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Abstract of the doctoral thesis

„Investigation of electron-phonon coupling and superconductivity in selected materials using ab initio methods"

The aim of is work is the investigation of superconductivity with *ab initio* methods in selected materials: Heusler phases $MgPd_2Sb$, $LiGa_2Ir$, $LiPd_2X$ (X=Si,Ge,Sn), $ScAu_2Al$ and resonantly doped semiconductors $Sn_{1-x}In_xTe$ and $Pb_{1-x}Tl_xTe$. Thanks to the collaborations with experimentalists groups lead by prof. Tomasz Klimczuk (Gdańsk University of Technology, Poland) and prof. Robert Cava (Princeton University, USA), published papers combined author's theoretical results with experimental ones.

The thesis consist of three parts: Theoretical introduction, Results and Appendix. In the first part main tools used in calculations are presented: density functional theory employed to obtain the electronic structure, density functional perturbation theory (DFPT) for phonons and electron-phonon matrix elements, BCS theory and density functional theory for superconductors (SCDFT).

First group of selected materials belong to the Heusler family which remains a very popular field of research because of the plethora of physical properties. Heusler compounds crystallize in face centered cubic structure which can be imagined as an AB sublattice NaCl-type with atoms C filling the tetrahedral voids. The investigation of $MgPd_2Sb$ began by chance during the synthesis of another compound $Mg_2Pd_3Sb_4$ when unidentified traces of a superconducting phase where observed. Then $LiGa_2Ir$ was examined following the discovery of superconductivity in an isoelectronic $LiGa_2Rh$. In $LiPd_2X$ series strong phonon softening was observed in the calculated phonon dispersion relation which suggest structural instability. However, there were indications of structural phase transitions above 1 K in heat capacity, electrical resistivity and magnetic susceptibility measurements. Moreover, the strongest softening observed in $LiPd_2Ge$ correlates with highest T_c=1.96 K so it probably enhances superconductivity. $ScAu_2Al$ exhibits the highest Tc=5.12 K and strongest electron-phonon coupling constant among Heusler compounds. In superconducting Heuslers the valence electron count per atom (VEC) plays an important role. One can find two maxima of Tc for VEC=4 and VEC=7. $LiGa_2Ir$ has VEC=4, $ScAu_2Al$ VEC=7 and $LiPd_2X$, $MgPd_2Sb$ VEC=6.75 so these compounds were selected as promising candidates for superconductors in experimental research.

In selected Heusler compounds the electron-phonon coupling was confirmed to be the pairing mechanism. Calculated electron-phonon coupling constant λ for $MgPd_2Sb$ and $LiGa_2Ir$ are equal λ=0.61 and λ=0.68, respectively. Calculated T_c remains in a very good agreement with the experiment, 2.16 K for $MgPd_2Sb$ and 3.57 K for $LiGa_2Ir$. The influence of hydrostatic pressure was investigated and the calculated change of T_c with is p $\frac{\Delta T_c}{p}$=-0.27 K/GPa in $MgPd_2Sb$ and $\frac{\Delta T_c}{p}$=-0.05 K/GPa in $LiGa_2Ir$ which are exactly equal experimental ones. Additionally, mechanical properties were calculated, including bulk modulus B=106 GPa in $MgPd_2Sb$ and B=139 GPa in $LiGa_2Ir$. Spin-orbit coupling (SOC) turned out to visible affect

the phonon structure of $LiGa_2Ir$. In the $LiPd_2X$ series due to imaginary phonon frequencies for (X=Ge,Sn), the λ and T_c could be only roughly estimated, but they qualitatively agree with the experiment. Especially, calculations suggest superconductivity in $LiPd_2Si$ below 1 K which was later confirmed by repeating experiments in lower temperatures. Systematic studies of causes for the appearance of the soft mode in $LiPd_2Ge$ ruled out the Fermi surface nesting, the structure modulation (charge density wave phase) and static distortion related to atom movement for **q**=(1/3,1/3,0) located near the minimum if the soft mode. The probably cause of the soft mode is anharmonicity of the potential which can be seen by displacing single Li and Ge atoms in a supercell. In $ScAu_2Al$ obtained λ=1.25 places the compound in the strong coupling regime. Calculated T_c=5.43 K remains in good agreement with the experiment. The main factor influencing superconductivity of $ScAu_2Al$ is a softened phonon mode in Γ-X direction which is caused by the Fermi surface nesting. Moreover, SOC significantly changes the electronic and phonon structure, including atoms' movement pattern near the X point which results in 30% of λ compared to value computed with SOC neglected (0.97). To the best of author's knowledge, anisotropic superconducting gap in $ScAu_2Al$ was calculated for the first time in Heusler compounds. $ScAu_2Al$ is a two-band superconductor with s-wave superconducting gap with moderate asymmetry which can be seen in the unusual shape of the quasiparticle density of states curve. Obtained T_c=5.16 K remains in an excellent agreement with the experiment. A large ratio $\frac{2\Delta}{k_b T_c}$=4.14, much greater than the characteristic value of 3.53 from the BCS theory, confirms strong electron-phonon coupling. An influence of spin fluctuations was and they slightly lowered T_c by 0.37 K.

The second group of selected compounds consists if resonantly doped semiconductors SnTe and PbTe which crystallize in NaCl-type structure. They have been intensively investigated for 50 years because of their exceptional thermoelectric performance. The resonant dopants, for example In in $Sn_{1-x}In_xTe$ and Tl in $Pb_{1-x}Tl_xTe$, modify the electronic structure in a particular way which greatly enhances thermopower. The pristine PbTe is not superconducting, but SnTe is with small T_c<0.1 K which is due to vacancies on Sn positions. Interestingly, the resonant dopants greatly enhance superconductivity, because with little dopant concentration they noticeably increase the Tc which reaches over 4 K in $Sn_{1-x}In_xTe$ and approximately 1.5 K in $Pb_{1-x}Tl_xTe$ for the optimal doping. Because of very low carrier concentration in the order of 10^{20} cm^{-3} it is often discussed that superconductivity in these compound is unconventional. For $Pb_{1-x}Tl_xTe$ there is a model of superconductivity induced by the negative U, nonetheless, it cannot explain transport and thermoelectric properties in normal state and it does not describe the resonant state. In this work the calculation of electron-phonon interaction in $Sn_{1-x}In_xTe$ and $Pb_{1-x}Tl_xTe$ was performed as it could provide valuable insight into superconductivity in these materials.

The choice of the exchange-correlation functional in SnTe was presented because it strongly affects the electronic structure, phonons and thermopower. Similar difficulties are present in PbTe. Atomic positions relaxation was checked in $Sn_{1-x}In_xTe$ and $Pb_{1-x}Tl_xTe$ which visibly lowered average phonon frequencies and increased electron-phonon coupling near the dopant atom. Using the Rigid Muffin Tin Approximation, the electron-phonon coupling constant was calculated. Obtained values λ=0.1-0.2 in $Sn_{1-x}In_xTe$ and λ=0.04-0.07 in $Pb_{1-x}Tl_xTe$ prove that this approximation is not valid to describe superconductivity in these compounds. DFPT calculations in $Sn_{31}In_1Te_{32}$ supercell resulted in λ=0.22 and in a finite T_c of the order of 0.1 K which is still lower by approximately 0.2 compared to the experimental value. Rhombohedral distortion in SnTe was investigated, as this structure is preferred in low temperatures, and it increased λ by about 3%. Performed calculations cannot determine whether the electron-phonon interaction is the pairing mechanism in these compounds.

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