

Information on the scientific activity, research, and achievements

1 Basic information

1.1 Personal data

Name and surname: Urszula Danuta Wdowik

Academic education:

- Higher education at Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Kraków, Poland graduated with MSc in Technical Physics, 1986-1991
- Degree of Doctor of Philosophy in Condensed Matter Physics, Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Kraków, Poland, 1998
title of PhD thesis: Emission Mössbauer spectroscopy in rutile single crystals
thesis supervisor: Professor Krzysztof Ruebenbauer
- Postgraduate studies, Computer Science, Pedagogical University, Kraków, Poland, 2005

1.2 Academic career and employment

1991-1998 - assistant, High Pedagogical School, Kraków, Poland, Department of Mathematics, Physics, and Technology, Institute of Physics and Computer Science

1998-2003 - associate professor, Pedagogical University, Kraków, Department of Mathematics, Physics, and Technology, Institute of Physics and Computer Science

since 2003 - associate professor, Pedagogical University, Kraków, Department of Mathematics, Physics, and Technology, Institute of Technology

2 Scientific achievements within collection of original articles

The following collection of six original papers devoted to cobalt oxide (CoO) constitutes my dissertation entitled **Ab initio study of the strongly correlated electron system with point defects:**

E1 Lattice dynamics of CoO from first principles

U. D. Wdowik and K. Parlinski, Physical Review B **75**, 104306 (2007)

E2 CoO under pressure from first principles

U. D. Wdowik and D. Legut, Journal of Physics and Chemistry of Solids **69**, 1698 (2008)

E3 Electronic structure of cation-deficient CoO from first principles

U. D. Wdowik and K. Parlinski, Physical Review B **77**, 115110 (2008)

E4 Ab initio study of point defects in the strongly correlated system CoOU. D. Wdowik, Physical Review B **84**, 064111 (2011)**P1 Lattice dynamics of cobalt-deficient CoO from first principles**U. D. Wdowik and K. Parlinski, Physical Review B **78**, 224114 (2008)**P2 Lattice dynamics of Fe-doped CoO from first principles**U. D. Wdowik and K. Parlinski, Journal of Physics: Condensed Matter **21**, 125601 (2009)**2.1 Abstract**

A detailed description of the collection of six original papers is provided in Appendix V (*Report* entitled **Ab initio study of the strongly correlated electron system with point defects**). A brief summary of accomplishments is given below.

Reported works concern perfect and decorated with point defects CoO crystal. They provide an insight into the local modifications of the electronic and magnetic structure of this oxide due to the incorporated defects. An influence of point defects on dynamical properties of the CoO lattice is analyzed and discussed as well. The perfect CoO system is also examined under external pressure.

An influence of such point defects like cobalt vacancies, Fe, Al, and In impurities as well as vacancy-impurity complexes on the structural and electronic properties of CoO has been investigated in [E3, E4]. Theoretical results are discussed with respect to the experimental data obtained from the emission Mössbauer spectroscopy. *Ab initio* calculated isomer shifts and quadrupole splittings for the substitutional Fe impurities were used to identify impurity valence state in CoO and Co_{1-x}O and to probe the local environment of dopants in the host matrix. The parameters of the hyperfine interactions at the Fe impurity nucleus in CoO and Co_{1-x}O have been determined by density functional theory (DFT) method for the first time. They are also very likely to be the first obtained theoretically for the strongly correlated electron system with point defects.

A coexistence of divalent and trivalent states of Fe cations in CoO has remained a long-debated issue (*Report* [43-55]) since the work of Wertheim published in 1961 (*Report* [44]). Despite few suggestions (*Report* [56-61]) to correlate a valency of Fe impurity in CoO with the preexisting lattice defects, such an idea was only partly supported by some atomistic simulations (*Report* [62-64]). The present DFT studies provide an explanation of the origin and stabilization mechanism of aliovalent states of Fe cations in the host CoO matrix.

Ab initio calculations of the lattice dynamics of CoO have been unsuccessful for a long time since contributions arising from the strong electron correlations have not been taken into account. The work [E1] shows that employing the Hubbard energy U to handle the strong electron correlation effects allows one to obtain the dispersion relations of phonons and the phonon density of states in antiferromagnetic CoO that agree well with those determined in experiments (*Report* [142]). Theoretical studies reported in [E1] are probably the first of this kind carried out for antiferromagnetic CoO by DFT+ U method.

A special *filter* enabling description of the phonon dispersion relations in defected system was proposed [P1, P2] (details can be found in *Report*). It also allowed to trace changes experienced by the CoO lattice due to incorporation of point defects. Moreover, the *filter* could be also successfully applied to setup neutron scattering experiments on stoichiometric samples (private communications with the neutron scattering group, Institute Laue-Langevin, Grenoble, France). Theoretical investigations on both Co_{1-x}O and Fe-doped CoO indicate

that point defects affect mostly the high-frequency optic vibrations of these systems, while the crystal environment more distant from defects tends to reflect the properties of the defect-free lattice. These studies showed that the long-wavelength acoustic phonons are insensitive to point defects. Detailed analysis of the phonon spectrum from Fe-doped CoO revealed that Fe dopant introduces its own force constants into the system that differ from the force constants of the host cations. This gives rise to an appearance of additional modes in the doped system. Moreover, the dynamical effects arising from the substitution of Co by Fe atom cannot be explained by the mass defect between the host and substitutional cations. They can be, however, accounted for by the force constant defect between those cations. It should be mentioned that the temperature evolution of the amplitudes of the thermal motion of Fe impurity in CoO correspond very well to the respective evolution obtained from the recoilless fraction measurements on Fe-doped CoO performed by the emission Mössbauer spectroscopy (*Report [60]*).

Ab initio studies of the behavior of the ideal CoO crystal under external pressure [E2] provide an additional information on the electronic and magnetic properties of this transition-metal oxide. The insulating antiferromagnetic phase of CoO was found to undergo transition to metallic, nonmagnetic phase at pressure of about 80 GPa. Such a transformation is accompanied by a decrease in crystal volume of 6-7 %. This remains in a very good agreement with the experimental data (*Report [145]*). It was also shown that magnetic collapse in CoO and the band gap closure that occur simultaneously during transformation are due to a loss of strong electron correlations in the system which results in delocalization of 3d Co electrons. Calculations shown that delocalization process proceeds gradually with crystal compression due to the band gap broadening with pressure. Moreover, an influence of the Hubbard potential U on the transformation pressure in CoO has been investigated. It occurs that the lower Hubbard U the lower the transition pressure. More details can be found in the *Report (Appendix V)*.

Finally, it can be mentioned that I am the co-author of the emission Mössbauer spectroscopy studies on the CoO system (*Report [60-61]*).

3 Scientific activity

My scientific activity can be divided according to the following terms (descending in time):

- from 2006 till now
- from 1998 to 2005
- from 1991 to 1997.

The first term is related with my theoretical research concentrated at the condensed matter physics and investigations using density functional theory (DFT). During the second period I was engaged in both experimental and theoretical investigations in the field of condensed matter physics, where my experimental experience is mainly associated with the Mössbauer spectroscopy. Finally, the last period relates to my research before PhD and here, I was also involved in some theoretical and experimental investigations based on the Mössbauer spectroscopy.

My scientific achievements are presented below with respect to the published papers. The published papers are listed in Appendix VII.

3.1 Research fields and the most important scientific achievements

Scientific activity 2006-2011

1. *DFT study of the electronic structure and lattice dynamics of perfect and defected systems with strong electron correlations*

This research topic is described in section 2 as well as in the *Report* (Appendix V).

Moreover, similar calculations have been performed for MnO crystal (Appendix VII [10]), which is also classified as the strongly correlated electron system. An influence of the Hubbard potential on the force constants and the phonon spectrum of MnO were analyzed in detail. An important role of the Hubbard potential in predicting frequencies of the optical phonon modes was confirmed. It was shown that theoretical results obtained with too weak or neglected strong electron correlation effect are unable to match experimental data. This applies also to such quantities as lattice contribution to the system heat capacity or atomic thermal motions in the system that are dependent on the phonon density of states.

2. *DFT investigation of systems under high pressure*

- 2.1 *Influence of pressure on the electronic structure of the strongly correlated electron systems*

These studies were aimed at the perfect CoO crystal. They are described in section 2 as well as in the *Report* (Appendix V).

- 2.2 *Structural stability and thermal properties of the nonmagnetic materials from the quasiharmonic approximation*

Phase diagrams of some technologically important ceramic materials, e.g., BeO (Appendix VII [8]) and AlN (Appendix VII [18]) have been calculated from first principles. For both cases, such computations including the temperature effects are performed for the first time. Anharmonic effects introduced via the quasiharmonic approximation allowed to establish stable structures for both BeO and AlN compounds. Results of these investigation indicate that the wurtzite structure is the most energetically stable structure for both crystals at the normal pressure and temperature conditions. The wurtzite phase transforms solely to the rocksalt structure at elevated temperature and pressure, while the zincblende structure, suggested by some DFT calculations neglecting lattice vibration effects, is the energetically less stable structure in the whole temperature and pressure ranges investigated theoretically.

Lattice vibrations play an important role in predicting structural stability of many systems, as it was also shown for MgAl₂O₄ (Appendix VII [19]). *Ab initio calculations* performed for MgAl₂O₄ proved that the free energy of phonons affect decomposition pressure of MgAl₂O₄ to oxides of periclase and corundum.

A negative thermal expansion (NTE) material, ReO₃, has been the subject of theoretical studies (Appendix VII [6]) as well. These investigations were carried out within collaboration with experimental group from Institute Laue-Langevin, Grenoble, France which was responsible for performing inelastic neutron scattering measurements. Thermal properties of ReO₃ crystal have been calculated using the quasiharmonic approximation for the first time. Theoretical results remain in close agreement

with experimental data, e.g., theoretically determined temperature at which the lattice constant of ReO_3 is minimal corresponds to the experimentally obtained value. It was shown that the negative thermal expansion in ReO_3 is closely related to the anisotropy of the oxygen thermal motion, whereas the latter anisotropy is due to the anisotropy of the force constants at the oxygen site. It was proved that oxygen atom vibrations in the direction perpendicular to the Re-O bond significantly contribute to the anisotropy of the atomic thermal motion. The anisotropy is consistent with the M phonon mode which represents the class of low-frequency lattice vibrations, i.e., RUMs (Rigid Unit Modes). Theoretical results show that the M phonon has a large negative value of the Grüneisen constant. This additionally confirms that NTE phenomenon in ReO_3 can take place below the room temperature.

3. *Lattice dynamics of systems exhibiting Jahn-Teller effect*

This theoretical and experimental research has been devoted to LaMnO_3 which is a typical example of Jahn-Teller system (*Appendix VII [2]*). These investigations have been performed in collaboration with the experimental group from Institute Laue-Langevin, Grenoble, France which carried out measurements using neutron diffraction technique. The approach of quasiharmonic approximation has been applied for theoretical studies of temperature dependencies of structural distortions originated from the Jahn-Teller effects. First principles calculations have been done for the low-temperature orbitally ordered phase of LaMnO_3 . Results of calculations agree well with the experimental data. Comparing theoretical and experimental results one finds that some residual distortions of MnO_6 octahedra are present in the LaMnO_3 system above the Jahn-Teller transition ($T_{\text{JT}} \sim 700 - 750$ K) and they are described by small, albeit non-zero value of the overall distortion parameter. This also indicates that some partial orbital ordering persists on a local scale in LaMnO_3 above T_{JT} . Furthermore, the reported studies confirm the most recent experimental data [*Phys. Rev. Lett.* 98, 137203 (2007), *Phys. Rev. Lett.* 99, 155503 (2007)] and they provide additional insight into the physics underlying the Jahn-Teller phenomenon in LaMnO_3 .

4. *Electronic structure and lattice dynamics of one-dimensional magnets*

This research topic is carried out in collaboration with Institute of Physics of Materials, Academy of Sciences of the Czech Republic. *Ab initio* calculations of the electronic structure, lattice dynamics, and elastic properties of the quasi-one-dimensional magnet, CsNiF_3 , has been performed (*Appendix VII [5]*). Theoretical studies took into account some possible magnetic phases of the CsNiF_3 system. Results of calculations enabled us to identify the most energetically stable magnetic phase of CsNiF_3 . The calculated elastic constants indicate that this compound belongs to the class of rather soft materials. The calculated tensor of atomic thermal motion proves that quasi-1D magnetism in CsNiF_3 is due to *stiff rods* formed by Ni cations. It should be noted, that *ab initio* lattice dynamics calculations have been done for that system for the first time. Moreover, the electronic and magnetic structure, as well as the lattice dynamics of another 1D-magnet exhibiting Jahn-Teller effect are being performed.

5. *Calibration of the isomer shift for Mössbauer resonance lines by ab initio methods*

Calibrations of the isomer shift for the 57.60-keV in ^{127}I , 27.72-keV in ^{129}I , 77.34-keV in ^{197}Au , and 14.41-keV in ^{57}Fe have been performed from first principles (*Appendix VII [7]*,

13, 16]). Calculations allowed also to determine electric quadrupole moments for ^{127}I , ^{129}I , ^{197}Au , and ^{57}Fe nuclei. Calibration constants as well as electric quadrupole moments of ^{127}I , ^{129}I , and ^{197}Au have been determined using first principles methods for the first time. A very good correlation between theoretical and experimental results was achieved. It should be mentioned, that calibration calculations were carried out in collaboration with Institute of Physics, Pedagogical University, Kraków and Institute of Physics of Materials, Academy of Sciences of the Czech Republic.

6. *Effects of magnetic and nonmagnetic impurities on charge and spin densities in α -Fe*

Despite many advances in developing the lightweight alloys, the conventional alloys based on iron (steels) are still technologically important materials. Such systems, as well as α -Fe doped with various impurities have been a subject of intensive experimental research. A great number of investigations has been done using the Mössbauer spectroscopy. Influence of magnetic and nonmagnetic impurities on the charge and spin densities of α -Fe has drawn a lot of attention in recent years. Therefore, a number of theoretical and experimental attempts have been undertaken to study the impurity effect on charge and spin densities in iron (Appendix VII [3, 4, 9]). It was shown that an impurity modifies charge and spin densities of α -Fe atoms up to the 3rd coordination sphere around impurity. The DFT results also show that for some impurities, experimental data can be well described by purely phenomenological model of Miedema and van der Woude [A. R. Miedema and F. van der Woude, Physica B 100, 145 (1980)]. Results of such investigation are of a great importance for a large material science community dealing with the properties of steels.

7. *Theoretical investigation of ion mobility in lightweight compounds*

The research specified above was undertaken in September 2011. It is carried out in collaboration with Institute of Nuclear Physics, Polish Academy of Sciences, Kraków and EMPA Swiss Laboratories for Material Science and Technology, Dübendorf, Switzerland. The project is aimed at investigations of the fundamental transport properties in Li-based complex hydrides to understand and improve their performance with respect to potential applications as solid state electrolytes or hydrogen storage media. The complexity of addressed questions requires close collaboration between experimental insight and theoretical description.

Scientific activity 1998-2005

1. *Investigation of crystal defect structure, valence states and dynamics of dopants in monocystals by Mössbauer spectroscopy. Experimental study of microscopic mechanism of diffusion using Mössbauer spectroscopy.*

Cobalt oxide and titanium dioxide monocystals have been investigated using Mössbauer spectroscopy to probe the defect structure of these compounds, valence and spin states of Fe dopants in the CoO and TiO₂ matrices, and to look upon diffusion mechanism in these materials (Appendix VII [20-23]). Experimental methodology of incorporating radioactive ^{57}Co into the CoO and TiO₂ matrices has been developed. Results of the emission Mössbauer spectroscopy measurements allowed to describe evolution of the valence states of ^{57}Fe impurity versus temperature and oxygen partial pressure. Dynamics of ^{57}Fe impurity in these systems was described and the measured recoilless fraction of the 14.41-keV

radiation was used for this purpose. The measured broadening of Mössbauer lines provided required information for a determination of the diffusivity of ^{57}Fe in CoO and TiO_2 . Additionally, a methodology of producing Co_3O_4 and metallic cobalt from CoO was developed. Similar measurements as reported above were performed on Co_3O_4 and metallic cobalt (Appendix VII [20, 21]). Evolution of the defect structure of the Co-O system as a function of temperature and oxygen partial pressure was established. Mössbauer spectroscopy results provided very useful information for subsequent DFT studies of the CoO defect structure and dynamical properties of Fe in CoO.

Measurements performed on TiO_2 (Appendix VII [23]) showed that (i) ^{57}Co (^{57}Fe) dopants can enter the rutile structure substitutionally and interstitially, (ii) the high-spin Fe^{3+} is born at the substitutional site undisturbed by the oxygen vacancy, (iii) the high-spin Fe^{2+} is created at the substitutional site disturbed by the oxygen vacancy, (iv) the low-spin Fe^{2+} is found at the interstitial sites with the oxygen vacancy in its neighborhood. Results of Mössbauer spectroscopy experiments showed that interstitial Fe impurity is a fast diffuser, while the diffusivity of the substitutional Fe impurities remains very low. The most interesting result is a presence of unusual Fe^{1+} charge state. The *exotic* monovalent Fe is a result of radioactive decay of parent ^{57}Co ion diffusing rapidly along the open channels of the rutile structure. Monovalent Fe represents a metastable state which can be observed below 400 K. The monovalent Fe can be found only at the ideal (free of intrinsic defects) interstitials, i.e., perfect channel sites.

2. Study of lattice dynamics and microscopic mechanism of diffusion in crystalline materials by Rayleigh scattering of synchrotron radiation

In the mid of 90-ties, Professor James G. Mullen from Department of Physics, Purdue University, West Lafayette, U.S.A. had at his disposal Mössbauer super-sources with activities reaching 60-70 Ci. The 46.5-keV Mössbauer radiation from ^{183}W was intended to study diffusive motion of atoms and the lattice dynamics of systems that do not contain resonant nuclei. The Rayleigh scattering of the Mössbauer radiation (RSMR) was used for this purpose. Measurements could be performed either in energy or time domains. The experimental group of Professor J. G. Mullen measured the recoilless fraction from NaCl crystal as a function of temperature and at various Bragg reflections using the RSMR technique. Experimental results showed that at temperature high enough to neglect anisotropy of the ionic form factors there is some anisotropy in the thermal motion of Na and Cl ions. Based upon the experimental results supplied by Professor J. G. Mullen a detailed analysis of the recoilless fraction from NaCl has been done. The general formalism describing experimental data was proposed. According to this formalism, the quartic anisotropy of the thermal motion of atoms in the cubic crystal was proved theoretically. This research was supervised by Professor Krzysztof Ruebenbauer from Institute of Physics, Pedagogical University, Kraków.

The problem of experimental observation of diffusive atomic motions in the time domain and by using synchrotron radiation was considered in (Appendix VII [25]). This theoretical work showed how to measure atomic motions in monocrystals that do not contain resonant nuclei, i.e., via the Rayleigh scattering of the Mössbauer synchrotron beams scattered at Bragg angles, and how to use the NRSR (Nuclear Resonant Scattering of Synchrotron Radiation) interferometer for that purpose. A general formalism describing diffusional motion of atoms in a crystal lattice which is observed experimentally at Bragg

conditions was presented. It should be mentioned that, theoretical research reported in (Appendix VII [24, 25]) attained quite a great interest of experimental community using synchrotron radiation to study diffusion processes in various materials.

Scientific activity 1991-1998

Theoretical models (Appendix VII [26, 27]) describing diffusion of substitutional and interstitial impurities in the rutile structure of TiO_2 were developed. Relaxation of the electric field gradient tensor due to impurity diffusive motion has been taken into account as well. The basic model presented in (Appendix VII [27]) was extended to model described in (Appendix VII [26]). The extended model is basically nonequilibrium model able to trace redistribution of impurities upon radioactive decay. Both models were used to predict Mössbauer spectra from substitutional and interstitial impurities diffusing within the TiO_2 lattice.

It was proposed to use a formalism of semi-invariants to expand vibrational self-correlation function describing a recoilless fraction, i.e., dynamics of the localized impurity (Appendix VII [28]). An anisotropy of the recoilless fraction was predicted for cubic crystals and it was further confirmed experimentally for NaCl crystal [C. K. Shepard, J. G. Mullen, and G. Schupp, Phys. Rev. B 57, 889 (1998); C. K. Shepard, J. G. Mullen, and G. Schupp, Hyperfine Interact. 110, 151 (1997)].

A modern Mössbauer spectrometer MsAa-1 (1st generation of the modern Mössbauer spectrometer) was developed and implemented in cooperation with RENON, Kraków, Poland. Innovative engineering design of the MsAa-1 spectrometer has been reported in (Appendix VII [29]).

A review of merits and drawbacks of the experimental methods sensitive to energy and momentum transfers that can be applied to study diffusion in solids at the microscopic (atomic) scale was done in (Appendix VII [30, 31]). A comparison between Mössbauer spectroscopy (QMS) and the time-dependent perturbed angular correlation (TDPAC) (Appendix VII [30]) as well as between Rayleigh scattering and the quasielastic incoherent neutron scattering (QNS) (Appendix VII [31]) was made.

A majority of scientific works performed between 1991 and 1998 was supervised by Professor Krzysztof Ruebenbauer, Institute of Physics, Pedagogical University, Kraków, Poland.

Additional information on my scientific activity (list of international and domestic research projects, information on international and domestic collaboration) is given in Appendix IX.

A handwritten signature in black ink, appearing to read "Andrzej P. Ruck". The signature is written in a cursive, flowing style.