PREFACE

In the last few years, the number of compounds known to show incommensurate (misfit) structures has been increasing very rapidly. The first examples of such compounds were found among minerals. These misfit materials exhibit low dimensional structures that can be described in the following ways:

-- for two-dimensional (2D) types: Layer structures composed of two layer types A and B which regularly alternate along a stacking direction. The in-plane periodicities of both layers are mutually incommensurate along 1 or 2 directions in the plane. This is the case, for instance, of the brucite-like hydroxide / metal sulfide compounds such as Valleriites, Tochilinites....

-- for one-dimensional (1D) types: Separate columns of two different structure elements; e.g., the so-called "chimney ladder" alloy phases or the synthetic series of compounds $A_{1-p}Cr_2X_{4-p}$ (A=Ba,Sr,Eu,Pb; X=S,Se; p=0.29) described by BROUWER and JELLINEK. For the synthetic series, a framework of linked CrX_6 octahedra contains two different types of channels centered around a sixfold and a threefold axes. The periodicities along the framework and the two channel directions are different and mutually incommensurate.

More recently, many new synthetic compounds have been reported with incommensurate features. One can mention for instances the sulfide derivatives $(MS)_nTS_2$, where M= Sn,Pb,Bi,Rare Earth Metal and T= Ti,V,Cr,Nb,Ta with $1.08<n<1.23$; their structures are similar to those found for the first studied member of this family, $(LaS)_{1.2}CrS_2$, frequently reported as " $LaCrS_3$" (KATO et al). One has also to introduce the new high T_c superconductor oxides (e.g., the bismuth derivatives) with structures also found to be incommensurate. These two new series of compounds show a typical 2D. structure type.

A structural model which considers an intergrowth phenomena between entities (chains or slabs) of different nature could lead to the notion of a composite crystal. The incommensurate structures of these phases are solved, truly or approximately, through three different analyses using:

-- a superspace-group symmetry: Only this method is to be used to get a correct solution when the ratio of periodicities along the misfit direction is irrational.

-- a supercell description which is correct when the ratio is truly rational; if not, one gets an approximate solution.

-- a composite approach: The structure determination is done in parts, each one related to the subsets A and B with their own unit cell dimensions and symmetries. Of course, this leads to the description of the basic structures (average structures), without modulation. However, atomic displacive modulation is induced by the mutual interaction of both subsystems. This approach, which is the simplest one, was largely followed for the $(MS)_nTS_2$ family.

The reasons for the tremendous increase in the number of incommensurate examples probably is to be found in the use of new equipment or improved techniques (e.g., a higher resolution in electron microscopy, the use of synchrotron radiation...) and of efficient and fast programs (the possibility to perform very complex calculations in a short time). These programs appeared primarily after a theoretical work on superspace group symmetry > 3D done by De WOLFF, JANNER and JANSSEN (around 1980). One can also think that the need to better understand physical properties has been a major factor for the recognition of such a structural particularity. In any case, accurate structure determination is absolutely necessary for a critical discussion of the high T_c superconducting properties exhibited by some oxides.

The occurrence of misfit compounds raises several questions: i, Is such a feature exceptional or rather is it a normal consequence of stacking two different rigid entities in forming a composite material?.

ii, How strong must the structural rigidity be within sets A and B to prevent small adjustments and the resulting commensurability?.

iii, How strong are the bonds at the A-B interface, and consequently what is the importance of the anisotropy?. For the $(MS)_nTS_2$ compounds, the interaction between (MS) the electron donor and (TS_2) the electron acceptor is primarily related to electron transfer.

The main object of this book is to focus on some new families of compounds, perhaps choosing the most recent examples, rather than to draw exhaustive lists of many compounds showing misfit structures. Four main parts are then devoted to:

1- a general overview of minerals and synthetic compounds which exhibit a 2D misfit structure. The classification of different misfit-type structures is recalled.

2- a detailed presentation of a new family of sulfide derivatives complete with an electron microscope study. In this part, a theoretical approach on the superspace-group symmetry illustrated by some solved examples is given.

3- a description is presented of some incommensurate structures of high T_c superconducting oxides and relevent electron microscope studies. The role of incommensurability is discussed from a theoretical point of view.

4- finally, a review is given on the physical tools which can be used for the study of incommensurate systems. The various techniques are illustrated through some examples taken in the wide field of incommensurate organic compounds.

This book is intended to be of interest for chemists, physicists, students and well trained researchers specifically concerned by incommensurate structures occurring in low-dimensional materials (mostly 2D sandwiched misfit layer structures).

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