Electronic structure of some layered compounds, intercalates and misfit layer compounds
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SUMMARY

The electronic structure of solids, which is the behavior of the valence electrons in terms of wave functions and energies, can be studied by theoretical methods like band structure calculations. Experimentally insight in the electronic structure is obtained by study of the physical properties like the electrical conduction, and in particular by photo electron spectroscopy. In this thesis band structure calculations are reported on some layered transition metal dichalcogenides \( TX_2 \), which are built of a stacking of sandwiches \( TX_2 \), and their intercalates. Intercalates are compounds in which foreign atoms (alkali metals, post-transition metals) or molecules like \( \text{NH}_3 \) are present in the space between \( TX_2 \) sandwiches. A new group of such intercalates are the misfit layer compounds in which a double layer of composition \( MX \) is present between the \( TX_2 \) sandwiches. They have the composition \( (MX)_{n+1}(TX_n) \); \( M \) can be any of the elements Sn, Pb, Sb, Bi; \( T = Ti, V, Cr, Nb, Ta; X = S, Se \). For \( n = 1 \) each of the gaps between the sandwiches are filled, for \( n = 2 \) every second gap is filled, etc. So far compounds with \( n = 1, 2, 3 \) were synthesized. The misfit layer compounds belong to the class of incommensurate composite crystals which all have the peculiar property that there is no three-dimensional periodicity in the crystal structure. In the structure one can recognize two or more structural building units, each with its own three-dimensional lattice and space group. The misfit layer compounds are planar intergrowth compounds with two subsystems, viz., the MX and the \( TX_2 \) subsystem, as building units.Layers of MX and \( TX_2 \) are stacked upon each other. Because the two building units are present in one composite lattice, there is a relation between the lattice vectors of the two subsystems.

The \( TX_2 \) layers (\( T = Ti, V, Cr, Nb, Ta \)) in the misfit layer compounds are sandwiches with the X atoms as the slices and the T atoms as the spread. The 3d metals Ti, V, Cr are in trigonal-antiprismatic (approximately octahedral) coordination. The Nb and Ta atoms are in trigonal-prismatic coordination. The same coordination is for both types found in \( TX_2 \) compounds and their intercalates.

The MX layers in the misfit layer compounds consist of double layers, resembling a slice of NaCl type structure with a thickness of half the cell edge. The MX layers are corrugated with the M atoms at the outside, making it possible to have bonding interactions with the X atoms of the \( TX_2 \) layers. Each M atom is coordinated to five X atoms of the MX layer and one or two X atoms of the neighbouring \( TX_2 \) sandwich.

The aim of this thesis is to understand the stability, the nature of the interactions between the theoretical (band structure calculations) and experimental methods (photo electron spectroscopy). The selected materials are \( TiSe_2 \) with \( M = Sn \) for the \( d \) electron interaction between the layers, and \( TiS_2 \) with \( M = Sn \) for the transfer of the \( d \) electron from the layers to the intercalates. Since band structure calculations with \( d \) electrons are difficult, the compounds studied are here \( TiSe_2 \), \( Cr \), being semimetallic, \( Nb \), being semimetallic, and \( Ta \), being semiconducting.

Besides the band structure calculations with \( TiSe_2 \), for \( 2F \) compounds

Chapter 3: LSW and ASLW calculations with \( TiSe_2 \), for \( 2F \) compounds

Chapter 4: TiS\(_2\) and \( 1T-TiS_2 \) calculations with LSW and ASLW calculations with \( TiSe_2 \) compounds smaller with \( 2F \) compounds

Band structure calculations with \( TiSe_2 \) compounds with a gap of 0.7 eV are completed.

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between the layers, the physical properties such as the electrical conduction by theoretical (band structure calculations, valence bond analysis) and experimental methods (photo electron spectroscopy) of some selected misfit layer compounds and layered transition metal dichalcogenides and three-dimensional periodic intercalates. The selected misfit layer compounds are members of four types of compounds, viz., a type with M = Sn or Pb and T = Nb or Ta which show p-type metallic conduction and a weak interaction between the layers and a small charge transfer from MX to TX, the second with M = Sn or Pb and T = Ti, with n-type metallic conduction and with minor charge transfer, the third with M a rare earth metal (Ln) and T = Nb or Ta with p-type metallic conduction with large charge transfer (Ln is Ln³⁺) and the fourth with M = Ln and T = Cr, being semiconductors with a large charge transfer (Ln and Cr both trivalent). The compounds studied were (SnS)₁₋₁,₇NbS₂, (SnS)₁₋₁,₂₀TiS₂, (LaS)₁₋₁,₄₅NbS₂ and (LaS)₁₋₁,₂₀CrS₂. Since band structure calculations can only be performed of compounds with three-dimensional periodicity, the band structure calculations were performed in a large supercell which approximates fairly the real incommensurate structure.

Besides the electronic structure of the misfit layer compounds, band structure calculations were performed for the bulk, the surface and thin layers of 1T-TiS₂ and 1T-TiSe₂, for 2H-NbS₂, LaS, 1T-CrSe₂, KCrSe₂ and compounds Sn₁₋₁,₃NbS₂ and Pb₁₋₁,₃TaS₂.

In chapter 2 an introduction into ab-initio band structure calculations is given. The LSW and ASW methods are used for the calculations.

Chapter 3 describes the electronic structure of bulk, thin layers and the surface of 1T-TiS₂ and TiSe₂. Bulk TiS₂ and TiSe₂ show semimetallic properties. However, the calculations show that TiS₂ thin films are semiconductors while TiSe₂ thin films are semimetallic. The indirect gap for single slab TiS₂ is about 1.0 eV, and the gap becomes smaller with increasing number of layers. When the number of layers becomes eleven, the thin films become semimetallic.

Band structure calculations of CrSe₂, VSe₂ and KCrSe₂ are discussed in chapter 4. Calculations for KCrSe₂ show that the compound is a magnetic semiconductor with a band gap of 0.7 eV. The potassium atoms are nearly completely ionized. The Cr 3d (t₂g) states are completely spin polarized. The electronic configuration of Cr is 3d⁹ with a local magnetic moment of 3 μₜₚ per Cr. For 1T-CrSe₂, which only exists in a metastable state, the calculations show that the total energy for the ferromagnetic state is 0.29 eV lower than for the non-magnetic state. The total magnetic moment of 2.17 μₜₚ on the Cr atoms consists of 3.28 μₜₚ for spin-up electrons and 0.84 μₜₚ for spin-down electrons; the total number of 3d electrons per Cr is 4.12, more than expected for Cr(IV), 3d⁸. The Cr 3d based band overlaps significantly the Se 4p bands, which implies strong covalency. CrSe₂
is a magnetic metal. Similar calculations for 1T-VSe₂ show a very small energy difference between the ferromagnetic and non-magnetic state, in agreement with experimental evidence that 1T-VSe₂ is a non-magnetic metal.

Chapter 5 describes the crystal structure determination and band structure calculation of intercalates Pb₁₀₃TaS₂ and Sn₁₀₃NbS₂. Post-transition metal atoms occupy one-third of the trigonal-antiprismatic holes between sandwiches NbS₂ and TaS₂. The Nb and Ta atoms are in trigonal-prismatic coordination by sulfur, as in 2H-NbS₂ and 2H-TaS₂. Band structure calculations show that the rigid band model is approximately valid. The main difference with 2H-NbS₂ and 2H-TaS₂ is the presence of Sn 5s and 5p (Pb 6s and 6p) bands and a larger S 3p/Nb(Ta) 4d (5d) gap in the intercalates. The Sn 5s (Pb 6s) bands are at the bottom (bonding) and top (antibonding) of the valence bands. The conduction bands are composed of Nb 4d₂ or Ta 5d₂ orbitals hybridized with S 3p. These bands are filled to about 0.3 holes per Nb (Ta) corresponding to a donation of two electrons per Sn (Pb).

In chapters 6 to 9 the electronic structure of the above mentioned misfit layer compounds are discussed.

For (LaS)₁₄-NbS₂ the band structure is compared with that of the components NbS₂ and LaS (Chapter 8). The calculations show that the electronic structure of (LaS)₁₄-NbS₂ can be regarded as that of LaS intercalated into the host NbS₂. The interlayer interaction is more ionic than covalent. There is a transfer of about 0.7 electrons per Nb from the LaS to the NbS₂ layers, some electrons remain in La 5d orbitals. The states at the Fermi level are dominated by Nb 4d₂ orbitals; there are about 0.3 holes per Nb. The conclusions are in good agreements with experimental results for the rare earth misfit layer compounds. X-ray and ultraviolet photoelectron spectra obtained for the valence bands of some late rare earth misfit layer compounds (LnS)₁₄-TS₂ (M = Dy, Ho, Er, Tb; T = Nb, Ta) are in good agreement with the band structure calculations except for the 4f multiplet structure shifting to a lower energy about 2 eV, as compared with the rare earth metals (Chapter 11).

Compounds MX (M = Sn, Pb; X = S, Se, Te) with M ns² (n is the main quantum number of the s orbital) "inert lone s² pair" are semiconductors. The bottom and the top of the valence band of SnS are mainly composed of the Sn 5s bonding and antibonding states, respectively; since both are occupied they do not contribute to the net bonding. The calculated band structure of (SnS)₁₄-NbS₂ and (SnS)₁₄-TiS₂ can be regarded approximately as a superposition of the calculated bands of the two components SnS and NbS₂ (TiS₂). There is a small transfer of about 0.2 to 0.3 electrons per Nb (Ti) from the SnS to the NbS₂ (TiS₂) subsystem. The stability of the misfit layer compounds (SnS)₁₄-TS₂ is mainly due to covalent bonding between Sn atoms and S atoms of the NbS₂ (TiS₂) subsystem, and to the electric field gradient in the rare earth layers. The misfit layer compounds are some examples as that of Pr₆S₉, which is one of the most stable with a structure in which the rare earth sublattice is stabilized by a strong electric field in the interlayer layers, and the misfit layer compounds are some examples as that of Pr₆S₉, which is one of the most stable with a structure in which the rare earth sublattice is stabilized by a strong electric field in the interlayer layers.
The contribution of electrostatic interactions, as a result of charge transfer, is much smaller. The calculated electronic structure is in good agreement with the electrical transport properties and photoelectron spectra.

The misfit layer compounds with CrX₂ sandwiches, which occur only for M = Bi, and the rare earth metals, are magnetic semiconductors. For (LaS)₁₂₀CrS₂ the calculation results are compared with those of LaS and the intercalates KCrSe₂ and NaCrS₂ (Chapter 4). The calculations show that the electronic structure of (LaS)₁₂₀CrS₂ can be regarded as that of LaS intercalated into the host CrS₂ (Chapter 9). The Cr atoms are almost spin-polarized. There is a transfer of 1.2 electrons per Cr from the LaS to the CrS₂ layers, and La is 3+ and (LaS)₁₂₀CrS₂ is a half-metal with a magnetic moment 3.2 of μₜ per Cr atom. The interaction between Cr and S(CrS₂) atoms is rather covalent. The semiconductor behavior of the misfit layer compound is explained by the fact that there are some vacancies in the La sites and the real composition may be (La₀.₇₄S₀.₆₆S)₁₂₀CrS₂ with charge balance between La³⁺, Cr³⁺ and S²⁻.

Synthesis and crystal structure determination of some erbium compounds, viz., F-Er₂S₃, Er₂Se₃ and the misfit layer compound (ErS)₁₂₄NbS₂ are described in chapter 10. F-Er₂S₃ is one of the several modifications of Er₂S₃ and isostructural to F-Tm₂S₃. Phase relationships are discussed. The F modification is a high pressure form, presumably stabilized by some Nb present during synthesis. Er₂Se₃ has the Se₂S₃ structure with Er in octahedral coordination by Se while Se is coordinated to Er atoms at four of the six vertices of an octahedron; vacancies are in cis position. (ErS)₁₂₄NbS₂ is a misfit layer compound and shows orientation variants of both subsystem, similar to that observed for the corresponding dysprosium and terbium compounds.