University of Groningen

Incommensurate structures and physical properties of antimony, bismuth and lanthanum misfit layer compounds.

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Publication date:
1996

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Already before the discovery that crystals diffract X-rays, the morphology of crystals was explained with the three-dimensional (3D) repetition of a smallest unit. After this discovery (1912) the difraction pattern could be explained with 3D periodicity and crystal structures were determined on basis of a unit cell and a space group. However, it was also known that the morphology of some crystals did not obey the laws for 3D periodicity. An example is AuTe$_2$ for which it was known already in 1902 that some of the crystal planes could not be indexed with the three integer Miller indices appropriate for most of the planes. This leaded to the discovery of incommensurately modulated crystals. They show a diffraction pattern that consists of the main reflections of a 3D periodic lattice and in addition weak extra reflections, satellites. The complete set of reflections can be indexed with three integer indices for the 3D lattice and an extra index for a modulation wave vector. Because a 3D periodic repetition is absent and there is yet a sharp diffraction pattern, the crystals are called quasi-periodic.

A second group of quasi-periodic crystals are the composite or intergrowth compounds. In contrast to the incommensurately modulated crystals the diffraction pattern consists of main reflections of two (or more) 3D patterns, and in addition satellites. One finds composite structures for inorganic as well as organic compounds. Subject of this thesis are the so-called misfit layer compounds which are built of a stacking of sandwiches with composition $\mathcal{TX}_2$ and double layers with compostion $\mathcal{MX}$; the formula giving the composition of the composite crystal is $(\mathcal{MX})_{1+\delta}(\mathcal{TX}_2)_n$. $\mathcal{M}$ can be one of the elements Sn, Pb, Sb, Bi and the rare earth metals; $\mathcal{T}$ the transion elements Ti, V, Cr, Nb, Ta; $\mathcal{X}$ is S or Se. The index δ depends on the constituents $\mathcal{MX}$ and $\mathcal{TX}_2$ in the compounds. The two types of building units, each with a unit cell and space group, are called the subsystems. The three-layer thick $\mathcal{TX}_2$ sandwiches are similar to those in the pure dichalcogenides $\mathcal{TX}_2$. The $\mathcal{MX}$ subsystem consists of a double layer with a structure resembling a two-atom thick slab in NaCl type MX; some pure compounds $\mathcal{MX}$ are also known, most of them have the NaCl-type structure. Besides compounds with a stacking of one $\mathcal{TX}_2$ sandwich followed by one $\mathcal{MX}$ layer, there are also compounds with a stacking of two or even

three $T\mathcal{X}_2$ sandwiches followed by one $\mathcal{M}\mathcal{X}$ double layer, etc. Such staged structures are also found for intercalation compounds of the transition metal dichalcogenides; they have foreign atoms or molecules in the gap (van de Waals gap) between the $T\mathcal{X}_2$ sandwiches. When all gaps are filled one has stage-1 compounds; if the gaps are alternatingly filled and empty, a stage-2 compound. The misfit layer compounds can be considered to be a special kind of intercalation compounds of the transition metal dichalcogenides $T\mathcal{X}_2$. The $\mathcal{M}\mathcal{X}$ lattice is pseudo-tetragonal, the $T\mathcal{X}_2$ lattice pseudo-hexagonal. For that reason the two types of layers do not fit. There in one direction ($\vec{a}$ axis) along which the atoms of the two subsystems run parallel, however, with a different periodicity (the misfit). The relation between the unit cell vectors of the two subsystems can most simply be expressed in reciprocal space, viz., there is a common reciprocal plane, which is the ($\vec{b}^*, \vec{c}^*$) plane. The common $\vec{c}^*$ is due to space filling (layers which are stacked along the c axes cannot intersect); the common $\vec{b}^*$ by the interaction between the sublattices along the parallel $\vec{a}$ axes. Both lattices modulate each other incommensurately; it means that the atoms are somewhat displaced from their positions in the 3D unit cell. This modulation gives rise to satellites in the diffraction pattern. For the composite crystals a new crystallography was developed by Janner and Janssen as an extension of the theory for incommensurately modulated crystals developed by de Wolff, Janner and Janssen. The theory makes use of higher dimensional (super) space. The theory was extended by van Smaalen, Kato and Yamamoto. A program (JANA) for the structure determination of composite crystals from X-ray data was developed by Petricek.

The first compound of the class of misfit layer compounds is $(LaS)_{1.20}CrS_2$ discovered by Kato *et al.* (1977). Investigations starting at about 1988 showed that there is large number of misfit layer compounds. Compounds with $Nb\mathcal{X}_2$ or $Ta\mathcal{X}_2$ sandwiches are orthorhombic or monoclinic; the Nb (Ta) atom is in approximately trigonal-prismatic coordination by chalcogen. These compounds show metallic type electrical conduction. Compounds with $Ti\mathcal{X}_2$, $V\mathcal{X}_2$ or $Cr\mathcal{X}_2$ sandwiches have the tramsition metal in approximately octahedral coordination by chalcogen. They have monoclinic or triclinic subsystems. Compounds with a $Cr\mathcal{X}_2$ subsystem only occur with Bi or a rare earth metal; they were found to be semiconductors.

The chemical bonding has been elucidated in particular by photoelectron spectroscopy and recently by band structure calculations. For compounds with Sn, Pb, Bi there is a slight electron donation from the $\mathcal{M}\mathcal{X}$ to the $T\mathcal{X}_2$ layers and the weak bonding between the layers is mainly covalent. A large electron donation from the $\mathcal{M}\mathcal{X}$ to the $T\mathcal{X}_2$ sandwiches and strong interlayer interaction is found if $\mathcal{M}$ is a rare earth metal.

This thesis describes the syntheses, structure determinations in superspace symmetry and physical properties of a number of new misfit layer compounds. The first examples of compounds with SbS double layers and TiS₂ sandwiches were prepared, viz.,

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$(SbS)_{1.15}(TiS_2)_2$, with $n = 1$ and 2 (stage-1 and stage-2 compounds, respectively). The SbS layers have much more complicated structure than the $\mathcal{MX}$ layers found in the Bi compounds $(Bi\mathcal{X})_{1+\delta}T\mathcal{X}_2$ with $T =$ Nb or Ta. The SbS layers are interface modulated due to antiphase boundaries. These antiphase boundaries are perpendicular to the diagonal in the $(\vec{a}, \vec{b})$ plane; for the Bi compounds they are perpendicular to the incommensurate $\vec{a}$ axis. As a consequence of this modulation a (3+2)D triclinic superspace group is needed to describe the structure. The refinement of the structure showed that there are zig-zag chains of mainly Sb atoms with distances as in Sb metal and zig-zag chains of mainly sulfur atoms with distances corresponding to van der Waals interaction. A photoelectron spectroscopy study showed that there are two types of Sb atoms, those in a coordination by sulfur as for a normnal SbS layer and those in the zig-zag chains; the ratio 22 : 78 is as was found from the structure determinations using X-ray diffraction. The valence band spectrum studied with XPS and UPS showed a peak just below the Femi level corresponding some Ti $3d$ electrons in the TiS$_2$ conduction band. The electrical transport properties of both compounds (resistivity, Hall effect and thermopower) were measured in the temperature range $4 - 350$ K. Both compounds showed metallic behavior. The Hall effect showed a donation of electrons from the SbS to the TiS$_2$ layers (~ 0.6 electron/Ti for $n = 1$ and ~ 0.3 e/Ti for $n = 2$). The resistivity in the (ab) plane shows a temperature dependence given by $\rho = \rho_0 + A_{ee}(T/T_F)^2\ln(T_F/T)$ for electron-electron scattering of a two-dimensional Fermi-liquid system. From the fit T_F is obtained. The optical reflectivity showed that a much better fit is obtained for a Fermi liquid behavior compared to the Drude model for which the scattering rate is frequency independent.

The compound $(BiS)_{1.11}VS_2$, the first example of a compound with a Bi$\mathcal{X}$ double layer and a VS$_2$ sandwich, shows an interface modulated BiS lattice, similar to that found in Bi$\mathcal{X}$ compounds with Nb$\mathcal{X}_2$ or Ta$\mathcal{X}_2$ sandwiches. The complete structure could not be elucidated due to disorder in the BiS structure.

Vanadium compounds are interesting because in the series of compounds with $T\mathcal{X}_2$ sandwiches a transition occurs from metallic behavior for $T =$ Ti to semiconducting behavior for $T =$ Cr. Vanadium compounds are intermediate, metallic behavior was found for $(BiS)_{1.11}VS_2$.

An accurate structure determination in (3+1)D superspace of a compound with an LaSe double layers and VSe$_2$ sandwiches showed that there is a large charge transfer from the LaSe to the VSe$_2$ layers, as also found in other misfit layer compounds with a $Ln\mathcal{X}$ double layer ($Ln =$ rare earth). The structure determination showed that there are vacancies in the La lattice such that charge balance exists between La^{3+}, V^{3+}, and Se^{2-}. The largest displacements of the atoms due to the mutual modulation of the two subsystems are remarkably found at the vanadium atoms, which is quite unusual since in all other cases the largest displacements are found for the atoms close to the

interface of the two subsystems. The displacements are such that in the vanadium layers relatively short and long V$\cdots$V distances occur. The semiconducting behavior is explained with a Mott localisation of the electrons in the VSe$_2$ sandwiches.

A first example of a misfit layer compound with an LnX double layer and a paired Ti$\mathcal{X}_2$ sandwich is (LaSe)$_{1.20}$(TiSe$_2$)$_2$. The intralayer La-Se distances are as in misfit layer compounds with an LaSe double layer and NbSe$_2$ or TaSe$_2$ sandwiches. One may conclude to a large charge transfer between the layers. The compound shows disorder in the TiSe$_2$ sandwiches which was taken into account in the structure refinement.

Samenva

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