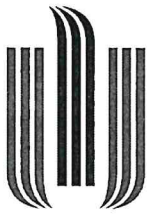

AGH AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE

SUMMARY OF THE DOCTORAL THESIS

Investigation of electronic structure, electron-phonon interactions and superconductivity of materials containing heavy elements

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The aim of this dissertation was to theoretically investigate the electronic structure, electron-phonon interactions, and superconductivity of several different families of materials containing heavy elements, namely the binary compound LiBi, Laves phases $SrIr_2$ and $SrRh_2$, alloy $Pb_{0.64}Bi_{0.36}$, and actinide/rare-earth compounds $ThIr_3$ and $CeIr_3$. For comparison and a more complete analysis of the obtained results, calculations were also carried out for NaBi, metallic Ir and Rh, and Pb.

A common feature of these materials is the occurrence of low-temperature superconductivity and the presence of elements with high atomic numbers, indicating the expected strong effects of spin-orbit coupling in these materials. Furthermore, in the Ce and Th compounds, strong electronic correlations are expected. Moreover, the investigated materials exhibit other interesting properties resulting from the combination of their crystal structure and composition. These include very strong electron-phonon coupling in the Pb-Bi alloy and the realization of an interesting "phonon engineering" mechanism leading to strongly coupled superconductivity in the Laves phases.

This work was done in collaboration with groups that conducted experimental studies in parallel, especially the group from the Gdańsk University of Technology under the direction of Prof. Tomasz Klimczuk. During her internship with this group, the author participated in some of the measurements. In addition, the experimental research involved teams led by Prof. Dariusz Kaczorowski from the Institute of Low Temperature and Structural Research of the Polish Academy of Sciences in Wrocław and Prof. Robert Cava from Princeton University. Thanks to this collaboration, the theoretical results were always compared with the experimental ones and formed the basis for their further analysis.

The thesis consists of three parts: a Theoretical Introduction, Results and Appendix.

In the first part I have introduced the theoretical background of my calculations, namely:

- The density functional theory (DFT), which allows to determine the electronic structure, and its implementations such as pseudopotentials and plane-wave methods;
- Phonons and density functional perturbation theory (DFPT) including the derivation of the electron-phonon part of dynamical matrix;
- Theories of superconductivity: Eliashberg theory and density functional theory for superconductors (SCDFT);
- Electronic correlations: LDA+U *vs.* dynamical mean field theory (DMFT) methods;
- Discussion of the relativistic effects and spin-orbit coupling.

Then I have described programs which I wrote to analyze and visualize the results of computations:

- Mayavi FS, which allows one to plot a 3D Fermi surface, colored with desired quantity, eg. orbital character. The purpose was to avoid the perspective projection which is programmed in Fermisurfer and which sometimes causes the troubles, eg. when focusing on nesting.

- The PH atom motion, which allows us to visualize phonon normal modes as arrows and as motion of atoms in crystal structure, in the direction pointed by polarization vector, and with given frequency.

- Program analyzing the force constants. The force constants contain an information about atomic bondings, however, they are obtained in cartesian coordinates, which usually do not coincide with bonding directions. To overcome this problem, the program transforms force constants matrix to desired coordination system and chooses the most interesting parts of this matrix.

In the second part I have focused on analysis of electronic structure and superconductivity of the four chosen groups of materials, all having heavy elements, which gave the opportunity to investigate the influence of spin-orbit coupling. Each of the materials was prepared and measured by the experimental group; in one case I participated in that process. In each chapter, one material (or a group of materials) is discussed, namely:

- LiBi - the compound consisting of the lightest and heaviest stable metallic elements, which crystallize in a tetragonal structure that is a distortion of the regular structure. The most important results of this chapter were published in Ref. [3] in the list below. The main results are as follows:

  - confirmation of the electron-phonon mechanism of superconductivity
  - investigation of the influence of structural distortion on electronic, phononic, and electron-phonon properties, and as a consequence, on superconductivity.
  - explanation of the topologically trivial electronic structure of LiBi, in contrast to the topologically non-trivial electronic structure of NaBi.
  - discussion of the influence of replacing Li with the heavier Na on the crystal structure and superconductivity
  - discussion of the influence of applied pressure on the investigated physical properties.
  - determination of the isotope effect.

- $SrIr_2$ and $SrRh_2$ - representatives of a large family of AM_2 Laves phases with characteristic crystal structure. We focus on the influence of this type of structure on physical properties. Most of the presented results were published in the paper [2] from the list below. The main results are as follows:

- Analysis of the crystal structure of SrM_2 shows that it is derived from the fcc crystal structure of elements M consisted of close-packed tetrahedron, by replacing the half of tetrahedrons with Sr atom.
- Observation of the key role of the tetrahedral subnetworks of M atoms for the properties of SrM_2 and comparison with the properties of elemental metals M.
- Capture of the "phonon engineering" mechanism, in which the relaxation of the tetrahedral network, compared to the elemental M, leads to a decrease in the frequencies of the key phonon branches, while maintaining a strong electronic contribution to the coupling constant. This explains the high values of the electron-phonon coupling constant and critical temperature in Laves phases, compared to metal M, and proves to be a more general mechanism that occurs in other Laves phases.
- Observation of the presence of the Kohn anomaly in $SrIr_2$ by analyzing the generalized susceptibility.
- Demonstration of the significant role of spin-orbit coupling in the stability of the cubic structure of $SrIr_2$.

- Pb and Pb-Bi alloy: the $Pb_{0.64}Bi_{0.36}$ alloy has the strongest electron-phonon coupling among crystalline materials at ambient pressure ($\lambda > 2$). Moreover, as Pb is a two-gap superconductor, studies of the superconducting gap were undertaken for the Pb-Bi alloy. Our main results:
  - Analysis of the fcc-hcp structural transition with increasing bismuth concentration in the alloy $Pb_{1-x}Bi_x$, based on calculations of total energy, changes in electronic structure, and occupation of 6p orbitals.
  - Confirmation of the strongly coupled electron-phonon mechanism of superconductivity.
  - Explanation of the mechanisms of the increase in λ and T_c in Pb-Bi compared to Pb.
  - Identification and description of phonon Kohn anomalies.
  - Demonstration of the strong anisotropy of the superconducting gap in Pb-Bi (with a value of $\frac{\Delta}{k_B T_c} \sim 5$ at $T = 0$ K) and its analysis with respect to Pb.
  - The properties of Pb-Bi are shown to be not determined by the chemical pressure of the Bi atoms, and the electronic mechanism of the changes is confirmed.

- $ThIr_3$ and $CeIr_3$ are compounds consisting of an actinide/rare earth element and a transition metal. Th atom has an empty $5f$ shell, while Ce has $4f$ shell occupied with one electron. This gives the opportunity to check the interplay of $4f$ state and

superconductivity. Most of the results presented in this chapter were published in papers [1, 4, 7] from the list included below. The main results are:

- Analysis of the electronic structure and relativistic effects.
- Analysis of the critical temperature value and the renormalization parameter of the electronic specific heat in $ThIr_3$, which shows that explaining the value of the critical temperature and the Sommerfeld coefficient requires the assumption of the presence of strong electron-phonon interactions ($\lambda \sim 1$) as well as electron-paramagnon interactions ($\lambda_{sf} = 0.1$), which is further supported by enhanced magnetic susceptibility and a quadratic temperature dependence of electrical resistivity.
- The electronic structure of $CeIr_3$ calculated using GGA and GGA+U methods leads to overestimated values of the electron-phonon coupling parameter ($\lambda =$ 1.47 and 3.4, respectively), which do not agree with the observed Tc value. Moreover, both methods give an incorrect occupation of the $4f$ state with respect to the experimental data.
- The correct electronic structure of $CeIr_3$ was calculated using the dynamic mean field theory (DMFT) and allowed to obtain reliable values of the electron-phonon coupling parameter $\lambda \sim 0.8$ and suggesting the presence of weak spin fluctuations with $\lambda_{sf} = 0.05$.
- The occupancy of Ce $4f$ levels was determined to be 0.67 and seemingly contradictory results from XPS measurements and magnetic susceptibility were explained.

At the end I have summarized the effect of spin-orbit coupling on such parameters as electronic density of states, electron-phonon coupling constant, phonon frequency and critical temperature in all studied compounds. I have obtained the general rule that in the case of the compounds of transition metals (d-block of periodic table) such as $SrIr_2$ and $SrRh_2$ the spin-orbit coupling leads to higher frequencies and thus to lower electron-phonon coupling and critical temperature. It is caused by the expansion of d orbital, which is the indirect relativistic effect (it is the result of the contraction of p and s orbital due to spin-orbit coupling) and causes stiffer atomic bonding (higher force constants). On the other hand, in the case of p-block compounds (LiBi, Pb and Pb-Bi alloys), the phonon frequencies are lowered by spin-orbit coupling due to contraction of p orbital, which causes the weakening of atomic bonds, leading to lower phonon frequencies. This leads to a strengthening of the electron-phonon coupling and a rise of the critical temperature by the spin-orbit coupling.

The Appendix contains important supplementary information, excluded from the main course of the dissertation, so as not to distract the reader from its main content.

The results obtained for this thesis were published in 5 papers:

1. S. Gutowska, B. Wiendlocha "Electronic structure of $CeIr_3$ superconductor: DMFT studies", Journal of Magnetism and Magnetic Materials **547**, 168917 (2022).

2. S. Gutowska, K. Górnicka, P. Wójcik, T. Klimczuk, B. Wiendlocha "Strong-coupling superconductivity of $SrIr_2$ and $SrRh_2$: Phonon engineering of metallic Ir and Rh", Physical Review B **104**, 054505 (2021).

3. K Górnicka, S. Gutowska, M.J. Winiarski, B. Wiendlocha, W. Xie, R.J. Cava, T. Klimczuk, "Superconductivity on a Bi square net in LiBi", Chemistry of Materials **32**, 3150-3159 (2020).

4. K Górnicka, D. Das, S. Gutowska, B. Wiendlocha, M.J. Winiarski, T. Klimczuk, D. Kaczorowski, "Iridium $5d$-electron driven superconductivity in $ThIr_3$", Physical Review B**100**, 214514 (2019).

5. K Górnicka, E. Carnicom, S. Gołąb, M. Łapinski, B Wiendlocha, W. Xie, D. Kaczorowski, R.J. Cava, T. Klimczuk, "$CeIr_3$: Superconductivity in a phase based on Tetragonally Close Packed (TCP) clusters", Superconductor Science and Technology **32**, 025008 (2019).

Another publication on the Pb-Bi alloy is in preparation.