ELECTRON MICROSCOPY OF QUASI-CRYSTALS AND RELATED STRUCTURES

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ABSTRACT

Systematic electron microscopy of quasi crystals in an Al-14 at % Mn alloy has been carried out. High resolution imaging reveals fringes with spacings in the ratio of $1:\tau$. Besides 5-3-2 symmetry axes, other important zones of electron diffraction patterns are experimentally determined and compared with those generated by Landau generation technique and by projection technique. It has been shown that the 'T' phase, which often co-exists with quasicrystal, is closely related to it and can be treated as a two dimensional quasiperiodic crystal stacked periodically along an icosahedral vector of a true quasi crystal. Our results indicate that it is possible to have a general frame work of quasi periodic incommensurate modulation in three, two and one dimensions. The quasi crystal, the 'T' phase and vacancy ordered τ phases are the respective real life examples of such modulations.

INTRODUCTION

THE rapid solidification of alloys has been providing a stimulus to materials scientists the world over during the past quarter century. The latest, and probably the most exciting discovery so far, is the formation of a quasi-crystal from a melt of Al-14 % Mn under conditions of rapid solidification[1]. These quasi-crystals exhibit the crystallographically forbidden five-fold symmetry and have become the subject of feverish investigations. Following the original discovery, Ramachandrarao and Sastry[2] have used elegant principles of alloy design to synthesize the quasicrystal in a ternary Mg-Zn-Al alloy. For reviews on quasicrystals, the articles by Ramaseshan[3] and Nelson and Halperin[4] may be consulted.

As quasi-crystals, unlike glasses, give rise to discrete diffraction patterns, transmission electron microscopy (TEM) becomes an effective technique for their characterisation. We have carried out extensive TEM investigations on the nature of quasicrystals and related structures[5-7]. The present article summarises the results obtained by us so far. All the results discussed here pertain to Al[-14 at %]Mn alloy made from ultrahigh purity constituent elements. For rapid solidification, the twin roller technique was adopted[8] by us. For aluminium alloys, the cooling rate achievable is of the order of 10^5 to 10^6 Ks^{-1}.

ELECTRON MICROSCOPY

The rapidly solidified foils contain primarily the quasicrystals, embedded in an aluminium matrix. Twin roll quenching led to a markedly facetted morphology (figure 1). Diffraction experiments showed that many of them had a similar orientation, indicating a notable amount of texture. Previous investigators[1] had reported a nodular appearance for quasicrystals. The morphological and textural aspects are under a more detailed study.

High resolution electron micrographs have been obtained by combining diffraction spots seen in 5-fold and 2-fold symmetry positions[5]. Figure 2(a) shows the micrograph and the associated diffraction pattern. The fringe spacings
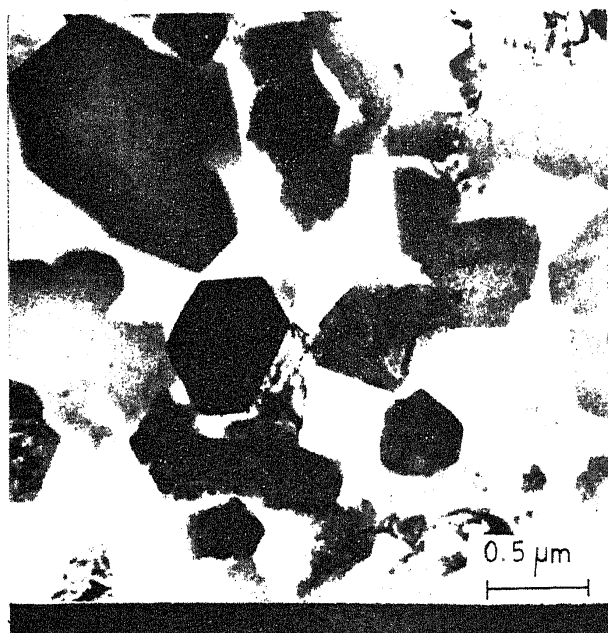
Figure 1. Transmission electron micrograph of rapidly solidified Al-14% Mn alloy showing quasicrystals with a facetted morphology.

are seen to alternate quasiperiodically in 1: τ fashion, where τ is the golden mean and equal to $(1 + \sqrt{5})/2$. This feature has been independently confirmed by Bursill and Lin[9]. Figure 2(a) may be compared with the Penrose pattern (figure 2(b)) generated by Duneau and Katz[10] for this structure.

The TEM observation of α-Al matrix and quasicrystals was confirmed by the x-ray diffraction patterns. The lines showed close agreement with those reported by Bancel et al[11]. No other phase was detected in the quenched foils.
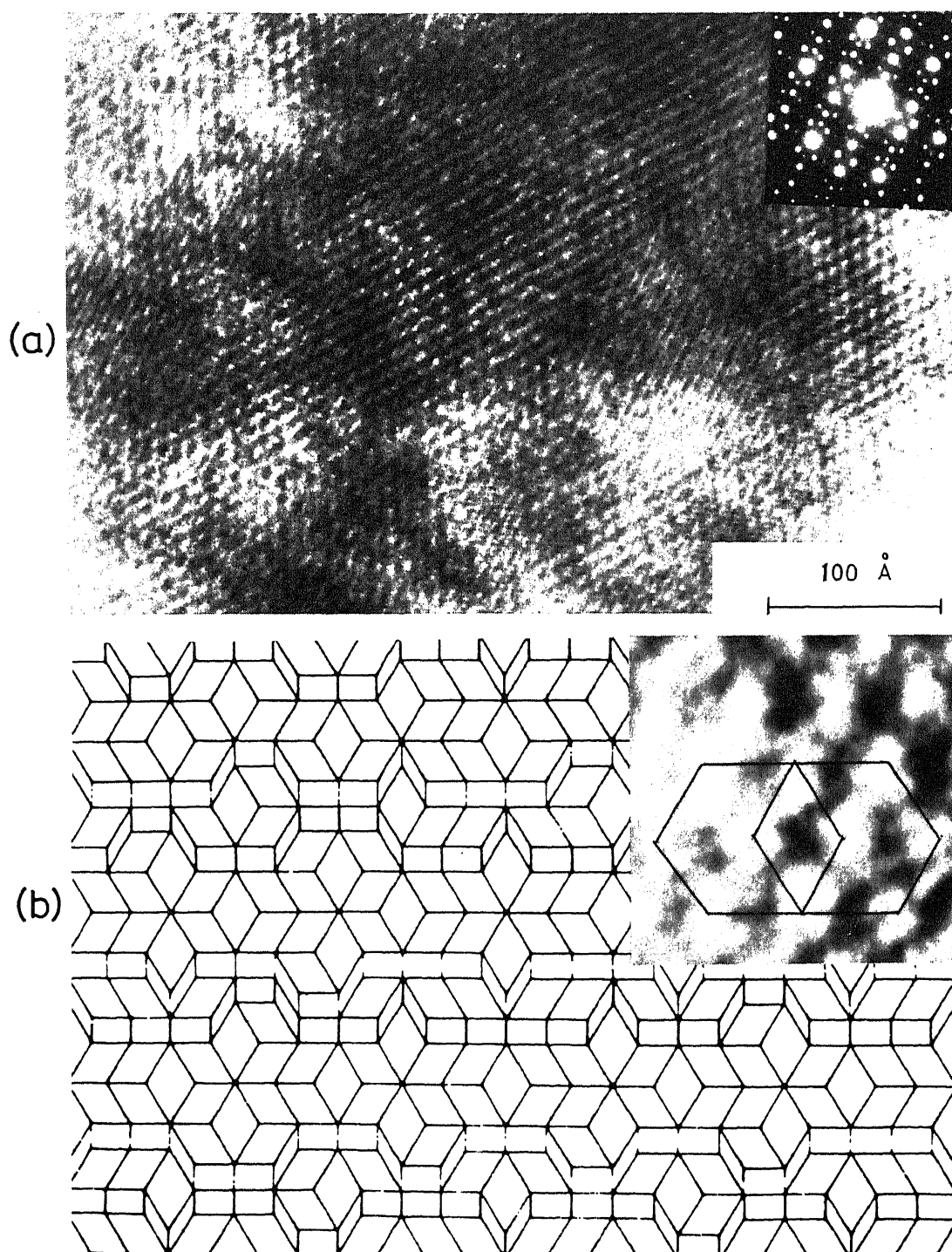
ELECTRON DIFFRACTION

The electron diffraction patterns from these crystals reveal the typical 5-3-2 symmetry[1]. However, we observed additional patterns. This led us to carry out a systematic investigation to identify all the relatively important zone axes possible in a quasicrystal. The most important relrods observed in quasicrystal diffraction patterns correspond to 5, 3, 2 symmetry vectors. Combination of these relrods leads to six possible zones which include the 5-3-2 symmetry zone axes. Additional zones in the decreasing order of importance can be obtained by the combination

of at least one of the above relrods with other reflections. Figure 3 gives the observed patterns, arranged in the unit stereographic triangle. Additional patterns may be seen in an earlier paper[6].

Nelson and Sachdev[12] have shown that all the reciprocal vectors can sequentially be generated by combining the six star vectors pointing to the vertices from the centre of the icosahedron. Qualitatively as the Landau generation increases, the intensities are expected to decrease.

Elser[13] has offered a more elegant solution to the calculation of intensities and spacings in the reciprocal space by projecting from the reciprocal space of a six dimensional periodic cubic crystal along the six vertices of the icosahedron. Duneau and Katz[10] have independently derived a similar methodology. The projections along the axes give the spacings, while the perpendicular component yields a measure of the intensity. The most intense reflections according to this formalism are those joining the centre of the icosahedron to the vertices, faces and edges. In the Cartesian scheme, the vectors pointing to the vertices are $[\pm 1, \pm \tau, 0]$, $[\pm \tau, 0, \pm 1]$ and $[0, \pm 1, \pm \tau]$. The vectors pointing to the edge and face centres are of the type $[1, 0, 0]$ and $[-\tau^2, 1, 0]$.

Figure 4 gives the computed patterns obtained by the Landau generation technique and ought to be compared with the experimental patterns of figure 3. While the intensity as well as the spacing matches well for the early generations, there is a curious reversal of intensity in the satellite row of spots flanking the icosahedral vector, as, for example, in the pattern corresponding to $[\bar{1}, 3\tau + 1, \tau]$ zone axis. Figure 5 gives a completely indexed theoretical pattern for this zone generated by Elser's formalism. Here again, the outer satellite row flanking the icosahedral vector ($\bar{1}\bar{2}\bar{1}$ 1 1 $\bar{1}$) is brighter than the inner satellite row. The generation scheme and Elser's formalism are for an essentially monatomic quasicrystal and thus ignore the effect of compositional ordering. They also do not take into account dynamical diffraction effects. The importance of these factors is underlined by the fact that for the ternary Mg-Zn-Al alloy, (see figure 3a of the paper by Ramachandrarao and Sastry[2]) the intensities of

Figure 2. a) High resolution transmission electron micrograph from a 2-fold symmetry pattern. b) Corresponding real space picture after Duneau and Katz[10].

the satellite rows agrees with predicted values.

Other notable features of diffraction were studied and reported by us[6]. As the reciprocal space is densely filled with Bragg spots, an infinite number of patterns can be obtained. However, the intensities follow a hierarchical order and

instrumental resolution will limit the number of patterns that can be observed. For example Elser[13] has identified 23 different types of spots as significant. We find that there are about 15 different relplanes, which are significant within the current resolution of our microscopes.
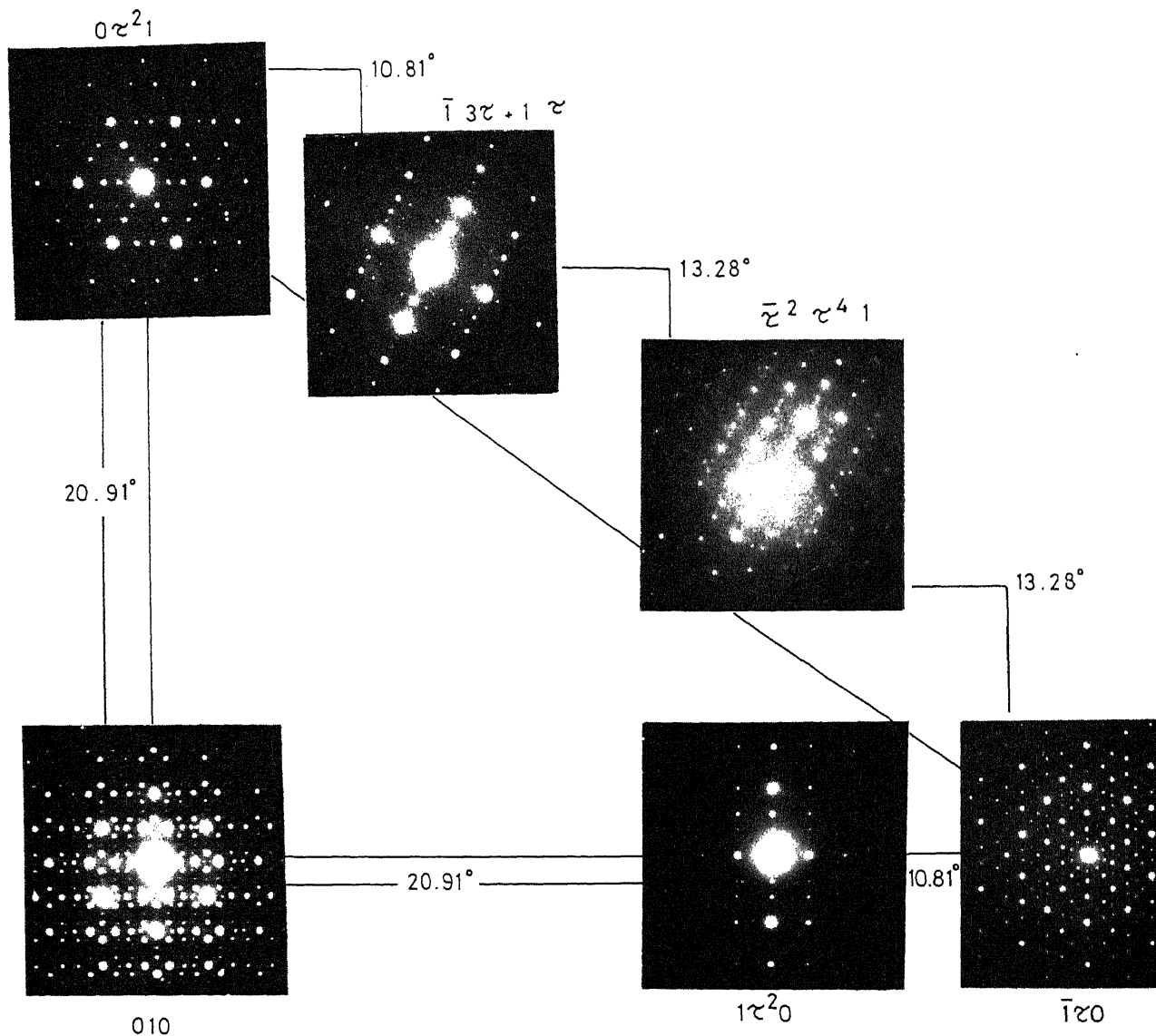
Figure 3. Diffraction patterns corresponding to $[010]$, $[\bar{1}\tau^2 0]$, $[\bar{1}\tau 0]$, $[\tau^2, \tau^4, 1]$, $[1, 3\tau + 1, \tau]$ and $[0\tau^2 1]$ z

Careful observation reveals that zone axes are arranged in an enantimorphous fashion around $[\bar{1}\,10]$ type zone axis. Thus the five fold pattern $[\bar{1}\tau\,0]$ has a counterpart in $[\bar{1}, 3\tau + 1, \tau]$ and the three fold pattern has a counterpart in $[\bar{1}\,\tau^2 0]$.

Inflation and deflation, first discovered for Penrose tilings by Conway [14] and stressed by Elser[13], play an important role in real and reciprocal space of quasicrystals. The sequence of patterns can be continued further based on inflation or deflation by τ or τ^3.

STUDIES ON THE T-PHASE

Together with the quasi-crystals, one often

observes in rapidly solidified Al-Mn foils, p which yield a set of characteristic diffra patterns beguilingly similar to those from q crystals. In an early study, predating the covery of quasicrystals, Shechtman *et al*[1] tained a pattern from a phase which they te as an unknown T-phase in a dilute Al-Mn Subsequently we obtained a similar pattern Al-14 % Mn alloy and observed that this pa showed periodicity in one direction and periodicity in other directions[5]. It is pertin note that patterns similar to those observ Shechtman *et al*[15] and by us[5] have been rep much earlier by Sastry *et al*[16] in an Al-6 alloy and an $Al_{60}Mn_{11}Ni_4$ alloy. In part
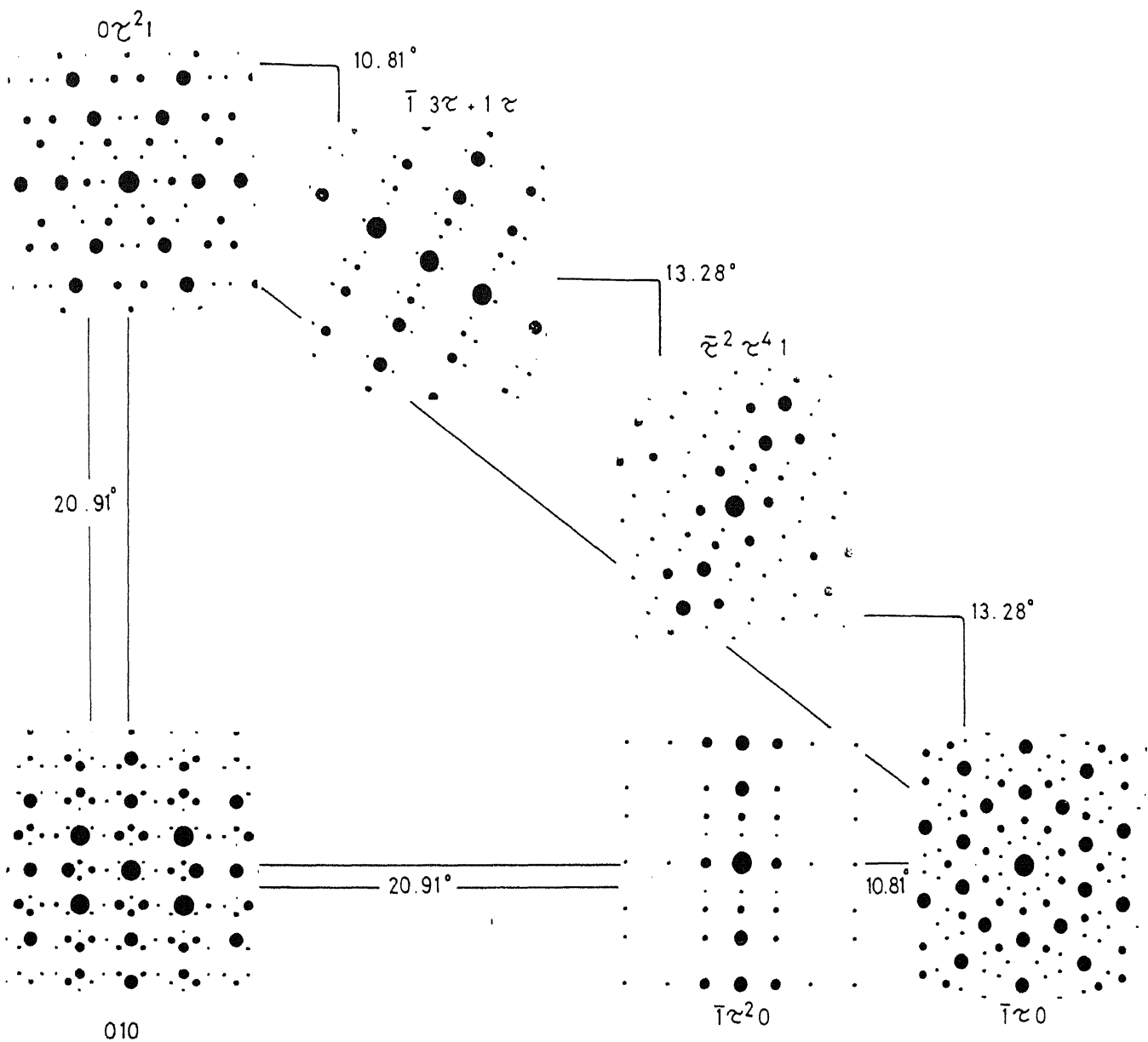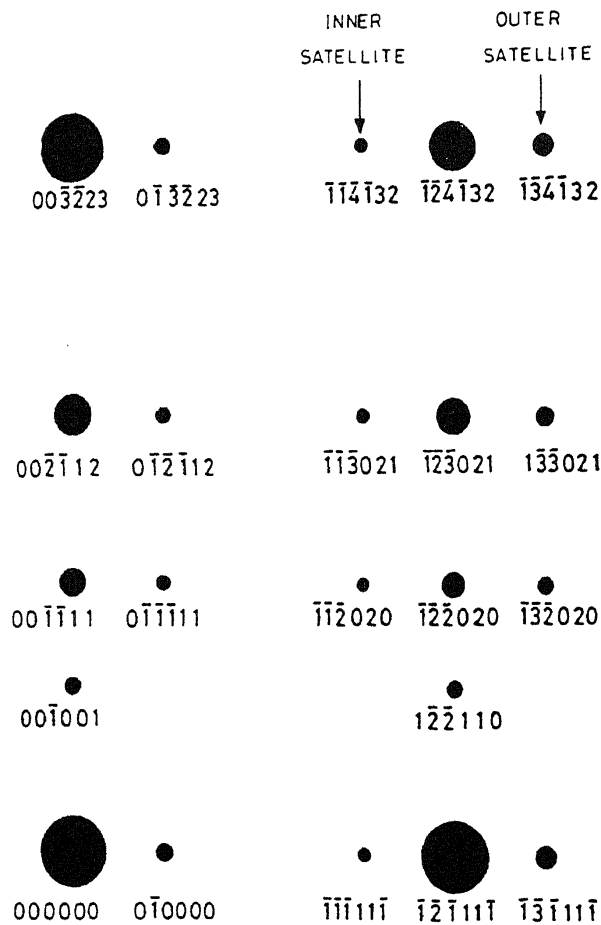
Figure 4. Computed diffraction patterns corresponding to the zones of figure 3: $[010]$, $[\bar{1}\tau^{2}0]$, $[\bar{1}\tau 0]$, $[\bar{\tau}^{2}, \tau^{4}, 1]$, $[\bar{1}, 3\tau + 1, \tau]$ and $[0\tau^{2}1]$ zones.

Sastry *et al* observed a pseudo-pentagonal symmetry in another orientation of the same phase and came tantalizingly close to the discovery of quasicrystals.

We have observed this T-phase in both as quenched foils as well as heat treated foils. In the latter the T-phase is seen to occur along with the equilibrium Al_6Mn phase and has a plate-like morphology. We have carried out a systematic investigation to elucidate the nature of this phase. Our results indicate T-phase to be closely related to the quasicrystals. Figure 6 gives the diffraction patterns for T-phase along with the angular

relationships. This must be compared with figure 3. The notable feature of the T-phase patterns is uniform streaking corresponding to the trace of one of the planes representing the five fold symmetry in the quasicrystal. While the relation of the 3-fold and 5-fold symmetry patterns of the quasicrystal to the corresponding streaked ones of the T-phase is obvious, the most interesting is the not-so-evident relation between the 2-fold pattern of the quasicrystal and its counterpart. A detailed analysis has been presented by us elsewhere[7]. This revealed that the T-phase can be treated as two dimensional quasi-periodic planes

INNER SATELLITE OUTER SATELLITE

003$\bar{2}\bar{2}$23 0$\bar{1}$3$\bar{2}$23 $\bar{1}\bar{1}\bar{4}\bar{1}$32 $\bar{1}\bar{2}\bar{4}\bar{1}$32 $\bar{1}\bar{3}\bar{4}\bar{1}$32

002$\bar{1}$12 0$\bar{1}\bar{2}\bar{1}$12 $\bar{1}\bar{1}$3021 $\bar{1}\bar{2}$3021 1$\bar{3}\bar{3}$021

00$\bar{1}\bar{1}$11 0$\bar{1}\bar{1}\bar{1}$11 $\bar{1}\bar{1}$2020 $\bar{1}\bar{2}\bar{2}$020 1$\bar{3}\bar{2}$020

00$\bar{1}$001 1$\bar{2}\bar{2}$110

000000 0$\bar{1}$0000 $\bar{1}\bar{1}\bar{1}$11$\bar{1}$ $\bar{1}\bar{2}\bar{1}$11$\bar{1}$ $\bar{1}\bar{3}\bar{1}$11$\bar{1}$

Figure 5. Diffraction pattern from [$\bar{1}$, $3\tau + 1$, τ] axis indexed on the six vector basis. Compare with the corresponding patterns in figure 4 and figure 5. The diameter of the spots are proportional to the calculated intensity.

stacked in a periodic fashion along one of the icosahedral vertex direction of the quasicrystal. In the derivative of the 2-fold pattern in the T-phase, this vector is divided into six parts (In the Al-Pd study of Sastry et al[16], this vector is divided into eight parts). All the observed diffraction patterns are consistent and support this conclusion. In addition, the diffraction patterns contain streaks of Bragg intensity. The analysis of these intensities indicates the existence of cylindrically shaped diffracting regions oriented along the stacking directions. These planes contain circular regions which can coherently diffract, separated by a relatively disordered region. A diffraction pattern with electron beam direction along the icosahedral vector normal to these planes will generate a perfect five fold pattern

with broadened Bragg peaks. The limitations or rotation available with the goniometer stage prevented us from obtaining evidence for this from a single T-phase. However, from another T-phase, we obtained this pattern (figure 7) lending strong support to our reasoning.

As the T-phase differs from the quasicrystal only in having developed strict periodicity in one direction, diffraction patterns and images from one can often be mistaken to arise from the other. Thus figure 3a in Ramachandra Rao and Sastry[2] is almost certainly from a T-phase derivative of the 2-fold symmetry pattern of a quasicrystal and again figure 5 in Portier et al[17] probably arises from a T-phase rather than a quasicrystal.

An electron micrograph from T-phase is shown in figure 8, revealing the periodic stacking along the icosahedral vertex vector direction.

THE NATURE OF QUASI-CRYSTALS

The literature features intense discussion about the nature of quasicrystals. An early proposal that the diffraction patterns can be explained on the basis of microtwinning[18] has not been supported by later investigations including ours[1-7]. An attractive possibility is that they represent a new class of solids exhibiting quasi-periodic icosahedral order – a point of view advanced by Levine and Steinhardt[19] and supported by Shechtman et al[20] on the basis of electron microscopic observations. A third proposal that merits attention is that of Bak[21]. He has persuasively advocated that they may be seen as a natural extension of "Smectic, rod like and cubic crystal structure". Thus the quasicrystals can be regarded as a special class of incommensurate phases. The distinction between these two proposals is subtle[20].

Our analysis inclines us to the view that quasicrystals can be treated as three dimensionally incommensurate phases with spacings and composition modulation following a Fibonacci sequence. If we extend this argument and look for incommensurate modulations in two and one dimensions, the description of the T-phase as revealed by our diffraction experiments places it
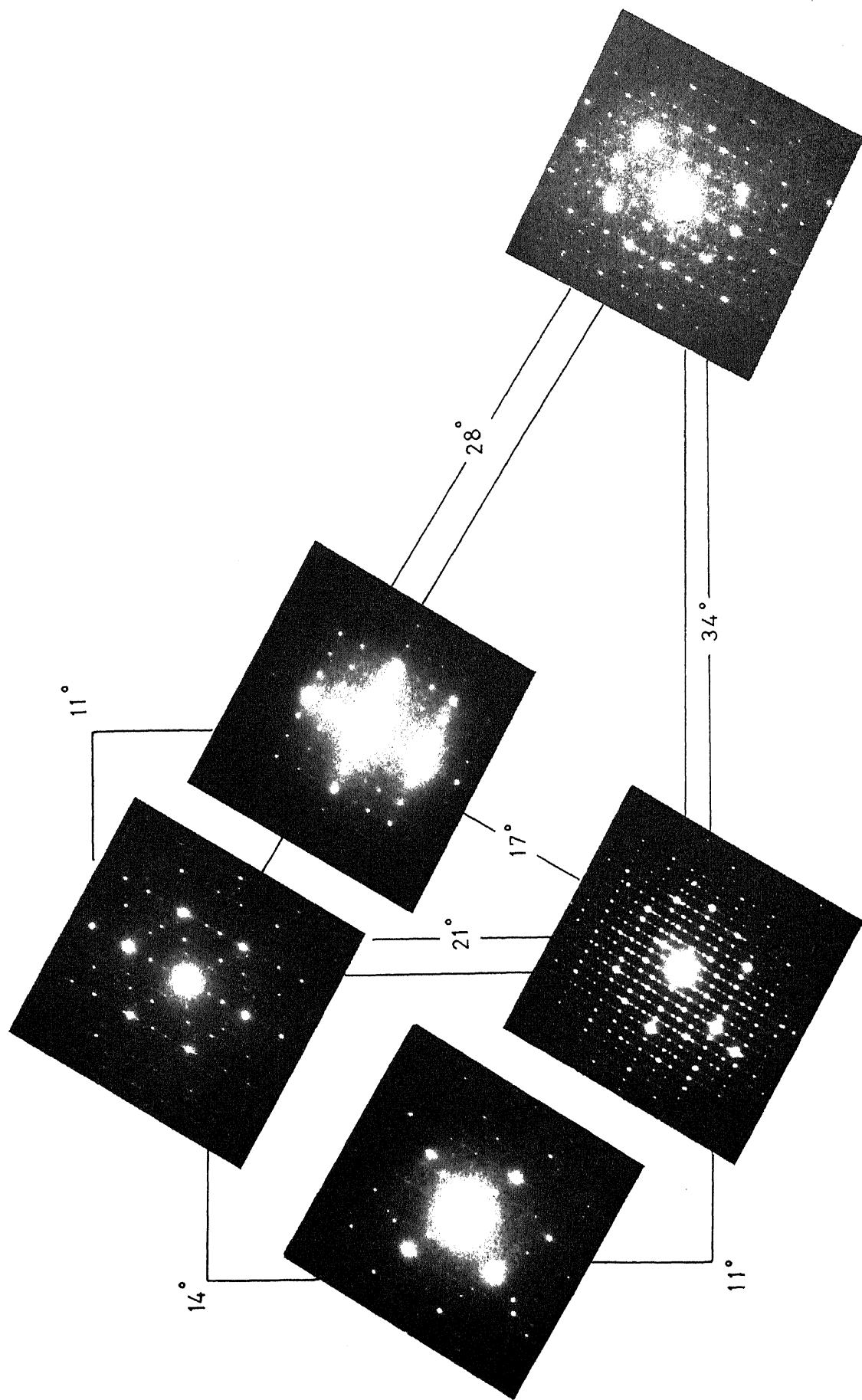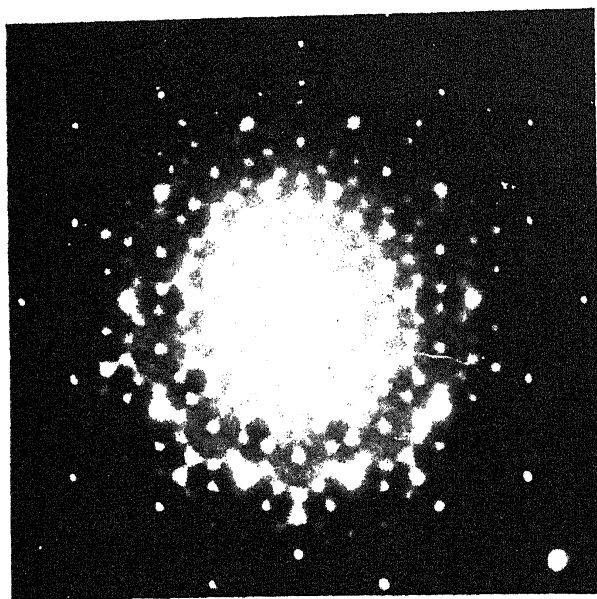
Figure 6. Diffraction patterns from T-phase arranged with appropriate angular relationships.
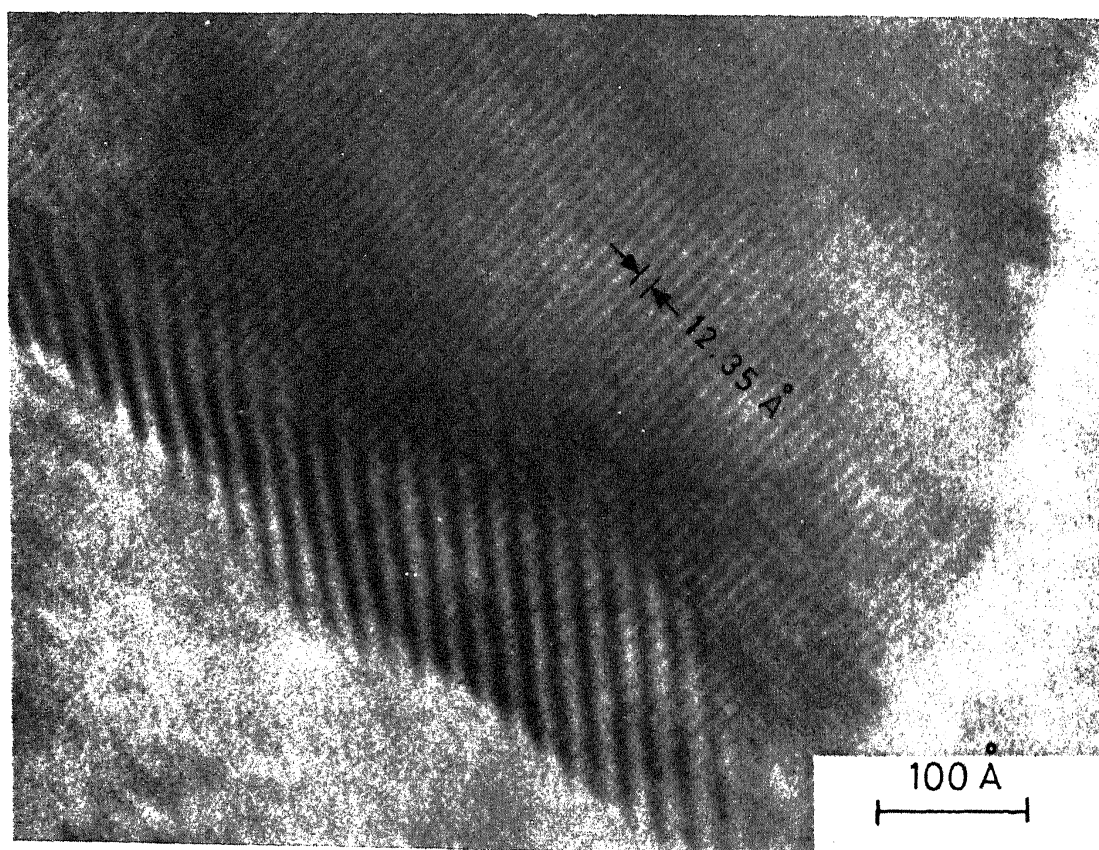
Figure 7. Diffraction pattern from T-phase indicating a possible unique five-fold symmetry.

in the category of a two dimensionally incommensurate phase. The vacancy ordered phases which occur in Al alloys appear to be an example of one dimensional incommensurate phase. In

particular the patterns observed by Sastry *et al*[22] in Al-Pd and by van Sande *et al*[23] in Al-Cu-Ni alloy have been interpreted as periodic phases where the stacking sequences have been labelled as τ_3, τ_5, τ_8 and τ_{13}. We noted that these numbers follow the Fibonacci sequence and indeed the spacing and intensity variation of the reported τ_{13} phase bear a startling similarity to a one dimensional quasi-periodic phase. This has been treated by us in detail elsewhere[7].

The quasiperiodic structures are best understood as regular structures in higher dimensions. As remarked earlier, a quasicrystal is a projection from a simple cubic crystal in six dimensions. Projection from a regular structure from five dimensions leads to the T-phase, while projection from four dimensions can allow us to analyse one dimensionally modulated vacancy ordered phases. Further experiments are required whether the description of quasicrystals requires concepts additional to those required in dealing with incommensurate phases.

It appears appropriate to conclude this article

Figure 8. HREM of T-phase.