12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

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A MODULATION WAVE APPROACH TO COMMISSURATURALLY MODULATED STRUCUTRES. By R.L. Withers*, J.G. Thompson, S.Schmidt, Research School of Chemistry, Australian National University, GPO Box 4, Canberra City, ACT 0200, Australia and A.D. Rae, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia.

Commissurately or incommensurately modulated structures can always be described in terms of an underlying parent structure (characterized in reciprocal space by a set of sharp Bragg reflections G) plus compositional and/or dispersive modulations thereof associated with independent modulation wave-vectors \((\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, ...)\) and characterized in reciprocal space by a set of sharp Bragg reflections at \(G + (\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3, ...)\), where \(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \ldots\) represent independent primary modulation wave-vectors and \(q_1, q_2, q_3, \ldots\) are integers. Given knowledge of the underlying parent structure, structure determination reduces to the determination of the compositional and/or displacement modulations (amplitudes and phases for each atom in the asymmetric unit of the parent structure) associated with each independent modulation wave-vector \((\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, ...)\). The symmetry-allowed structural degrees of freedom associated with each independent modulation harmonic are determined by the resultant space group (or the super-space group if the primary modulation wave-vectors are correctly chosen) in the case of a commensurately modulated structure or by the super-space group in the case of an incommensurately modulated structure.

An additional important feature of many such modulated structures is that the amplitudes associated with each independent modulation harmonic often fall off monotonically and fairly rapidly with increasing harmonic order (provided the correct choice of the primary modulation wave-vectors is made) so that there is a natural hierarchy as regards the symmetry allowed structural degrees of freedom. It is demonstrated, via Fourier decomposition of previously reported example superstructures phases, that a modulation wave approach to such superstructures almost invariably provides a much simpler structural parameterization than conventional superstructure refinements using independent atom-based parameters and that the latter, because they fail to take advantage of this natural hierarchy, are often grossly over-parametrized.

The use of such a modulation wave approach to the structural parameterization of incommensurately modulated structures is reviewed and recent developments in the understanding of such superstructures highlighted. Using examples, the advantages and possible disadvantages with respect to a conventional superstructure approach are discussed as regards the information content of reciprocal space, the possibility of false minima in conventional superstructure refinements and the possibility of homomorphic (i.e. indistinguishable but non-identical) structure solutions.

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A composite crystal structure is a generic name for mixed layer structures, intergrowth compounds, venier structures, and chalcopyrite-ladder structures, which have mutually interpenetrating two or more substructures with incommensurate (or commensurate) period along some (one or two) directions. It has been found in minerals, organic compounds, metals, and is particular in many sulfides. Each substructure is modulated by the interaction of the others. Therefore this is a general case of modulated structures and superspace groups introduced for usual modulated structures can be applied to its symmetry (Janner, A. and Jansen, T., Acta Cryst. 1989, A 36, 408-115). Recent several structure analyses were made on the basis of the superspace symmetry (for example, Kido, K., Acta Cryst. 1980, B 36, 39-44, Smidt, E. and Price, J. Phys. Cond. Mat. 1991, 3, 1947-1261) and the efficiency of the superspace group in the structure analysis has been proved. The diffraction pattern is indexable with more than 3 vectors for example, \(h + i + 2k + 4l + 4m + n + 6r + \ldots\) is as in modulated structures but is different from that of modulated structures. In the composite crystal, there are a few sets of main reflections corresponding to several substructures (Fig. 1). The main reflections of each substructure are at the same time the satellite reflections of the other substructure. The superspace group can be expressed by a pair (or triple) of the superspace group symbols, each of which specifies the symmetry of a modulated substructure. They are not independent but equivalent to each other as higher-dimensional space groups. The symbol of a superspace group depends on the setting, in particular, the selection of the wave vector of modulation waves. If we employ the wave vector of each modulated substructure within...