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INCOMMENSURATE PHASES IN CHARGE-DENSITY WAVE SYSTEMS.
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Charge-density waves (CDW), a coupled modulation of the conduction electron density and crystal lattice, have been reported in a large number of structurally anisotropic compounds. These CDW modulations, which are in general incommensurate with the periodicity of the undistorted lattice, occur in materials encompassing a wide range of chemical and physical properties. However, in spite of this diversity, many aspects of the observed CDW phenomena are remarkably similiar. In this paper, we will attempt to highlight this through an examination of two model CDW systems: the $TaTe_4$-$NbTe_4$ system and $NbSe_3$.

Extensive experimental and theoretical investigations of $TaTe_4$ and $NbTe_4$ have demonstrated that these compounds constitute a nearly prototypical CDW system. The compounds possess a quasi-one-dimensional crystal structure in which chains of metal atoms are centered within extended cages of Te atoms in square antiprismatic coordination. The observed lattice distortions, involving mainly longitudinal motions of the metal atoms along a chain, correspond to that of the classic CDW model. In addition, the compounds exhibit the full spectrum of possible CDW-driven phase transitions: commensurate to incommensurate (C to IC), commensurate to commensurate (C to C) and incommensurate to incommensurate (IC to IC). Despite this apparent complexity, it has recently been shown that the various phases occuring among the tetrachalcogenides are rather simply interrelated with each phase representing a member of a series of long period structures. In addition, transmission electron microscopy studies have revealed the important role of microstructure, including discommensuration arrays and antiphase boundaries, in this CDW system.

The crystal structure of $NbSe_3$ is considerably more complex than that of the tetrachalcogenides and, until recently, it had not been possible to precisely determine the nature of the IC modulations. In analogy with the tetrachalcogenide system, we have developed models for the incommensurate distortions found in $NbSe_3$. The implications of the new structural models for the observed sliding of CDW under the application of an electric field will be discussed.

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A MODULATION WAVE APPROACH TO COMMENSURATELY MODULATED STRUCTURES. By
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Commensurately 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 displacive modulations thereof associated with independent modulation wave-vectors $\{mq_1 + nq_2 +...\}$(and characterized in reciprocal space by a set of sharp Bragg reflections at $G \pm \{mq_1 + nq_2 +...\}$,where $q_1,q_2,...$ represent independent primary modulation wave-vectors and m,n,.. are integers). Given knowledge of the underlying parent structure, structure determination reduces to the determination of the compositional and/or displacement modulation patterns (amplitudes and phases for each atom in the asymmetric unit of the parent structure) associated with each independent modulation wave-vector $\{mq_1 + nq_2 +...\}$. 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 superstructure 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-parameterized.

The use of such a modulation wave approach to the structural parameterization of commensurately 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 homometric (i.e. indistinguishable but non-identical) structure solutions.

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SUPERSPACE SYMMETRY OF COMPOSITE CRYSTALS. By
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A composite crystal structure is a generic name for misfit layer structures, intergrowth compounds, vernier structures, and chimney-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 in particular in many sulfides. Each substructure is modulated by the interaction to 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 Janssen, T., Acta Cryst. 1980, A 36, 408-415). Recently several structure analyses were made on the basis of the superspace symmetry (for example, Kato, K., Acta Cryst. 1990, B 46, 39-44, Smaalen, S. van, J. Phys. Cond. Mat. 1991, 3, 1247-1263) 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 $ha_1* + kb* + lc* + ma_2*$ etc.) as in modulated structures but is different from that of modulated structures. In the composite crystal, there are several 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 triplet) 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

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a*, b* and c* of the other substructure, a nonambiguous symbol is obtained (Yamamoto, A., Acta Cryst, 1992, B 48, 476-483). The symbol shows the number of substructures, the superspace group of each substructure and implies the relation of the unit axes between substructures. The superspace groups of the substructures are obtained from the diffraction pattern by the same method as in modulated structures even when the satellite reflections are not observed, because the main reflections of one substructure can be regarded as the satellite reflections of the other substructure. The equivalence relation for the superspace groups of composite crystals is however not completely solved. In an exceptional case where substructures are transformed to each other by a symmetry operator, the total symmetry may be higher than the substructure symmetry. Such a case is found in $[Hg]_x[Hg]_x[AsF_6]$, where two Hg-monoclinic substructure is related by a glide plane and the total symmetry is orthorhombic.

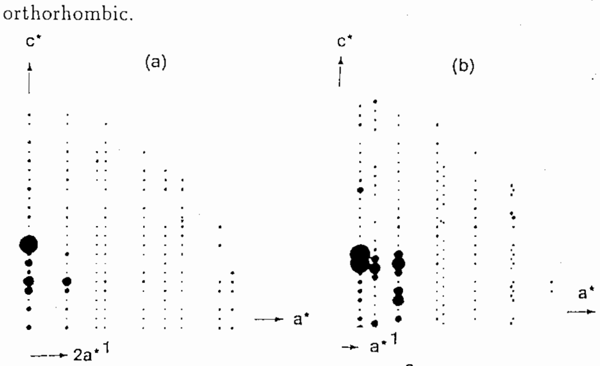

Fig. 1. Diffraction patterns of $[PbS]_x[VS_2]$ in (a) ($h0lm$) and (b) ($h1lm$) planes

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DIFFRACTION BY INCOMMENSURATE STRUCTURES IN THE SOLITON REGIME.

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Regarding a conventional diffraction experiment, the neighbourhood of a soliton regime could appear as a desirable structural state of an incommensurate (IC) phase. The main reasons being the expected increase of the primary distortion and the presence of high-order harmonics contributing to the modulation. As a result a sharpened diffraction pattern with higher-order satellites is anticipated. Consequently a deeper and more accurate structural insight could be achieved. Nevertheless the above reasoning line is based on an intuitive analysis of the structure factor formula for a sinusoidal regime. In this well-known formula a higher modulation amplitude implies more intense (predominantly first-order) satellites. On the other hand it is rather common to assume that the $n^{\underline{th}}$-order-satellite intensities are essentially governed by only the amplitude of the $n^{\underline{th}}$-order harmonic. These assumptions break when the IC structure evolves towards a soliton regime. Although it is true that the progressive stepping of the modulation functions requires the superposition of high-order harmonics, such additional harmonics must appear 'orderly' (by symmetry), not 'consecutively'. That is to say, the main distortion will be constituted by those harmonics having the same symmetry that the first harmonic present in the sinusoidal regime. Therefore, depending on the specific compound, the most intense satellites could not be the first, second, third and so on, but the sequence could be completely different. Hence in the case of Rb_2ZnCl_4 the most intense satellites should belong to the $(6m\pm1)^{\underline{th}}$ order (m integer). Furthermore the influence of harmonics on satellite intensities is not so simple as expected. As a rule, each harmonic influences (with different weights) all kind of satellites. As a consequence a higher amplitude of a determined harmonic does not signify simply a higher intensity of the corresponding (by order) satellite. In this way the intensities of some satellites will decrease as the soliton regime is approached. Eventually, new experimental difficulties could arise in the vicinity of the soliton regime On one hand the general tendency of the modulation wave vector to its lock-in value will imply a strong overlap of satellites around their commensurate positions. On the other hand kinetic processes that imply a constant-temperature variation of the solitonic structure (without any apparent crystallinity loss) have been already detected. This type of behaviour would indicate that some routinely tasks concerning data reduction of IC structures (as, for example, the internal scaling) should be revisited.

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THE MORPHOLOGY OF INCOMMENSURATELY MODULATED CRYSTALS.

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The study of the morphology is the origin of the science of Crystallography. Preceding X-ray diffraction it lead to the concept of a lattice periodic structure. The law of rational indices then states that all facets on a crystal have a face-normal vector given by three small integer indices hkl, representing a vector of the reciprocal lattice. Furthermore, it states that the morphological importance (MI) of a facet increases with decreasing length of hkl.

Several years ago it was found that incommensurately modulated crystals may show so-called incommensurate facets (1,2). That are facets which cannot be described by three small integers. As shown by Janner and coworkers (1,2), these facets can be described by four small integers, which define a reciprocal vector accoring to

$$\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$$

where $\mathbf{q}$ is the modulation wave vector.

The present contribution reports a surface free energy model, based on the Broken Bond Model. It provides a mechanism for the stabilization of incommensurate facets as due to surface pinning of the phase of the modulation wave. The stepped nature of the true surface restricts the stabilization to low-index facets. It is shown that the MI does not depend only on the length of $\mathbf{s}$, but also on the size of the modulation and the direction of the modulation wave vector. Applications to Rb_2ZnCl_4 and $AuTe_2$ are given.

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