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ELECTRON DIFFRACTION AND MICROSCOPY OF INCOMMENSURATE PHASES AND QUASI-CRYSTALS

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Abstract - We first review the application of transmission electron microscopy to incommensurate crystals drawing attention to the different techniques available. There follows a discussion of proposed differences between AlFe incommensurate and quasi-crystals introducing some new results on an AlFeCe quasi-crystal. Finally, a brief report is given of incommensurate phases recently identified in crystallized amorphous films of AlMn.

1. INTRODUCTION

Electron microscopy and diffraction have played an important role in recent studies of commensurate phases and quasi-crystals, but the complexity resulting from the strong interaction of electrons with matter can prove a barrier to the effective exploitation of the results. Several quite distinct techniques are now routinely available on modern transmission electron microscopes (TEMs): lattice imaging and satellite dark field (SDF) microscopy in real space, selected area diffraction (SAD) and convergent beam electron diffraction (CBED) in reciprocal space. We begin by reviewing the strengths and weaknesses of these techniques in studying incommensurate crystals and then examine some of the results generated by their application to quasi-crystals.

2. INCOMMENSURATE CRYSTALS

Electron diffraction from incommensurately modulated crystals tends to produce patterns with many weak satellites which tend to cluster together. The diffraction pattern frequently occurs in the form of a sub-set of strong reflections arising from the high temperature unmodulated phase decorated with weaker satellite reflections. High angular resolution is required to determine the satellite positions accurately and this is readily achieved by SAD. The resulting diffraction patterns are, at best, extremely unreliable for symmetry determination because of unavoidable averaging over thickness and angle within the illuminated area. Reliable information in SAD patterns is restricted to a plane in the reciprocal lattice perpendicular to the direction of incidence. Dynamical diffraction makes it almost impossible to decide from SAD patterns whether the modulation is by composition waves or displacement waves, of longitudinal or transverse character. Many of the limitations of SAD can be overcome by CBED. In this technique the diffraction patterns are generated with probe sizes in the range of 0.5-50nm, small enough to eliminate thickness and orientation averaging. CBED patterns are particularly effective in symmetry determination and in establishing the...
three-dimensional reciprocal lattice geometry, including the out-of-plane components of satellite vectors [1] [2]. In reality, symmetry is an ideal and in practice the question of near symmetry is a very important one in incommensurate systems. While these systems lack translational symmetry, it is always possible that an appropriately placed electron probe will detect point symmetry which can be retained. The symmetry or near-symmetry observed is closely related to the probe size, the incommensurate or discommensurate nature of the modulated state, the strength of the modulation and the presence of defects (accidents of history) in the modulated or parent structure. As an example IT VSe₂ exhibits a clear case of symmetry breaking at 80K while retaining its out-of-plane incommensurate modulation [3]. The diffraction symmetries observed in the patterns from this material are as precise as any encountered in studying high-quality unmodulated crystals. CBED patterns from other IT transition metal dichalcogenides have near-symmetry, but almost invariably contain features which break the symmetry when the patterns are subjected to rigorous scrutiny. An interesting example is provided by [0001] IT TaS₂ [4]. The diffraction patterns from the incommensurate (IT₁) state are close to 3m symmetry, those from the nearly commensurate state (IT₂) are near to 3 symmetry, those from the commensurate state (IT₃) are only approximately three-fold, while those from the incommensurate state (IT₄), formed on warming to 220K, clearly lack any symmetry. As the incommensurate phases of IT transition metal dichalcogenides have three-dimensional modulations CBED is useful in determining the out-of-plane components of the satellite vectors.

Lattice images have sometimes proved less helpful than might have been expected in distinguishing discommensurate from incommensurate modulations. Many attempts have been made to find discontinuities in the modulations of materials with charge density waves. ZnH₂Se₂, IT TaS₂, and NbSe₂ are three well-known examples of failure [5] [6] [7]. There are probably several contributing causes. The satellites in each of these cases are weak in diffraction from thin crystals although they become somewhat stronger in diffraction from thicker regions. The weakness is partly the result of the small atomic displacements and long associated extinction lengths and also contributed to by surface effects reducing the amplitude of the modulation. Interpretable lattice images need to be obtained from thin crystals, less than 20-30 nm in thickness [8]. The images obtained from the materials mentioned above showed such weak modulation that no departure from sinusoidal character could be detected. In contrast, modulated alloys have been successfully studied by lattice imaging. Here the sharp discontinuities associated with anti-phase boundaries can be detected easily in thin specimens [9]. In addition, fine probe CBED has been used to investigate local symmetries and discontinuities [10].

Satellite dark field electron microscopy is a relatively low magnification technique which is very useful for revealing inhomogeneities and discontinuities in a modulated state. It is particularly effective in the case of second order or near-second order phase changes when temperature dependent changes can be observed. It is also useful for studying the relative perfection of different samples and in following the dynamics of phase transitions. The interpretation of the images produced is not straight-forward in general. Even for a given choice of satellite, the images can change considerably with orientation, as dynamical couplings to the satellite change. However, in spite of these difficulties a reliable interpretation has been possible in some cases [11].

A new development which offers exciting prospects for future development arose out of the application of CBED to NiGeP, a modulated NiAs structure. Wide angle electron diffraction patterns (the Tanaka method) have made it possible to distinguish how intensity gets to each nearby satellite reflection in a cluster. Multiple diffraction routes are revealed as either systematic or cross-grating in character, compositional waves can be distinguished from displacive waves, longitudinal waves from transverse. In this particular case it was not only possible to show that the modulation was chiefly displacive, but also to deduce the phonon mode which softened and the nature of the atomic displacements from their ideal NiAs positions [7].

In nearly all the cases reviewed so far it was possible to distinguish sub-lattice from satellite reflections. Moreover the point symmetry was less than, or the same as, that of the parent structure. These two situations no longer persist when we consider the diffraction from quasi-crystals.
3. QUASI-CRYSTALS

It seems reasonable to suppose that the techniques found useful for examining incommensurate structures will also be of value in studying quasi-crystals. SAD has been widely used for examining icosaheiral phases over an ever increasing range of elements and compositions. Lattice imaging has generated a number of beautiful electron micrographs. However, it should not be forgotten that SAD is not an effective method of determining point symmetry and that lattice images of quasi-crystals can be expected to be very hard to interpret. In fact, the most rigorous electron diffraction calculations yet performed [12], indicate that, contrary to some expectations, lattice images are not very effective in deciding the atom locations in the AlMn icosahedral phase.

CBED results from AlMn and other icosaheiral phases have been most disappointing. The patterns generally not only lack five-fold symmetry, but also any evidence of three-dimensional diffraction. SDF images show considerable inhomogeneity of microstructure. The lack of three-dimensional diffraction is a clear indication of gross disorder in the quasi-crystals, as is also the structure of the SDF images and the rapid variation of CBED patterns when the probe is moved small distances. It has been argued [13] that lattice images lack dislocations, but of course the defects may be of a more subtle nature, like anti-phase boundaries or charge density wave dislocations in incommensurate 2HTaSe_2 [11]. Until we know the basic structure of an icosahedral phase, it will be hard to identify defects in it. On the other hand, highly defective quasi-crystals could easily defeat our efforts at determining the atomic positions. The single exception is provided by the recent results on an icosahedral phase of AlSiMn [14]. CBED patterns from this material show reasonable five-fold symmetry with mirror lines every 36° and three-dimensional diffraction. The SDF images are also relatively homogeneous and the SAD patterns contain a considerable number of additional weak reflections. The SAD pattern from the five-fold axis of this material is illustrated together with the equivalent pattern obtained from the wide range of other icosahedral phases in Fig. 1. Some caution should be exercised in referring to this figure, as most authors have failed to indicate the angular scale in publishing their diffraction results. We have therefore scaled the available results on the basis of comparable relative spot intensities in constructing the figure. The high quality of the AlSiMn results encourages a serious attempt at atom location for this particular icosahedral phase.

Another example of a quasi-crystal is provided by the uniaxial (planar) phase reported by Bendersky [15] for the AlMn system and called by him the decagonal phase. A very similar phase has just been reported by Fung and co-workers in the AlFe system, and we report yet another here for the AlFeCe system. The unique axis of these crystals produces SAD or CBED patterns which are related and somewhat different from the five-fold pattern of the icosahedral phases. The three patterns are compared with the two equivalent icosahedral patterns in Fig. 1. None of so-called decagonal crystals appear to be of sufficient quality to deduce their
symmetry with any degree of certainty, although they appear to be ten-fold with mirrors every 18°. The planar nature of these phases leads to reasonable order along the unique axis. Even if each layer plane has ideal 10mm symmetry, the symmetry of the crystals as a whole depends on the phasing of the planes with respect to each other.

Typical CBED patterns from the AlFeCe phase are shown in Fig. 2 and lattice images are shown in Fig. 3. The approximate composition of the phase is AlFeCe. The CBED patterns in Fig. 2 show reasonable 10mm symmetry, but cannot be regarded as very reliable. The particle from which the pattern was obtained was very small (Fig. 3a) and embedded in a crystalline matrix. The crystalline matrix accounts for the discrete reflections superimposed on the large angle CBED in Fig. 2b. In this case the particle was apparently homogeneous. Other particles were less homogeneous, with a central region like that in Fig. 3a, but becoming more regularly crystalline at the periphery with angular facets. An extreme example is illustrated in Fig. 3b, which shows a particle composed of ten reasonably crystalline segments. It would be interesting to pursue the relationship between the crystalline forms of the AlFeCe phase diagram in the vicinity of this composition in seeking an explanation for the quasi-crystalline interior. Unfortunately it appears that the relevant part of the phase diagram has not yet been explored.

Fig. 2a (above): CBED pattern taken with a small convergence angle to illustrate the zero layer diffraction from a decagonal AlFeCe phase.

Fig. 2b (upper right): Large angular view of CBED at the ten-fold axis of AlFeCe showing many HOLZ rings.

Fig. 3a (right): High resolution image of a small decagonal AlFeCe particle embedded in the matrix.
In a related discovery Ishimasa et al. [16] have reported a uniaxial quasi-crystal with 12-fold symmetry in the NiCr system. This particle has a morphology very similar to that illustrated in Fig. 3a for AlFeCe phases, except that there are twelve facets at the periphery, each associated with a phase in a different twin orientation. In fact, a previously unreported and highly defective hexagonal Frank-Kasper phase (F phase) has recently been discovered [17] [18] which is closely related to these observations. Anti-phase boundaries (discommensurations) in this material can occur in several different orientations (Fig. 4). If the anti-phase boundaries are regularly spaced, they generate o-phase (Fig. 5) and different orientations of antiphase boundaries generate twin related regions of o-phase. The distinction between quasi-crystals, incommensurate phases and twins is not clear in this case. A similar situation might be responsible for the observations just reported for the apparently 10-fold AlFeCe phase.

Some have sought to forge a distinction between quasi-crystals and incommensurate crystals with the argument that the incommensurate length scales are locked at particular ratios in quasi-crystals, but are continuous functions of external parameters such as temperature or composition of the incommensurate crystal, [13] and Steinhardt (unpublished). In fact, few incommensurate crystals of charge density wave origin obey this distinction, the length scales being fixed, independent of temperature. On the other hand it may be that the length scales are not fixed in the quasi-crystals. There are several pieces of evidence which lead to this conclusion. First there is the evidence presented above. In addition careful high resolution SAD experiments (Tanaka et al, to be published) reveal that the AlMn pattern is not composed of discrete sharp spots but that each apparent spot can be resolved into a cluster of closely spaced satellites. In addition, recent work in Bristol on crystallised AlMn films has revealed incommensurate structures, described in the final section.
4. CRYSTALLISATION OF AMORPHOUS AlMn FOILS

Amorphous AlMn films with composition about that of the icosahedral phase were grown by evaporation onto a liquid N$_2$-cooled substrate. When these electron-transparent films were heated to 350°C, we have observed the nucleation and growth of several related incommensurate phases with unknown structures (Fig. 6), which will be described in detail elsewhere. A preliminary identification of the first phase (I) was based on measurement of SAD patterns taken parallel to a prominent zone axis close to the film normal (Fig. 7a).

The reflections were labelled with hko indices (h+k even) and differed by only a few percent from the [001] zone axis pattern expected for the C-centred orthorhombic cell of MnAl$_6$ (see Table). Also, the hko intensities were at least qualitatively consistent with a structure assembled by stacking the pentagonal atomic nets common to MnAl$_6$ and other related phases [19]. These conclusions were modified when the geometry of higher-order Laue zone (HOLZ) reflections in [001] CBED patterns was examined (Fig. 7b). Although the spacing of reciprocal lattice planes measured from HOLZ ring diameters was apparently consistent with the MnAl$_6$ structure, reflections in the first HOLZ ring were displaced relative to the zero layer, split into pairs, streaked and also showed a clear minimum of intensity normal to the displacement vector. By comparison, reflections in the second HOLZ
ring were not split and projected directly onto the hkO reflections in the zero layer.

Subsequent tilting experiments demonstrated that the recrystallised film contained a fine-scale domain structure defined by two alternative four-fold stars of q-vectors directed out of the layer plane. The geometry in reciprocal space of the subcell reflections and of the associated q-vectors within a single domain is sketched in Fig. 8, where an equivalent set of reflections for MnAl₆ is included for comparison. A formal description of the subcell was given by a set of nominally monoclinic (pseudo-orthorhombic) basis vectors \( a_m, b_m, \) and \( c_m \) \((\theta=10^\circ)\), which were chosen to be consistent with the reduced symmetry of the four-fold star of q and the consequent domain structure. In terms of the equivalent pseudo-orthorhombic lattice vectors \( a, b \) & \( c \), as listed in the Table, we have \( a_m=(b+a)/2, \)

\( c_m=(b+a)/2 \) and \( b_m=c \), for the two domain orientations.

The reciprocal lattice of a monoclinic subcell was decorated by a four-fold star of q-vectors chosen to lie in the \( a^*_m, b^*_m \) plane, perpendicular to \( c^*_m \). The precise magnitude and direction of q was not well defined (see Fig. 9), but was always close to the commensurate positions \( \pm (a^*_m+\pm b^*_m)/2 \). Direct evidence, not only for the displacive character of q, but also the direction of atomic displacements, was given by the azimuthal intensity distribution within the first HOLZ ring in Fig. 6b, which contained only incommensurate reflections from a single domain. The dashed line represents the projected direction of the q-star plane. The reduced intensity of HOLZ reflections in radial directions normal to this line in the first (but not in the second) HOLZ ring was interpreted as evidence of a principally longitudinal character for the displacements associated with q.

The domains were imaged by tilting the film about the [010] (orthorhombic) axis, so that incommensurate reflections in the reciprocal lattice plane defined by the two dashed lines in Fig. 8 were excited. The SAD pattern for this axis is shown in Fig. 9, where the subcell reflections were common to both domains, and the incommensurate reflections were separated into distinct sets. The corresponding dark-field images are shown in Fig. 10, where the film was tilted slightly to improve the contrast.

We have no direct proof for the atomic structure within the subcell, but the dimensions were consistent with the simplest possible stacking of centred pentagonal nets described by Pearson [19] for CoAl and FeAl₆, equivalent to continuous columns of interpenetrating icosahedra parallel to the orthorhombic c-axis. In MnAl₆, these icosahedra are arranged in a more complex arrangement of stepped rows [20], which may be less accessible to atoms in a thin film recrystallised at the lowest possible temperature.

Fig. 6: Micrograph of partially recrystallised Mn-Al film showing dendritic growth of large grains into the amorphous areas.
Table: Comparison of lattice parameters (Å) for the subcells of the MnAl phase with some other orthorhombic cells with related lattice ratios. Figures listed for phase I are based on a limited sample, and may be subject to some revision.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>a/b</th>
<th>Reference</th>
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<td>Phase I</td>
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<td>4.18</td>
<td>1.21</td>
<td>This work</td>
</tr>
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<td>6.50</td>
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<td>[21]</td>
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<td>C</td>
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<td>6.40</td>
<td>4.20</td>
<td>1.20</td>
<td>[22]</td>
</tr>
</tbody>
</table>

Fig. 7: Diffraction patterns from [001] axis of Mn-Al Phase I. (a) SAD pattern showing characteristic intensity distribution, and (b) CBED pattern from a single domain showing absence of intensity normal to the plane of q-star (dashed line) in the first HOLZ ring.
Fig. 8: Reciprocal lattice for Phase I, indexed for the pseudo-orthorhombic cell. One cluster of incommensurate reflections and the monoclinic basis vectors are included in the diagram. The squares represent MnAl₆ reflections not observed here.

![Reciprocal lattice diagram](image)

Fig. 9: SAD pattern from Phase I, normal to the reciprocal lattice plane defined by the dashed lines in Fig. 8, where subcell reflections are labelled with orthorhombic indices. The two alternative monoclinic repeat units, including incommensurate reflections, are outlined above.

![SAD pattern image](image)

Fig. 10: Dark-field micrographs from the two clusters of incommensurate reflections circled in Fig. 9, demonstrating that some Mn-Al grains contained two distinct sets of domains.

![Dark-field micrographs](image)
Finally, we note here that both the axial ratio and also the atomic positions at the vertices of distorted pentagons forming the primary layers in MnAl₆, CeAl₂, Fe₂Al₃, WAl₄ and Mn₄Al₆ [19] are reproduced almost exactly (to within 0.1Å) by decoration at golden ratio positions within a rhombic motif (one obtuse plus two acute rhomb with edges equal to 4.0Å for MnAl₆) extracted from the 2-D Penrose tiling (Fig. 11). Similar coincidences linked to hyperspace projections have been described by Yang and Kuo (to be published) for some Frank-Kasper phases where the pentagonal anti-prisms share both edges and faces, and also by Henley [23] for other Al-transition metal phases.

Fig. 11: Mapping of Al atoms (open circles) onto golden ratio positions within three Penrose tiling rhombs. The dotted lines outline the primitive cell.

References