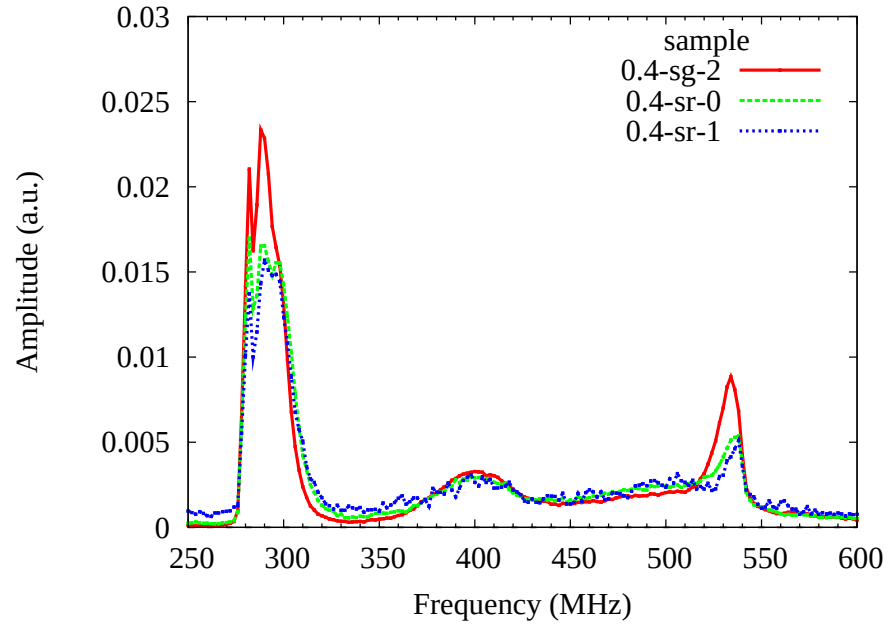


Figure 11.14: NMR spectra at 4.2 K of the samples (*0.4-sg-2*), (*0.4-sr-0*), (*0.4-sr-1*) normalized to unity area.

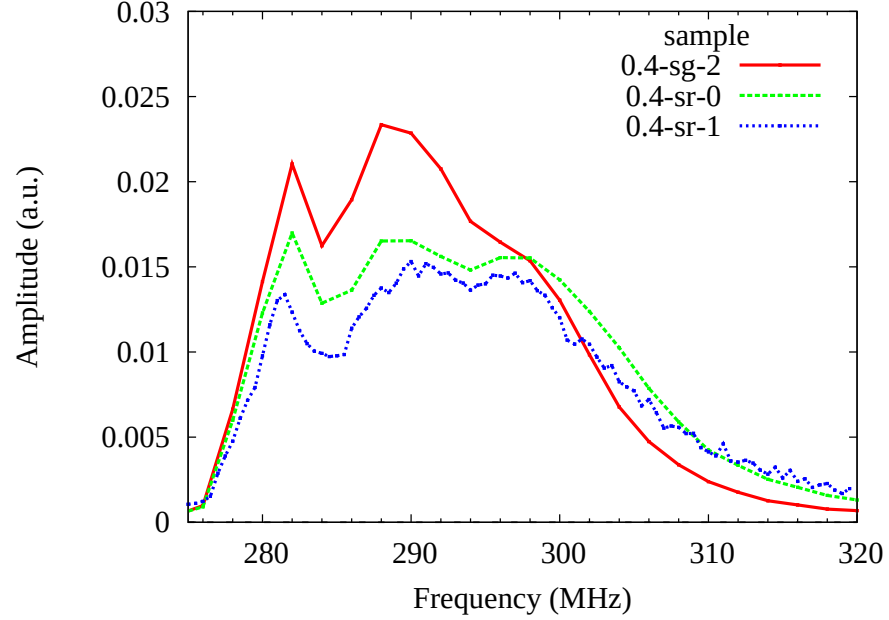


Figure 11.15: NMR spectra at 4.2 K of samples (*0.4-sg-2*), (*0.4-sr-0*), (*0.4-sr-1*) normalized to unity area, details of Mn^{4+} line.

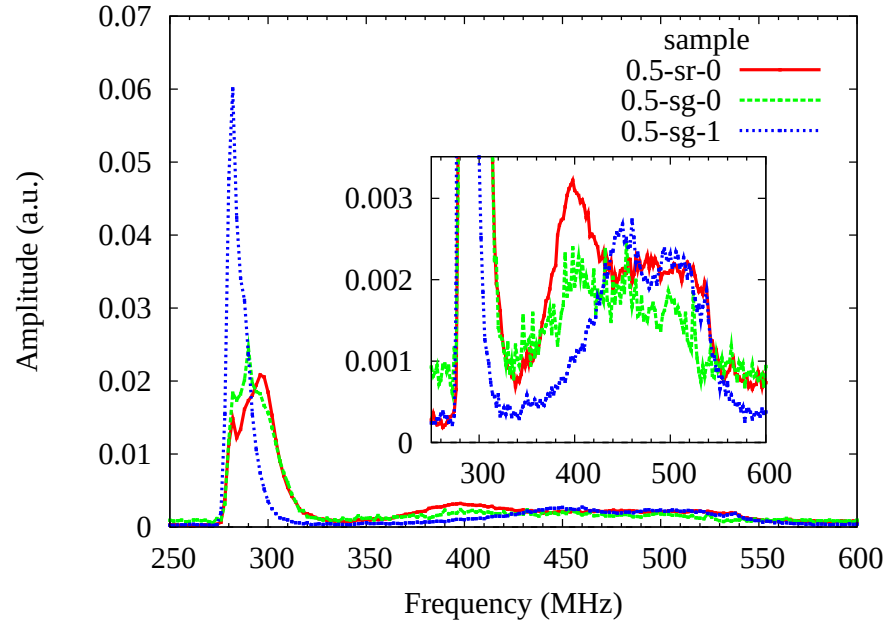


Figure 11.16: NMR spectra of samples *0.5-sg-0*, *0.5-sg-1*, *0.5-sr-0* at 4.2 K. Spectra are normalized to unit area.

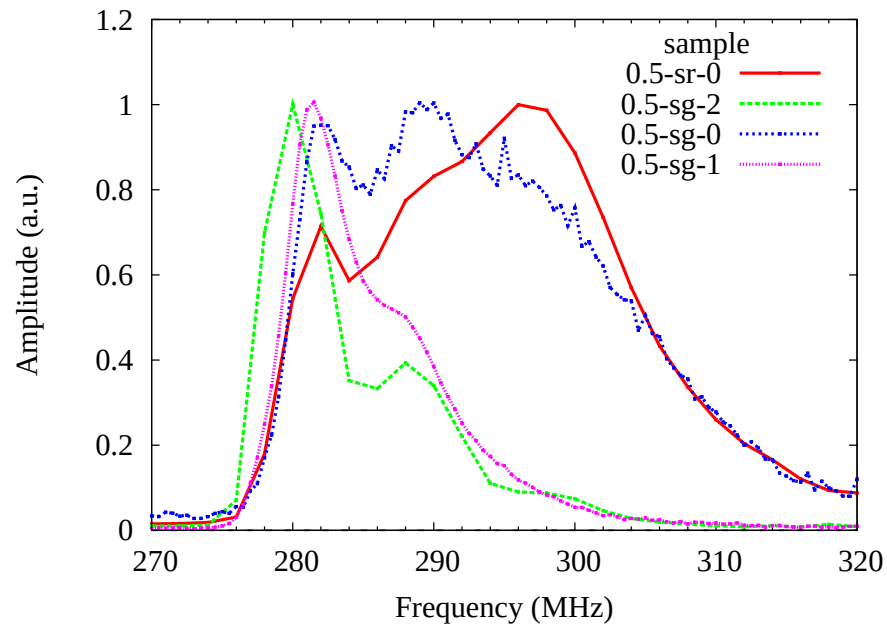


Figure 11.17: NMR spectra of samples *0.5-sg-0*, *0.5-sg-1*, *0.5-sg-2*, *0.5-sr-0* at 4.2 K, details of Mn^{4+} line. Spectra are normalized to maximal amplitude.

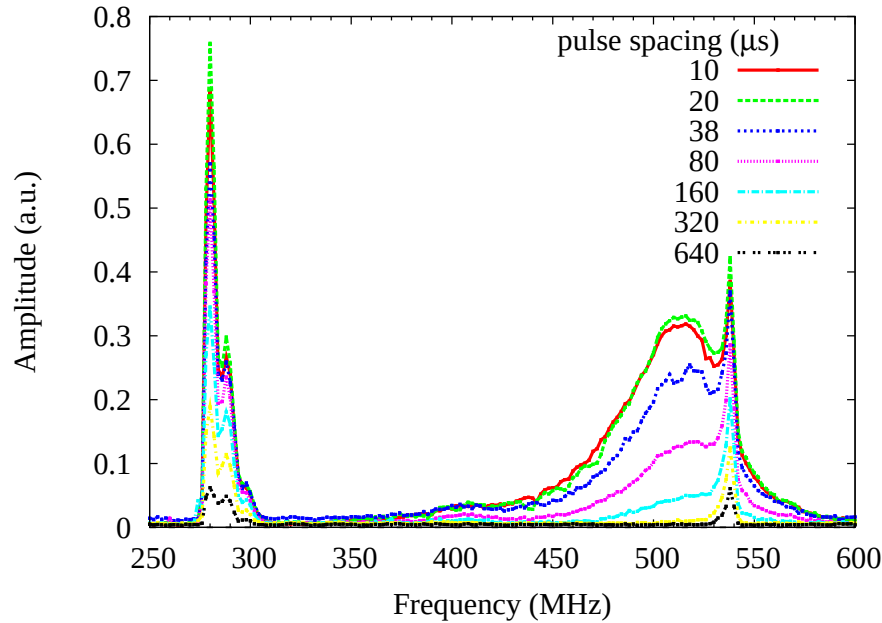


Figure 11.18: NMR spectra of the sample *0.5-sg-2* measured at 4.2 K with different pulse spacing

ing of ions in the material studied. On the other hand the NMR spectrum of the samples (prepared using SG method) is dramatically affected by heating at 750°C in oxygen atmosphere. With thermal treatment the Mn^{4+} line becomes narrow and splits, a structure consisting of three lines is observed in the range from 350 MHz to 600 MHz, one line at 450 MHz (II), next at 500 MHz (III) and very narrow line at 538 MHz (IV), the line IV has small intensity in the case of sample *0.5-sg-1* and higher intensity in the case of sample *0.5-sg-2*, see Figure 11.18.

In order to check if the spin-spin relaxation time is different at different frequencies, spectra measured with different pulse spacing were normalized to their maximal amplitude. Normalized spectra for the sample *0.5-sg-2* are shown in Figure 11.19 and for the sample *0.5-sr-0* in Figure 11.20. The spectral lines II and III have approximately the same relaxation time which is on the other hand much shorter than the relaxation time of lines I and IV for both samples.

Mn^{4+} lines measured with different pulse spacing for samples *0.5-sg-2* and *0.5-sr-0* are presented in Figures 11.21 and 11.22, respectively.

NMR spectra of sample *0.5-sg-2* in the external magnetic field of 0, 3 and 5 Tesla are plotted in Figure 11.23. There is an evident shift of signals I, II, IV to lower frequencies. On the other hand the line III (which is the broadest) shifts to higher frequencies. This behavior is the same as in the case of samples with lower x . Therefore, the ions contributing to NMR lines denoted as II and IV are parallelly ordered with Mn^{4+} while the ions which contribute to signal in the region II are

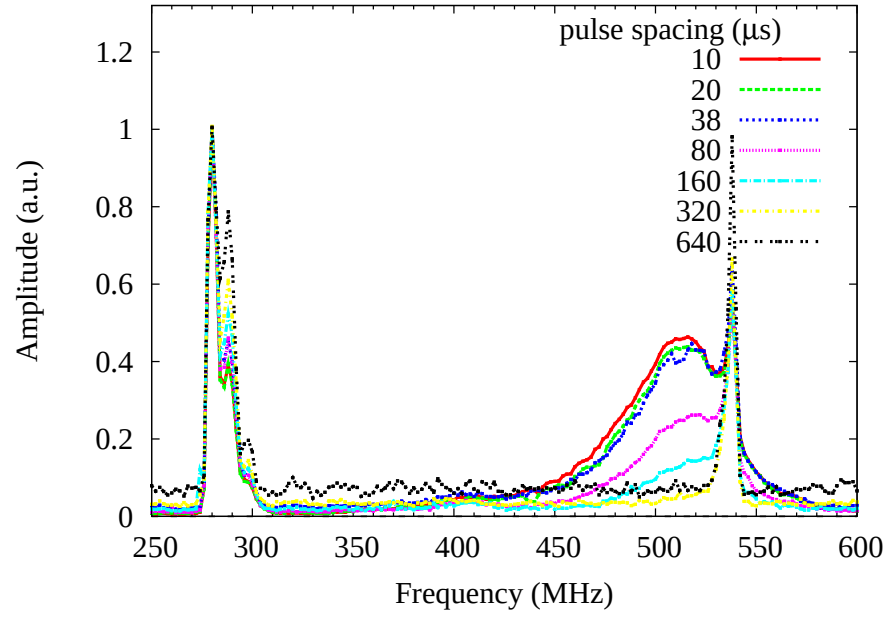


Figure 11.19: NMR spectra of the sample *0.5-sg-2* measured with different pulse spacing, spectra are normalized to the amplitude of Mn⁴⁺ line.

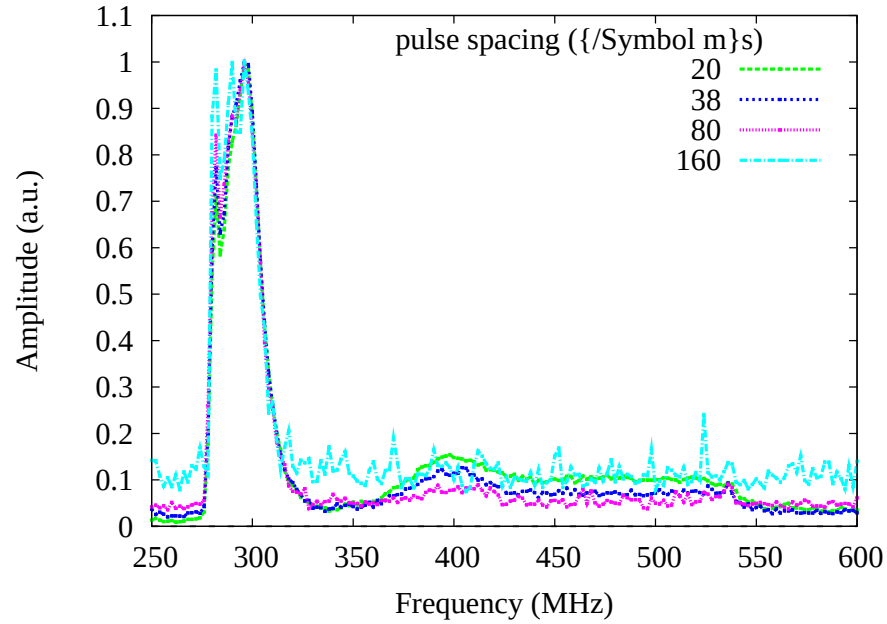


Figure 11.20: NMR spectrum of the sample *0.5-sr-0* measured with different pulse spacing.

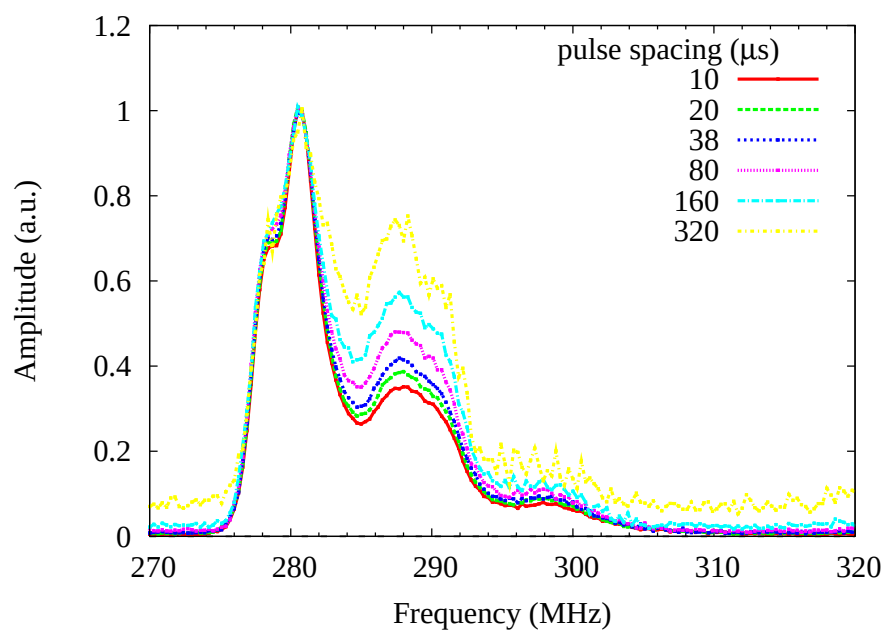


Figure 11.21: NMR spectra of the sample *0.5-sg-2* measured with different pulse spacing, Mn^{4+} line in detail.

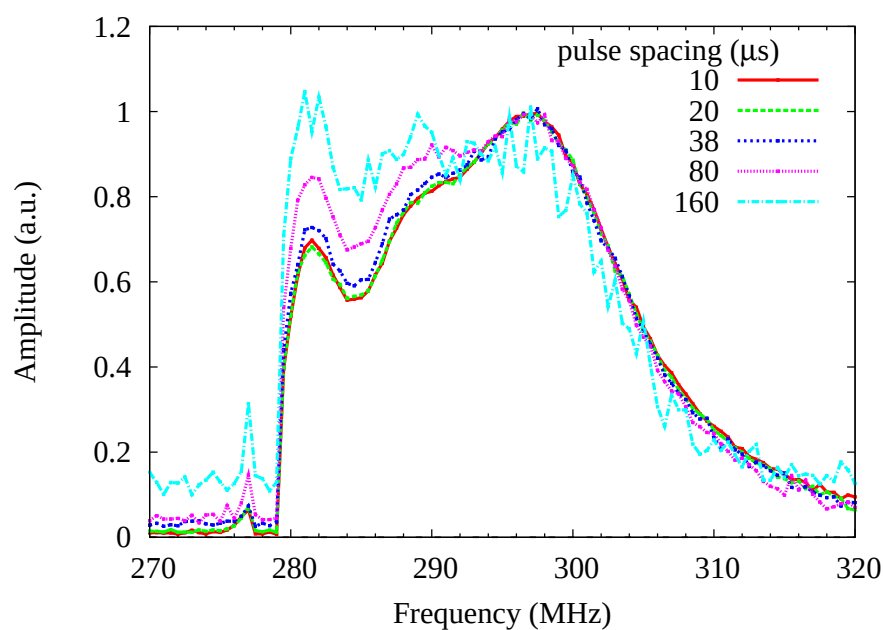


Figure 11.22: NMR spectra of *0.5-sr-0* sample measured with different pulse spacing, Mn^{4+} line is shown in detail.

antiparalelly ordered with Mn^{4+} .

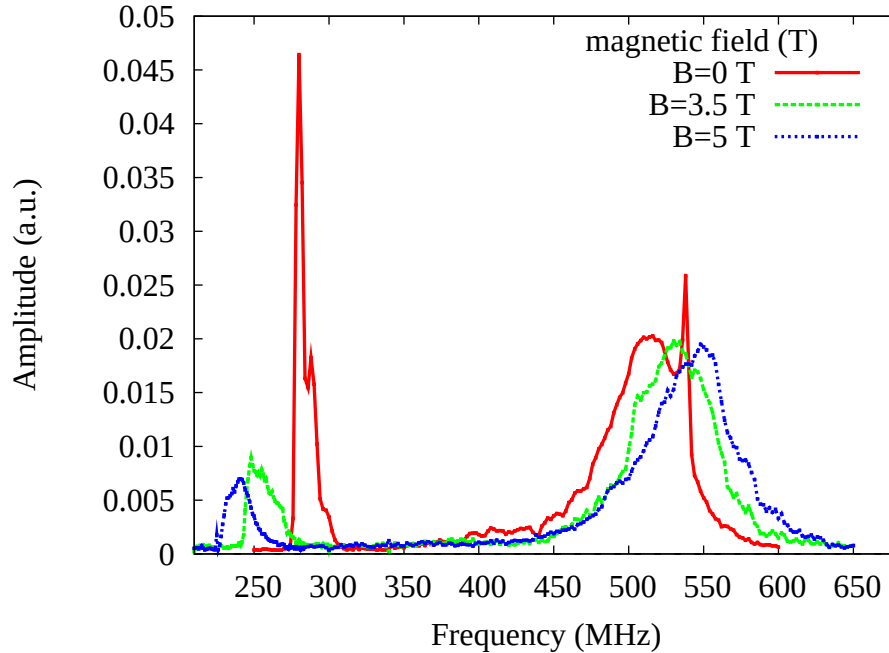


Figure 11.23: NMR spectrum *0.5-sg-2* in the external magnetic field of 0-5 Tesla.

In order to find the origin of the narrow line (IV), it was measured at several values of external magnetic field ranging from 0 to 5 T with long pulse spacing. The pulse spacing was chosen taking into account to the spin-spin relaxation time T_2 in such way that the broad line at 506 MHz is no longer observable (see Figure 11.19) and we can clearly observe the shifting of the narrow line. The narrow line at different magnetic field is shown in Figure 11.24 for fitting this line we used a Gaussian curve. The dependence of the central frequency of this line on the applied magnetic field is shown in Figure 11.25.

We see that the central frequency of the narrow line decreases linearly with increasing applied field. In the Figure 11.24 values from 2 T are plotted only (the demagnetization field was found to be smaller than 1.5 T). The field dependence of the central frequency was fitted using a liner function and the parameters of the fit were evaluated. A gyromagnetic ratio, which amounts to $\gamma = 10.46 \pm 0.4$ MHz/T was obtained. The possible sources of this signal are ^{55}Mn and ^{57}Co ions. However, it cannot be decided with absolute certainty whether this line originates from manganese or cobalt nuclei.

As in the case of Mn^{4+} line of sample *0.4-sg-2* also in the case *0.5-sg-2* we tried to analyze the Mn^{4+} line splitting by means of ordered disordered model of manganese and cobalt arrangement in the sample. The ordered model in this case results in

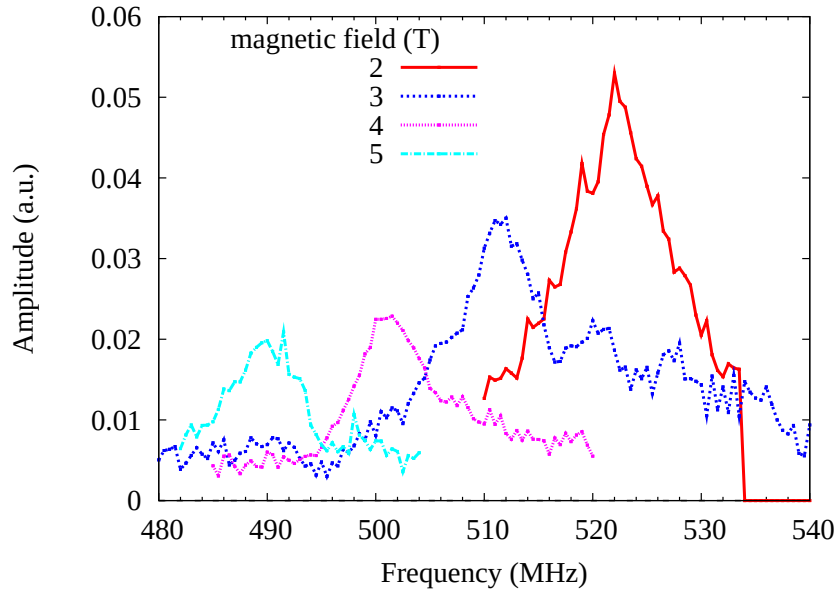


Figure 11.24: The shift of NMR line IV of sample *0.5-sg-2* in the external magnetic fields, the line III was reduced by setting pulse spacing time $320 \mu\text{s}$.

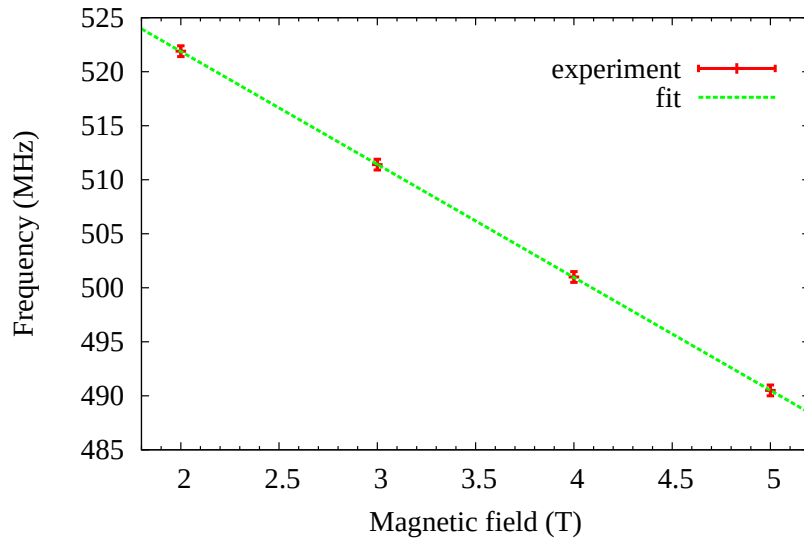


Figure 11.25: The dependence of the central frequency of the narrow line (IV, sample *0.5-sg-2*) on the external magnetic field, points are from measurements and the dashed line is a fit. Parameters of fitted linear function are: 10.46 (slope) and 542.8 (y-intercept), where the slope is related to the gyromagnetic ratio. Gyromagnetic ratio of $\gamma^{55}\text{Mn} = 10.58 \text{ MHz/T}$ and of $\gamma^{59}\text{Co} = 10.07 \text{ MHz/T}$.

one line, as it was mentioned in [Nish1995], while in the case of disordered sample the line intensities should follow the binomial distribution. Even the mixture of ordered and disordered phase cannot describe properly the spectrum of the sample. Authors of [Nish1995] published Mn^{4+} spectrum of sample $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ and the spectrum exhibited similar splitting as in our case. However, the authors discussed the influence of Mg doping and they do not provide any explanation of the Mn^{4+} line splitting in $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ compound.

11.6 $\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$

The NMR spectrum of sample $\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$, where part of the Co ions are replaced with magnesium ions is presented in Figure 11.26. There are four lines in the spectra, one symmetric line around 300 MHz with complicated but badly resolved structure, two weak lines at 400 MHz and 500 MHz and one weak narrow line at 543 MHz (see Figure 11.27). The NMR spectrum in frequency range 270–320 MHz of a compound with the same composition is presented in [Nish1995]. Spectrum reported in [Nish1995] is also more or less symmetric, but it exhibits splitting to four lines, not to two lines as in our measurement. The reason for observing only two lines could be due to higher dipole-dipole broadening caused by disorder in our sample.

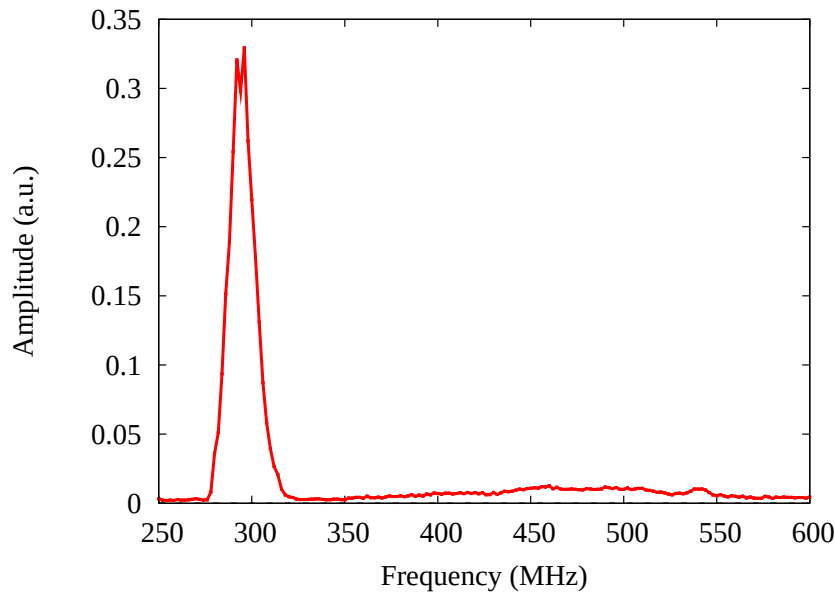


Figure 11.26: NMR spectrum of sample $\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$ measured at 4.2 K

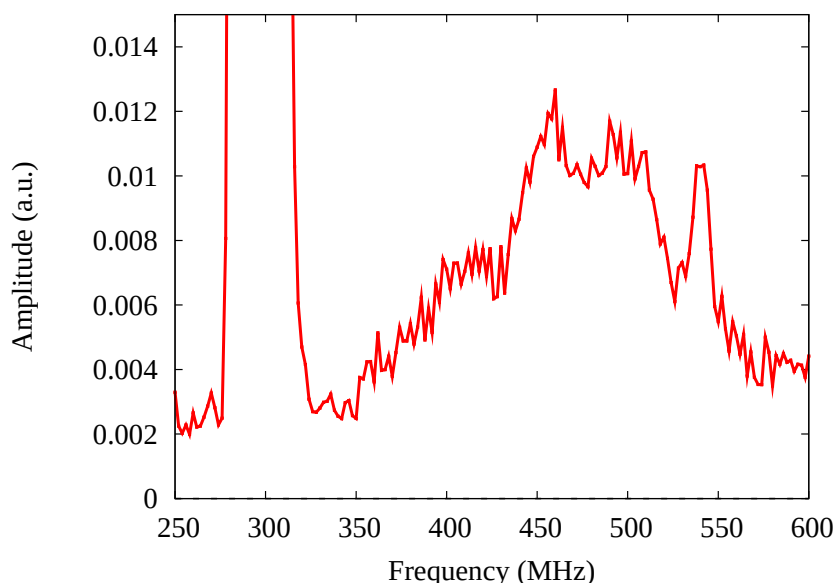


Figure 11.27: NMR spectrum of sample $\text{LaMn}_{0.5}\text{Co}_{0.2}\text{Mg}_{0.3}\text{O}_3$ measured at 4.5 K, enlarge y scale.

11.7 Influence of cobalt doping on the NMR spectra

In previous sections we described the NMR results for samples $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0, 0.2, 0.3, 0.4, 0.5$, prepared using different methods. This section presents a comparison of NMR spectra of samples with different Co content in order to analyze the influence of Co doping and assignment of the spectral lines to given ions.

Spectra of samples prepared using SR and SG method are plotted in Figures 11.28 and 11.29, respectively. With increasing of Co content there is an evident shift of the Mn^{4+} line to lower frequencies for samples 0.2-sr-0 and 0.4-sr-0 , while the Mn^{4+} line for samples 0.4-sg-0 and 0.5-sr-0 is located at the same frequency. Moreover, the decrease of Mn^{4+} line frequency with increasing Co content is also evident for all samples prepared by the sol-gel method (0.2-sg-0 , 0.3-sg-0 and 0.5-sg-0). The Mn^{4+} line is shown in more detail in Figure 11.30. Observed frequency shift indicates decreasing of the hyperfine field of Mn^{4+} . The signal intensity in the range III increases with increasing Co content. Due to large line width it is difficult to say if there is a frequency shift with increasing Co content.

Spectra of samples prepared by the sol-gel method with additional treatment are plotted together in Figure 11.31. One can see that the manganese 4+ line is much more narrow in the case of sample with $x = 0.5$. As in the case of samples without additional treatment the center of gravity of the Mn^{4+} line shifts to lower frequencies with increasing cobalt content. There are big differences between spectra of samples

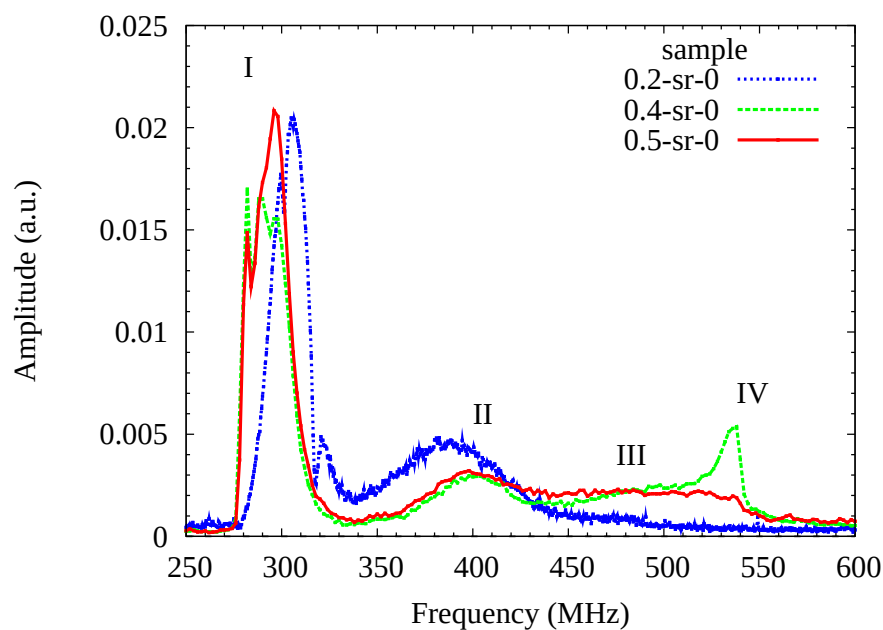


Figure 11.28: NMR spectra of samples prepared using the solid state reaction method measured at 4.2 K.

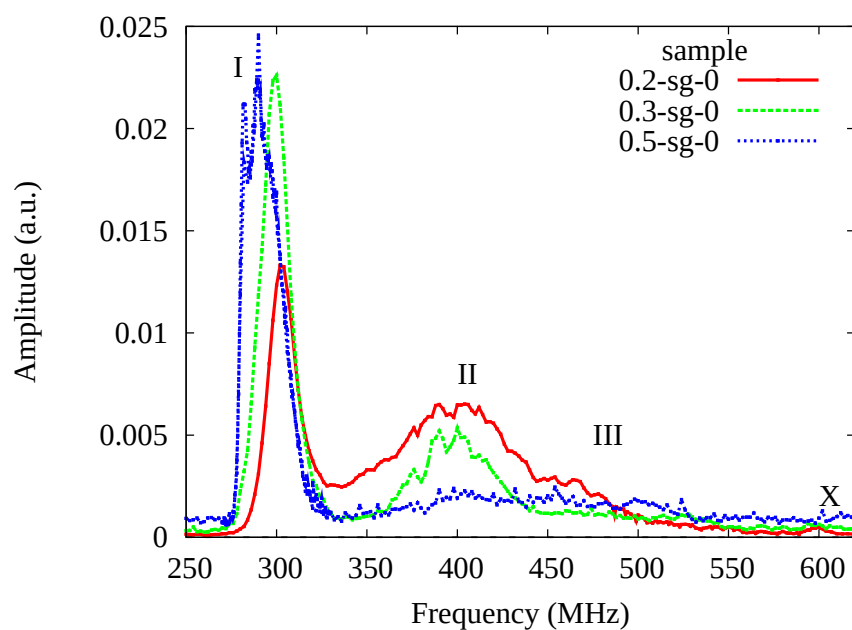


Figure 11.29: NMR spectra of samples prepared by the sol-gel method without additional treatment.

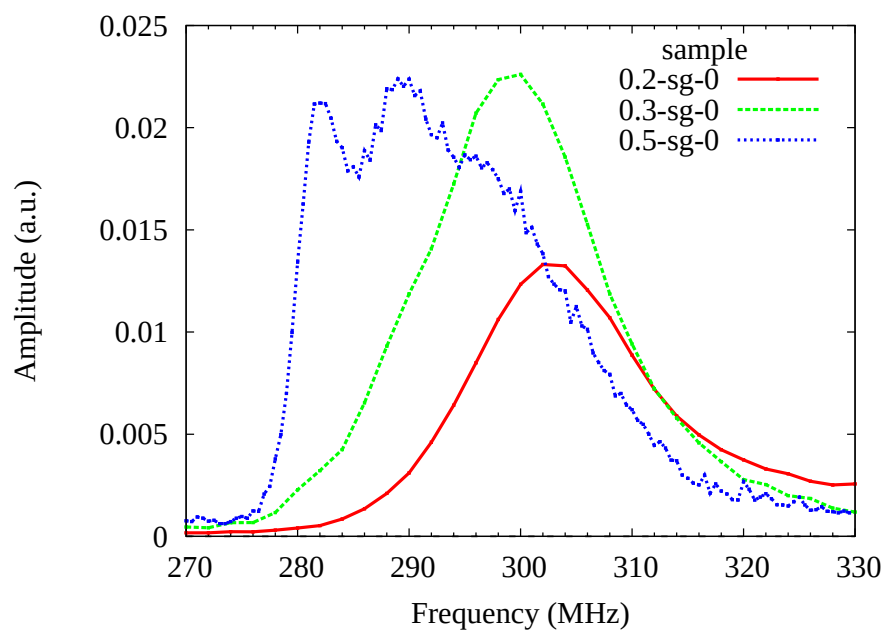


Figure 11.30: NMR spectra of samples prepared by the sol-gel method without additional treatment, Mn^{4+} line in more detail.

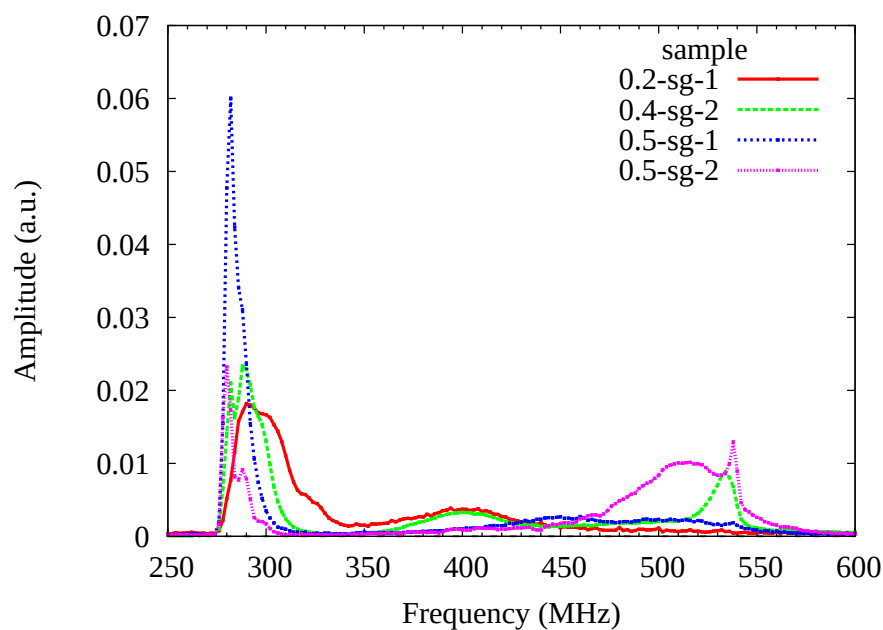


Figure 11.31: NMR spectra of samples prepared by the sol-gel method with additional treatment.

0.4-sg-2 and *0.5-sg-2* in the region from 350 MHz to 580 MHz. NMR spectrum of sample *0.4-sg-2* exhibits a broad line at 400 MHz (II), while for sample *0.5-sg-2* only weak signal in the region II is observed. Similar situation is observed in the region III, where the spectrum of sample with $x = 0.5$ exhibits one broad line (line width of 70 MHz) while in the spectrum of sample with $x = 0.4$ one can see only a low intensity plateau. Both samples exhibit the relatively narrow line in the region IV.

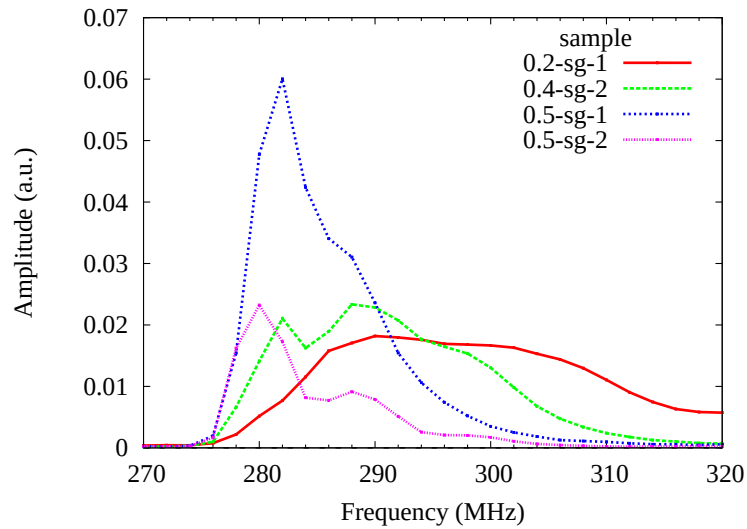


Figure 11.32: NMR spectra of samples prepared by the sol-gel method with additional treatment, Mn^{4+} line in more detail.

In samples which were additionally thermally treated in the oxygen atmosphere the narrowing and shifting of the Mn^{4+} line with increasing Co content is evident, see Figure 11.32. The Mn^{4+} line also splits for samples *x-sg-2*. The narrowing could be directly connected to the ordering in the material. In the case of disordered samples a higher inhomogeneity of the hyperfine field is expected and due to this the line width increases. This observation is also supported by the redistribution of intensity in the split Mn^{4+} line.

11.8 Discussion

NMR spectra of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ exhibit several spectral lines in the region 250–620 MHz. Considering literature reports (see chapters 2.2 and 2.6) we can suppose presence of Mn^{3+} , Mn^{4+} , Co^{3+} (IS, LS, HS) and Co^{2+} (HS) ions in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$. NMR frequency of manganese ions varies from 200 to 650 MHz and similarly ^{59}Co resonance frequency in various compounds was observed in the range 100–600 MHz.

Because all ions of Mn and Co presented in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with exception of Co^{3+} in LS state can resonate in the frequency range where lines II, III, IV and line X (sample *0.2-sg-0*) occur, an undoubtful assignment of signals to specific ions and spin states is very difficult.

The applied magnetic field experiments clearly show a ferrimagnetic character of all samples, i.e. structure consists of several sublattices with magnetic moments oriented paralelly or antiparalelly to the magnetization. Mn^{4+} magnetic moments are oriented parallel to the direction of magnetization. The same alignment of magnetic moments exhibit also ions contributing to the region II and IV, while magnetic moments of ions resonating in the region III and X (if present) are oriented antiparalelly to the magnetization. Ferrimagnetic ordering in the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compounds results from the competition of magnetic interactions in the Co doped manganite, i.e. ferromagnetic superexchange between $\text{Mn}^{4+}\text{--Co}^{2+}$, $\text{Mn}^{3+}\text{--Co}^{3+}$, antiferromagnetic superexchange interaction between $\text{Mn}^{4+}\text{--Mn}^{4+}$, $\text{Mn}^{3+}\text{--Mn}^{3+}$, $\text{Co}^{2+}\text{--Mn}^{3+}$, $\text{Co}^{2+}\text{--Co}^{2+}$, $\text{Mn}^{3+}\text{--Mn}^{4+}$ ions or double exchange interaction between $\text{Mn}^{3+}\text{--Mn}^{4+}$.

Although a detailed assignment of lines is a complex problem, considering magnetic interactions involved, possible interpretations of the spectra are discussed.

In the previous section it was mentioned that with increasing Co content the spectral intensity in the region II decreases and the spectral intensity in the region III increases. Considering the presence of Mn^{3+} , Mn^{4+} , Co^{3+} (IS, LS, HS) and Co^{2+} (HS) ions, we conclude that only amount of Mn^{3+} ions could decrease with increasing Co content. Mn^{3+} ions can contribute to the NMR spectrum significantly in the case of samples with $x = 0.2$ and 0.3 . According to NMR experiments in mixed-valence manganites with Sr and Ca doping [Kapu1999], [Kapu2000], [Shim2003a], [Shim2003b], where the manganese 3+ ions were reported to give signal between 300 MHz and 500 MHz, we assign the signal II which is observed in all samples in the region of 350-450 MHz to Mn^{3+} . Mn^{3+} is ferromagnetically ordered to the Mn^{4+} what is confirmed by shifting of the line to the lower frequencies in the applied magnetic field. Next spectral line (in the region III) could be assigned to Co^{2+} ions in the HS state which is antiferromagnetically ordered with Mn^{3+} ions (line shifts to higher frequencies in the applied magnetic field). According to [Siko2006] and [Good1961] only the interaction between $\text{Mn}^{3+}\text{--Co}^{2+}$ ions leads to antiferromagnetic ordering. This assignment is also supported by relaxation time T_2 which is comparable for the lines II and III.

The line denoted as IV was only observed for samples with the Co content higher or equal to the 0.4. The appearance of this line in the spectrum depends strongly on the sample preparation method and the thermal treatment. This line has similar spin-spin relaxation time, T_2 as the Mn^{4+} signal therefore it can be relatively strongly ferromagnetically coupled with the Mn^{4+} ions. We can speculate on the assignment. The line IV might be Co^{3+} signal. The spin state of Co ions is frequently discussed in the literature. Joy et al. discussed in [Joy2000] possible presence of the Co^{3+}

in the HS state in $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ compound. The appearance of the HS state of Co^{3+} depends then on preparation conditions. Samples with lower Co content have Co ions rather as Co^{3+} in the LS state while in the case of samples with more cobalt ($x = 0.4, 0.5$) the probability of Co^{3+} in the HS is state is much higher and then the signal of Co^{3+} in HS state can occur in the NMR spectrum.

In contrast to this suggestion, relatively large orbital moment of Co^{3+} in HS state usually results in broader spectral lines and faster relaxation. We cannot exclude also a presence of low amount of Mn^{2+} or Co^{4+} which both have zero orbital moment and for both of them we can suppose narrow resonance line above 500 MHz.

As it was mentioned in chapter 9.2 the X-Ray diffraction does not observe any other structural phases in the samples (with accuracy of 1%). On the contrary, NMR can detect even smaller amounts of impurities, owing to the enhancement effect in ferromagnetic materials. Therefore we have to take into account also this possibility in our discussion. Houston in [Hous1966] reported ^{55}Mn NMR in Mn_3O_4 at 554-560 MHz, which is close to the frequency range of line IV.

Regarding the Mn^{4+} line splitting which is observed mainly for thermally treated samples with higher x the suggested model considers presence of Mn^{4+} , Mn^{3+} , Co^{2+} and Co^{3+} ions in LS and HS states. It means that there are five possible types of neighbors located at 6 transition metal positions around given Mn^{4+} ion. Supposing that Mn and Co ions in sample with $x = 0.5$ can be ordered or disordered and considering distribution of valence states suggested by [Siko2006] and taking the spin moments according to [Joy2000] into account, one finds large number of possible arrangements where each of them can results in slightly different hyperfine field of Mn^{4+} occurring as a splitting of the line in NMR spectrum. The splitting of the Mn^{4+} line should be driven by charge or ionic ordering. Another possible mechanism of Mn^{4+} line splitting should be connected to spin ordering. Considering that Mn^{4+} is present in the HS state with $S = 1.5$, Mn^{3+} in the HS state with $S = 2$, Co^{2+} with $S = 1.5$, Co^{3+} in the LS state ($S = 0$), and also Co^{3+} in the HS ($S = 2$), ions with three different spins can be distributed on the transition metal sites. Mn^{4+} can be surrounded by different number of ions with different spins resulting in different hyperfine field.

Concerning the Mn^{4+} line splitting we can conclude that the splitting should be a result of charge, ionic or spin ordering in the compound studied, however, we are not able to conclude which of these mechanisms is dominant.

Chapter 12

Summary and conclusions

A study of mixed valence manganites and cobaltites with perovskite structure is presented. It was focused on the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained by two different preparation methods, solid state reaction and sol-gel method. The macroscopic magnetic and microscopic properties of the solid solution of the LaMnO_3 and LaCoO_3 were studied by means of NMR, EXAFS and SQUID magnetometry in order to determine the lattice, spin and electronic properties. Phase separation problem and possible structural changes induced by preparation method, thermal treatment and difference in composition of the samples were also studied.

A linear decrease of the saturation magnetization with x in the region $x > 0.2$ is confirmed and an increase of the coercive field is observed in the analysis of hysteresis loops. The coercive field also depends on the additional thermal treatment of the sample. The heating in oxygen atmosphere decreases the coercive field and the effect is especially strong for samples with $x = 0.4$ and $x = 0.5$.

In NMR experiments signals from both the ^{55}Mn and ^{59}Co isotopes are observed in a very broad frequency range. A new experimental approach was developed in order to obtain reliable, artifacts-free spectra. The excitation and detection processes during NMR experiment were thoroughly studied, with respect to broad frequency range and the frequency response problems at high frequencies. The procedure assuring constant excitation conditions during measurements in a broad frequency range was formulated and introduced into the practice. In parallel, the frequency dependence of receiving circuit sensitivity was being inspected and the procedure for estimation of its frequency response was applied and successfully verified during measurements.

EXAFS experiments on the Mn:K edge and Co:K absorption edge were carried out and the experimental data were analyzed using the software package FEFF. Great attention was paid to proper removal of the free atomic background and elimination of systematic errors due to experimental artifacts. The experimental results were fitted using theoretical simulations and the cobalt-oxygen distances

and manganese-oxygen distances were obtained for samples prepared using the SR method.

Results from EXAFS show a considerable decrease of cobalt-oxygen distances with increasing Co concentration, which is attributed to an increase of the mean Co oxidation degree. The data on manganese show an approximately constant character of Mn–O distances throughout the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ series. They do not exhibit expected decrease of the mean ionic radius of Mn induced by increase of its average oxidation level when x increases. This failure of a simple ionic picture in the case of Mn may point to increasing role of Co–O covalency with x in the series. The Co–O distances are in average bigger or close to Mn–O distances. The differences between the three Co–O distances for a given x in the orthorhombic structure are of comparable magnitudes to those for Mn–O.

From a detailed analysis of all NMR spectra measured in external field ranging from 0 to 5 Tesla it is found that the compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $0.2 \leq x \leq 0.5$ exhibit ferrimagnetic ordering, where ferromagnetic exchange interaction pairs $\text{Mn}^{3+}\text{--Mn}^{4+}$ and $\text{Mn}^{3+}\text{--Co}^{3+}$ and antiferromagnetic exchange interaction of $\text{Co}^{2+}\text{--Mn}^{3+}$ and $\text{Mn}^{3+}\text{--Mn}^{3+}$ are found to be responsible for the magnetic order.

Possible interpretations of NMR spectra were discussed and the most probable model of ionic arrangement was suggested. However, the situation can be more complicated than a simple $\text{Mn}^{4+}\text{--Co}^{2+}$ charge ordering, as a decreased local charge "disproportionation" is expected, related to a delocalization of valence electrons of Mn ions derived from EXAFS measurements.

NMR spectra have proven to be very sensitive to the local atomic arrangement in the material and it was possible to detect small changes in local arrangement connected with different preparation method or thermal treatment. Although many questions regarding interactions, magnetic ordering types in the studied compounds remain unanswered, the reported NMR experiments on the mixed valence manganites with a perovskites structure doped with transition metals at the B-site bring a new insight into the physical problems in mixed valence materials.

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List of Figures

2.1	Perovskite structure.	11
2.2	Rhombohedral structure with space group $R\bar{3}c$ of compounds with $x > 0.6$, blue ball - La, small green ball - oxygen, big green ball - Me.	11
2.3	Orthorhombic structure with space group $Pbnm$ of compounds with $x < 0.6$, blue ball - La, small green ball - oxygen, big green ball - Me.	12
2.4	Dependence of lattice parameters on Co content in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ series, [Autr2005].	12
2.5	Angular wave functions of the e_g and t_{2g} orbitals.	13
2.6	Scheme of energy levels of $3d$ ion in the crystal field, splitting of e_g and t_{2g} caused by Jahn-Teller effect.	14
2.7	Schematic diagram of the double exchange (DE) and super exchange (SE) in- teractions mechanism.	15
2.8	Diagram of transition metal content in the sample $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ derived from data published in [Siko2006].	18
3.1	Energy dependence of the absorption coefficient. The individual absorption edges are marked.	21
3.2	Emission of a core level electron due to absorption of the X-ray photon, $\rho(E)$ - density of states above Fermi energy.	22
3.3	Interference of photo electrons in the crystal.	23
3.4	Transmission mode (left side) and fluorescence mode (right side) of EXAFS measurement.	24
4.1	Pre-edge subtraction,	26
4.2	Example of normalized absorption spectrum.	27
4.3	Example of the $\chi(k)$ function	28
4.4	Example of the $\chi(k)k^3$ function	29
4.5	Example of the $\chi(R)$ function, $\chi(R) = \text{FT}(\chi(k)k^3)$	30
4.6	Path of a photoelectron during propagation in the crystal.	30

5.1	Zeeman multiplet. Splitting of energy levels of nucleus with spin $I=\frac{3}{2}$ in the magnetic field B_0 for positive gyromagnetic ratio.	36
5.2	Quadrupolar splitting in electrical field of axial symmetry. Splitting of energy levels for nucleus with spin $I = \frac{5}{2}$	39
5.3	Splitting of energy levels by electric and magnetic field for nucleus with spin $I = \frac{3}{2}$	41
5.4	Schematic diagram of regions for solution of Bloch equations.	43
5.5	Distribution function $g(\omega_0 - \bar{\omega}_0)$, $\Delta\omega_0$ is a width in half of maximum of the distribution function.	45
5.6	Spin-echo sequence.	46
5.7	Illustration of truncated FID detection limited by the dead time of the receiver.	46
5.8	Illustration of signals from nuclei in domains and from domain walls measured with different excitation conditions.	48
6.1	Concept diagram of Bruker AVANCE spectrometer used for NMR measurements. For details and abbreviations – see the text.	51
7.1	Fourier transform of a rectangular pulse at ω_{rf} . The formula is $FT(f(t)) \sim \frac{\sin(\frac{\tau(\omega - \omega_{rf})}{2})}{\frac{\tau(\omega - \omega_{rf})}{2}}$, $\tau = 1\mu s$. Only a narrow range close to pulse frequency is well excited.	54
7.2	Example of a broad frequency swept spectrum measurement.	54
7.3	A broad frequency swept spectrum measurement measured point by point.	55
7.4	Modelled frequency dependence of probehead current.	58
7.5	A schematic diagram of the probehead for NMR experiments. Top part - handle of connectors and a rod for tuning (in case of tune probehead), Middle part - usually stainless steel tube leading coaxial lines, Bottom part - handler for resonance circuit with sample.	60
7.6	Untuned resonance circuit, suitable for measuring broad frequency swept spectra, L - resonance coil, R - resistor, EXC. point where the resonance circuit is connected to the NMR spectrometer.	61
7.7	Schematic diagram of untuned probehead (a) and its connection to spectrometer. Configurations (b-d) are described in text. (T/R switch - transmitter/receiver switch, Oscillosc. - digital high frequency oscilloscope, Synthes. - input of power amplifier, see Figure 7.8, Terminat. - $50\ \Omega$ coaxial resistor, Sim. Imp. - element simulating the output impedance of synthesizer.)	62
7.8	Frequency dependence of voltage; a) input voltage of power amplifier, b) output voltage of power amplifier.	63
7.9	Frequency dependence of voltage on resistor in the probe (scheme on Figure 7.7b); a) before corrections, b) after corrections.	63
7.10	Frequency dependence of voltage on resistor (scheme on Figure 7.7c); a) before correction, b) after correction, c) detected by receiver.	65
7.11	NMR spectrum of $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ in zero external magnetic field at 4.2 K.	65

8.1	Screenshot of Emil software, software developed for NMR measurements analysis.	67
8.2	Screenshot from Emil, fitting two Gaussian curves	68
8.3	Screenshot from Emil, setting the plot parameters	68
9.1	Hysteresis loops of samples with $x = 0.2$, $T = 5K$	73
9.2	ZFC curves of samples with $x = 0.2$	74
9.3	Hysteresis loops of samples with $x = 0.3$, $T = 5K$	74
9.4	ZFC curves of samples with $x = 0.3$	75
9.5	FC curves of samples additionally thermally treated, <i>0.2-sg-1</i> , <i>0.3-sg-1</i> , <i>0.4-sr-1</i> , <i>0.5-sr-1</i>	76
9.6	Hysteresis loops of samples with $x = 0.4$, $T = 5K$	76
9.7	ZFC curves of samples with $x = 0.4$	77
9.8	Hysteresis loops of samples with $x = 0.5$, $T = 5K$	77
9.9	ZFC curves of samples with $x = 0.5$	78
9.10	Dependence of ordering temperatures T_{c1} and T_{c2} on Co concentration in the sample. Lines connecting the experimental points are the guide eyes only. . . .	79
9.11	Dependence of the saturation magnetization on Co concentration. Lines con- necting the experimental points are the guide eyes only. Errors do not exceed the size of point marks.	80
9.12	Dependence of the coercive field on Co concentration. Lines connecting the experimental points are the guide eyes only. Errors do not exceed the size of point marks.	80
9.13	Hysteresis loops at temperature $T=77$ K of samples with x ranging from 0 to 1 prepared by the solid state reaction method.	81
9.14	Hysteresis loops at temperature $T=300$ K of samples with x ranging from 0 to 1 prepared by the solid state reaction method.	81
10.1	Co K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method.	83
10.2	Co K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9, 1.0$ prepared by SR method.	83
10.3	Co K -edge absorption spectra of samples <i>1.0-sr-0</i> (rhombohedral) and <i>0.4-sr-0</i> (orthorhombic) symmetry, at room temperature.	84
10.4	Mn K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method.	84
10.5	Mn K -edge absorption spectra at room temperature of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8$ prepared by SR method.	85
10.6	Absorption on K :edge of manganese of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.8$ and 0.2 at room temperature. Compound with $x = 0.8$ has a $R\text{-}3c$ crystal structure and compounds with $x = 0.2$ has a $Pbnm$ crystal structure.	85

10.7	EXAFS functions $\chi(k) \cdot k^3$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method (<i>0.2-sr-0, 0.4-sr-0, 0.5-sr-0, 0.6-sr-0</i>).	86
10.8	EXAFS functions $\chi(k) \cdot k^3$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9, 1.0$ prepared by SR method (<i>0.6-sr-0, 0.8-sr-0, 0.9-sr-0, 1.0-sr-0</i>).	87
10.9	EXAFS function $\chi(k) \cdot k^3$ function measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0, 0.2, 0.4, 0.5, 0.6$ prepared by SR method (<i>0-sr-0, 0.2-sr-0, 0.4-sr-0, 0.5-sr-0, 0.6-sr-0</i>).	87
10.10	EXAFS function $\chi(k) \cdot k^3$ function measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9$ prepared by SR method (<i>0.6-sr-0, 0.8-sr-0, 0.9-sr-0</i>).	88
10.11	EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.2, 0.4, 0.5, 0.6$ prepared by SR method (<i>0.2-sr-0, 0.4-sr-0, 0.5-sr-0, 0.6-sr-0</i>).	88
10.12	EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Co:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9, 1.0$ prepared by SR method (<i>0.6-sr-0, 0.8-sr-0, 0.9-sr-0, 1.0-sr-0</i>).	89
10.13	EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0, 0.2, 0.4, 0.5, 0.6$ prepared by SR method (<i>0-sr-0, 0.2-sr-0, 0.4-sr-0, 0.5-sr-0, 0.6-sr-0</i>).	90
10.14	EXAFS functions $\chi(R)$ of the spectra measured at room temperature on Mn:K edge of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.6, 0.8, 0.9$ prepared by SR method (<i>0.6-sr-0, 0.8-sr-0, 0.9-sr-0</i>).	90
10.15	Result of the fitting procedure in the k space for cobalt K edge for LaCoO_3 . Experimental $\chi(k)$ function and the fit.	91
10.16	Result of the fitting procedure in the R space for cobalt K edge for LaCoO_3 . Experimental $\chi(R)$ function and the fit.	92
10.17	Values of cobalt-oxygen distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained from EXAFS.	94
10.18	Manganese-oxygen distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained from EXAFS.	94
10.19	Manganese-oxygen and cobalt-oxygen distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained by EXAFS.	95
10.20	Comparison of Co–O distances evaluated from EXAFS experiments (empty circles stand for rhombohedral structure, gray circles are a simple average of the three Co–O distances obtained for orthorhombic structure) with dependences based on XANES results of [Siko2006] and calculations described in text (full line for case (i), dashed for case (ii)).	97
10.21	Average Me–O distances in the series of compounds $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ obtained by EXAFS and X-ray diffraction.	97

11.1	NMR spectrum of sample <i>0.0-sr-0</i> . a) measured with pulse length 100 μ s, b) measured with pulse length 20 μ s, spectra normalized to unity area.	100
11.2	NMR spectra of sample <i>0.2-sg-0</i> measured with different pulse spacing at the temperature 4.2 K	101
11.3	Normalized NMR spectra of sample <i>0.2-sg-0</i> measured with different pulse spacing at temperature 4.2 K.	102
11.4	NMR spectra of samples <i>0.2-sg-0</i> , <i>0.2-sg-1</i> , <i>0.2-sr-0</i> at temperature 4.2 K, spectra normalized to unity area.	102
11.5	NMR spectra of samples <i>0.2-sg-0</i> , <i>0.2-sg-1</i> , <i>0.2-sr-0</i> at temperature 4.2 K, detail of Mn^{4+} line, spectra normalized to unity area.	103
11.6	NMR spectrum of sample $\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$ prepared by SG method (<i>0.2-sg-0</i>) measured at external field of 0 and 5 Tesla.	104
11.7	$\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$ sol-gel (<i>0.2-sg-0</i>) measured at external field ranging from 0 to 5 Tesla, the upper line is located at 600 MHz in 0 Tesla, at 619 MHz in 2 Tesla and at 637 MHz in 4 Tesla	105
11.8	NMR spectrum of $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ sol-gel (<i>0.3-sg-0</i>) in dependence on magnetic field 0–5 T.	106
11.9	NMR spectra of sample <i>0.4-sg-2</i> measured with different pulse spacing, at 4.2 K	106
11.10	Spectra of sample $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$ (<i>0.4-sg-2</i>), normalized to unit maximal amplitude and measured with different pulse spacing, at 4.2 K	107
11.11	Field dependence of NMR spectra of sample <i>0.4-sg-2</i> , at 3 K.	107
11.12	Spectra of $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$ (<i>0.4-sg-2</i>), details of Mn^{4+} line.	108
11.13	Spectra of $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$ (<i>0.4-sg-2</i>), details of Mn^{4+} line, normalized to maximal amplitude.	109
11.14	NMR spectra at 4.2 K of the samples (<i>0.4-sg-2</i>), (<i>0.4-sr-0</i>), (<i>0.4-sr-1</i>) normalized to unity area.	110
11.15	NMR spectra at 4.2 K of samples (<i>0.4-sg-2</i>), (<i>0.4-sr-0</i>), (<i>0.4-sr-1</i>) normalized to unity area, details of Mn^{4+} line.	110
11.16	NMR spectra of samples <i>0.5-sg-0</i> , <i>0.5-sg-1</i> , <i>0.5-sr-0</i> at 4.2 K. Spectra are normalized to unit area.	111
11.17	NMR spectra of samples <i>0.5-sg-0</i> , <i>0.5-sg-1</i> , <i>0.5-sg-2</i> , <i>0.5-sr-0</i> at 4.2 K, details of Mn^{4+} line. Spectra are normalized to maximal amplitude.	111
11.18	NMR spectra of the sample <i>0.5-sg-2</i> measured at 4.2 K with different pulse spacing	112
11.19	NMR spectra of the sample <i>0.5-sg-2</i> measured with different pulse spacing, spectra are normalized to the amplitude of Mn^{4+} line.	113
11.20	NMR spectrum of the sample <i>0.5-sr-0</i> measured with different pulse spacing.	113
11.21	NMR spectra of the sample <i>0.5-sg-2</i> measured with different pulse spacing, Mn^{4+} line in detail.	114
11.22	NMR spectra of <i>0.5-sr-0</i> sample measured with different pulse spacing, Mn^{4+} line is shown in detail.	114

11.23	NMR spectrum <i>0.5-sg-2</i> in the external magnetic field of 0-5 Tesla.	115
11.24	The shift of NMR line IV of sample <i>0.5-sg-2</i> in the external magnetic fields, the line III was reduced by setting pulse spacing time 320 μ s.	116
11.25	The dependence of the central frequency of the narrow line (IV, sample <i>0.5-sg-2</i>) on the external magnetic field, points are from measurements and the dashed line is a fit. Parameters of fitted linear function are:10.46 (slope) and 542.8 (y-intercept), where the slope is related to the gyromagnetic ratio. Gyromagnetic ratio of $\gamma^{55}Mn = 10.58$ MHz/T and of $\gamma^{59}Co = 10.07$ MHz/T.	116
11.26	NMR spectrum of sample $LaMn_{0.5}Co_{0.2}Mg_{0.3}O_3$ measured at 4.2 K	117
11.27	NMR spectrum of sample $LaMn_{0.5}Co_{0.2}Mg_{0.3}O_3$ measured at 4.5 K, enlarge <i>y</i> scale.	118
11.28	NMR spectra of samples prepared using the solid state reaction method measured at 4.2 K.	119
11.29	NMR spectra of samples prepared by the sol-gel method without additional treatment.	119
11.30	NMR spectra of samples prepared by the sol-gel method without additional treatment, Mn^{4+} line in more detail.	120
11.31	NMR spectra of samples prepared by the sol-gel method with additional treatment.120	
11.32	NMR spectra of samples prepared by the sol-gel method with additional treatment, Mn^{4+} line in more detail.	121

List of Tables

9.1	List of studied samples. Samples are labelled x - met - y where x denotes cobalt content in the sample, string met denotes the preparation method (sr- solid state reaction as a preparation method, sg- samples prepared by sol-gel method) and y means additional treatment, if any. Samples for which y amounts to 2 were not studied before an additional treatment in oxygen atmosphere. Samples labelled with 0 and 1 were prepared, measured before and after the thermal treatment. . .	71
9.2	Saturation magnetization of M_s (μ_B /formula unit), coercive field $H_c(Oe)$ for samples of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$, the ratio of saturation magnetization before and after additional thermal treatment M_{s0}/M_{s1} and the ratio of coercive field before and after additional thermal treatment H_{c0}/H_{c1}	78
10.1	Results of fits of Co: K -edge measurements.	93
10.2	Results of fits of Mn: K -edge measurements.	95
10.3	Effective ionic radii in octahedral coordination according to [Shan1976].	96
11.1	NMR isotopes and their parameters,[webeleme].	98
11.2	Relaxation times of sample 0.4 - sg - 2	109

List of publications

Publications related to the Thesis

1. M. Sikora, C. Kapusta, K. Knížek, Z. Jiráček, C. Autret, M. Borowiec, C. J. Oates, V. Procházka, D. Rybicki, D. Zajac, *X-ray absorption near-edge spectroscopy study of Mn and Co valence states in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ ($x=0-1$)*, Physical Review B 73 (2006), 094426.
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Other publications

1. B. Diouf, L. Gabillet, A. R. Fert, D. Hrabovský, V. Procházka, E. Snoeck, J. F. Bobo, *Anisotropy, exchange bias, dipolar coupling and magnetoresistive response in $\text{NiO-Co-Al}_2\text{O}_3\text{-Co}$ magnetic tunnel junctions*, Journal of Magnetism and Magnetic Materials 265 (2003), 204-214.
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Streszczenie

Praca przedstawia wyniki badań związków $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ (manganitów - kobaltytów) metodami makroskopowymi (dyfrakcja rentgenowska i pomiary namagnesowania) oraz mikroskopowymi (spektroskopia magnetycznego rezonansu jądrowego - ang. NMR i spektroskopia rozciągłej struktury absorpcji promieniowania X - ang. EXAFS). Bardzo interesujące właściwości magnetyczne i elektryczne tych związków, w tym kolosalny magnetoopór i bogactwo struktur magnetycznych, wynikają z powiązania między stopniami swobody uporządkowania sieci krystalicznej, ładunków oraz spinów.

Badane związki $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$, z x w przedziale od 0 do 1, zostały przygotowane w grupie Dr. Zdeňka Jiráka w Zakładzie Magnetyzmu Instytutu Fizyki Czeskiej Akademii Nauk metodami reakcji w stanie stałym (solid state reaction, SR) i zol-żel (sol-gel, SG). Próbki po przygotowaniu wygrzewano przez kilka godzin w temperaturze 1200°C w atmosferze tlenu, argonu lub próżni. Stosowano też dodatkowe wygrzewanie w atmosferze tlenu przy 750°C przez dwie doby.

Charakteryzację strukturalną przeprowadzono metodą rentgenowskiej dyfrakcji proszkowej i przeanalizowano otrzymane dyfraktogramy metodą Rietvelda. Dla $x > 0.6$ stwierdzono strukturę romboedryczną oraz dla $x < 0.6$ - strukturę rombową, przy maksymalnej ilości obcych faz mniejszej niż 1%. Nie stwierdzono wpływu dodatkowego wygrzewania w atmosferze tlenu na strukturę krystaliczną, niezależnie od metody przygotowania próbek.

W badaniach magnetometrycznych zmierzono pętle histerezy oraz krzywe: ZFC (pomiar podatności magnetycznej mierzonej podczas ogrzewania próbki po schłodzeniu bez przyłożonego pola magnetycznego) i FC (pomiar podatności magnetycznej mierzonej w ciągu ogrzewania próbki po schłodzeniu w niezerowym polu magnetycznym) w zakresie 5–300 K. Dla krzywej ZFC dla próbek $x = 0.2$ i próbki *0.3-sg-0* zaobserwowano jedno maksimum, podczas gdy dla krzywej ZFC próbki *0.3-sg-1* oraz próbek z $x > 0.3$ są wyraźnie widoczne dwa piki z temperaturą krytyczną T_{c1} oraz T_{c2} . Efekt został przypisany ferrimagnetycznemu uporządkowaniu w dwóch izostrukтурalnych fazach magnetycznych, głównej - z wyższą temperaturą T_c , oraz małym klasterom - z niższą T_c . Dodatkowe wygrzewanie w tlenie powoduje wzrost temperatury T_{c2} , podczas gdy temperatura T_{c1} pozostaje niezmienną. Namagne-

sowanie nasycenia maleje liniowo ze wzrostem x od 0.2 do 0.5, jest niezależne od metody przygotowania i rośnie po dodatkowym wygrzewaniu. Pole koercji H_c silnie wzrasta z koncentracją kobaltu, x , zależy od metody przygotowywania i silnie maleje po dodatkowym wygrzewaniu.

Pomiary NMR zostały wykonane na spektrometrze BUKER AVANCE NMR z szerokopasmową sondą przy temperaturze $T = 4.2$ K, w zewnętrznym polu magnetycznym od 0 do 5 T. Dla wszystkich linii obserwowanych w widmach dobierane były optymalne warunki wzbudzenia. Otrzymane widma mają linie rezonansowe w czterech obszarach częstotliwości, oznaczonych jako I-IV, gdzie mogą występować sygnały pochodzące od izotopów ^{55}Mn i ^{59}Co . W pierwszym obszarze (I) (od 270 MHz do 320 MHz) obserwowana jest silna linia, która pochodzi od Mn^{4+} . W drugim obszarze (oznaczenie II) od 350 do 450 MHz, pojawia się szeroka linia z maksimum przy około 400 MHz. Następna linia, z szerokością połówkową większą niż 50 MHz, jest obserwowana przy 475 MHz (obszar III, 450–530 MHz). Ostatni obszar, w którym pojawia się stosunkowo wąska linia przy około 540 MHz oznaczony jest jako IV. Dla jednej z próbek zaobserwowano dodatkowo linię o niskiej intensywności przy około 600 MHz oznaczoną jako X.

Linia Mn^{4+} przesuwana się w stronę niższych częstotliwości ze wzrostem zawartości kobaltu w próbce oraz pod wpływem wygrzewania w atmosferze tlenowej. Dodatkowe wygrzewanie powoduje zwięźenie tej linii, z wyraźnym rozszczepieniem, które jest prawdopodobnie związane z uporządkowaniem w próbce. W przypadku nieuporządkowanej próbki, ze zróżnicowanymi najbliższymi otoczeniami jonów Mn i Co o różnych stopniach utlenienia i różnych stanach spinowych oczekuje się większej niejednorodności pola nadsubtelnego, która odpowiada szerszej linii rezonansowej.

W widmach zmierzonym w zewnętrznym polu magnetycznym do 5 T linia Mn^{4+} (I) przesuwana się ze wzrostem pola magnetycznego w stronę niższych częstotliwości. Sygnał w obszarach II i IV przesuwana się też w stronę niższych częstotliwości, natomiast linie w obszarze III i X przesuwają się w stronę wyższych częstotliwości. Ponieważ pola nadsubtelne Mn i Co są antyrównoległe do ich momentów magnetycznych, wynika stąd, że linie I, II i IV odpowiadają momentom magnetycznym równoległym do wypadkowej magnetyzacji próbki, a linie III i X - momentom antyrównoległym do wypadkowej magnetyzacji. Z powodu małej różnicy czynników giromagnetycznych Mn i Co (5%) nie można jednak jednoznacznie określić z pomiaru NMR, czy linia rezonansowa odpowiada Mn, czy Co.

Ferrimagnetyczne uporządkowanie w $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ jest spowodowane konkurencją ferromagnetycznej nadwymiany $\text{Mn}^{4+}-\text{Co}^{2+}$, $\text{Mn}^{3+}-\text{Co}^{3+}$, antyferromagnetycznej nadwymiany $\text{Mn}^{4+}-\text{Mn}^{4+}$, $\text{Mn}^{3+}-\text{Mn}^{3+}$, $\text{Co}^{2+}-\text{Mn}^{3+}$, $\text{Co}^{2+}-\text{Co}^{2+}$ oraz podwójnej wymiany $\text{Mn}^{3+}-\text{Mn}^{4+}$. Ponieważ natężenie widmowe w obszarze II maleje, a w obszarze III rośnie ze wzrostem x , rozważywszy obecność Mn^{3+} , Mn^{4+} , Co^{3+} (stan niskospinowy - LS, o pośrednim spinie - IS, wysokospinowy - HS) oraz Co^{2+} (HS), tylko zawartość Mn^{3+} może maleć. Sygnał w obszarze II został więc przypię-

sany Mn^{3+} , który jest ferromagnetycznie sprzężony z Mn^{4+} . Linia w obszarze III została przypisana Co^{2+} w stanie HS który jest antyferomagnetycznie sprzężony z Mn^{3+} . Sygnał z obszaru IV został przypisany rezonansowi Co^{3+} w stanie wysokospinowym.

Widma NMR pokazały swoją wysoką czułość na lokalne uporządkowanie w badanych związkach, zależne od podstawiania manganu kobaltem, metody przygotowania próbek oraz dodatkowego wygrzewania.

Przeprowadzone w pracy badania perowskitów manganowo-kobaltowych podstawianych na miejscu metalu przejściowego wnoszą nowe informacje na temat uporządkowania strukturalnego, ładunkowego i spinowego oraz oddziaływań magnetycznych w złożonych tlenkach metali przejściowych z mieszaną walencyjnością.