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The Use of Electron Diffraction for the Structural Characterization of Modulated and Aperiodic Structures

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Very many traditional 'crystalline' compounds or line phases are known. Close inspection of a large and ever-increasing number of phases, however, has shown that many do not in fact fit into such a neat strait-jacket and are in fact modulated in one form or another [1]. The modulations in such materials can be short or long range ordered, have large or small amplitude while the associated occupational and displacive Atomic Modulation Functions (AMF's) required for complete structural characterization in superspace can be essentially sinusoidal, inherently square wave or saw tooth in form. Whatever the particular characteristics, an understanding of the local crystal chemistry as well as the associated physico-chemical properties of such phases can not be had until such modulations are recognized and properly taken into account. The Transmission Electron Microscope (TEM) is an extremely well-adapted instrument for the detection as well as the symmetry and structural characterization of such modulated structures. This is as a result of the sensitivity of electron diffraction to weak subtle features of reciprocal space, the ability to obtain such information from small local regions as well as the capacity to image in various modes with excellent spatial resolution and over a considerable range of temperature. In this contribution, the application of electron diffraction to the study of interface, composite, compositionally and/or displacively modulated structures (including hollandites, $LaSb_2Sn_x$, $Sn_{1-x}Sb_{1+x}$, fresnoites *etc*) will be discussed. The characteristic diffraction signatures associated with the different types of modulated structure will be highlighted along with the practical application of transmission electron microscopy to problems such as pseudo-symmetry and twinning, to indexation in (3+d)-dimensional superspace and to overall superspace symmetry and structural characterization.

[1] R.L.Withers, L.Norén and Y.Liu, *Z.Krist.* 219, 701-710, 2004.

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Modulations and worse in Sb-Zn and related systems

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The system Sb-Zn contains a number of phases that are all possible to consider as tetrahedrally close-packed arrangements of Sb with Zn in the interstices. The various compositions may be rationalized by Zintl-phase type arguments.The Zn-rich end contains some very complex phases, notably ht- and lt-Zn_3Sb_2, and a phase often referred to as Zn_4Sb_3. This latter phase has attracted a lot of attention due to its promising thermoelectric properties, and has recently [1] been shown to have a composition closer to $Zn_{13}Sb_{10}$, but it has a certain phase width. Given appropriate synthesis conditions, the compound will undergo reversible phase transitions at ca 245K and 235K respectively. The room temperature (β) phase is rhombohedral, the 245K structure (α-phase) is monoclinic (4-fold superstructure), and the low temperature α'-phase is an incommensurately modulated phase. Doping affects the thermal properties of this phase very strongly, and the formation of the α' and even the α phase may be suppressed completely. The corresponding Cd based system is even more complex. The systems offer an intriguing interplay between structural complexity and physical behaviour.

[1] Nylen, Andersson, Lidin and Häussermann, *J.Am.Chem.Soc.*, 2004,126,16306.