

Discommensurate Microstructures in Phason-Strained Octagonal Quasicrystal Phases of Mo-Cr-Ni

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Phason-strained octagonal quasicrystal phases of Mo-Cr-Ni have been studied by electron diffraction and dark-field imaging. Diffraction patterns of the twofold axes show that some spots are shifted and split along the fourfold axis. Discommensurations (DCs) observed in dark-field images of the split reflections are aligned perpendicular to the fourfold axis. The density of the DCs in widely separated and adjacent regions may vary by more than 1 order of magnitude. Our observations are consistent with some of the results of the two-dimensional octagonal random tiling model of Li, Park, and Widom.

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In the discovery of icosahedral quasicrystals by Shechtman *et al.* in a transmission electron microscope, dark-field images from the same grain were taken in order to dismiss the multiple-twin interpretation of the fivefold symmetrical diffraction pattern [1]. Typically, a dark-field image shows speckles in a uniform background. It was later noted that some of the quasicrystalline diffraction patterns were distorted. The shift and the broadening of the diffraction spots in the distorted diffraction patterns have been interpreted as the manifestation of phason strain in the quasicrystals [2]. Recently, in the study of a Mn-Si-Al octagonal quasicrystal with apparently undistorted diffraction patterns, domains and discommensurations (DCs) [3], or domain walls, have been directly observed by transmission electron microscopy in the dark-field images of certain reflections [4]. By analogy with incommensurate crystals [5] the diffraction spots are separated into basic and satellite reflections on the basis of the invisibility and visibility of domains and DCs. The domains and DCs have been interpreted as due to the ordering of Si and Al atoms in the quasilattice of the quasicrystal. In previous studies of the octagonal quasicrystal, multiple twins with the β -Mn structure have been found to coexist with the octagonal quasicrystal [6,7]. Distorted octagonal diffraction patterns have also been observed in the Cr-Ni-Si and Mn-Fe-Si systems [8,9]. We report in this Letter the splitting of certain reflections and the presence of DCs in the split reflections of the distorted octagonal Mo-Cr-Ni diffraction patterns. Regions with large differences in the densities of DCs have also been observed.

As in the case of the Mn-Si-Al octagonal quasicrystal, the Mo-Cr-Ni alloy obtained by melting the high-purity elements in argon atmosphere in an arc furnace was remelted and then solidified rapidly in the form of thin films using the piston-and-anvil method as reported previously [6]. Specimens for study in a Philips EM 420 electron microscope were prepared by ion milling the thin films to electron transparency.

Like the decagonal and dodecagonal quasicrystals [10-13], the octagonal quasicrystal is two dimensional with a periodic eightfold axis (A_8) and two sets of eight orthogonal twofold axes (A_{2D} and A_{2P}) [6]. While the symmetry of the Mn-Si-Al quasicrystal is eightfold [4], the symmetry of the Mo-Cr-Ni phase is fourfold (Fig. 1). The diffraction spots of the diffraction pattern of the fourfold axis (A_4) [Fig. 1(a)] are shifted, radially and/or tangentially out of alignment as in Cr-Ni-Si [8,9].

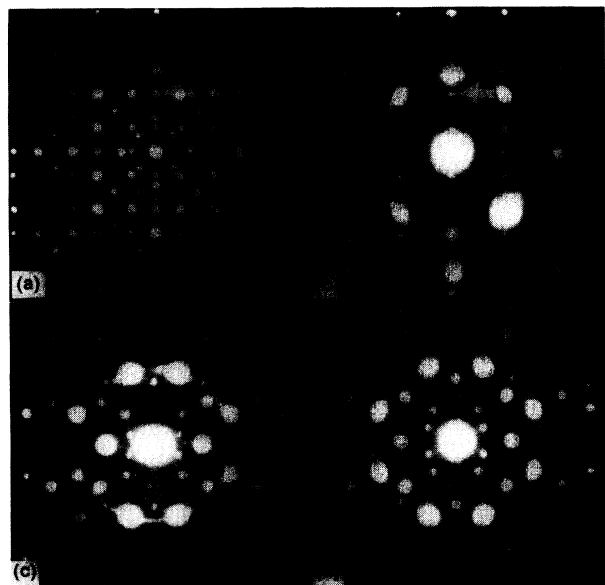


FIG. 1. (a) A_4 , (b) A_{2P} , (c),(d) A_{2D} diffraction patterns of phason-strained Mo-Cr-Ni quasicrystal. The diffraction spots are shifted out of alignment in the fourfold pattern and shifted and split in the twofold patterns. The corresponding spots in the A_4 and the orthogonal twofold patterns are marked by the same arrows. Note the splitting of Z in the A_{2D} pattern is twice that of X in the A_{2P} pattern. Inconsistent with the fourfold symmetry, the A_{2D} patterns are not equivalent.

Diffraction spots of the $A2D$ and $A2P$ patterns are also shifted, and in addition, some of the spots are split along the fourfold axis [Figs. 1(b), 1(c), and 1(d)]. The $A2D$ patterns 45° apart are no longer equivalent [Figs. 1(c) and 1(d)]. The $A2P$ pattern is not equidistant from adjacent inequivalent $A2D$ patterns. The shifting and splitting of the diffraction spots are more pronounced in the $A2D$ patterns. In fact, splitting in the $A2D$ patterns is twice that in the $A2P$ pattern. The corresponding spots in the $A4$ pattern and the $A2P$ and $A2D$ patterns are marked in Fig. 1. The splitting is not visible in the fourfold pattern since it is in the direction of observation. As in the case of the Mn-Si-Al quasicrystal, dark-field images taken with different reflections give different contrast. DC lines and DC dislocations are only visible in split reflections. The reflections which give images with no contrast correspond to the O reflections of the Mn-Si-Al quasicrystal while the split reflections of the $A2D$ and $A2P$ patterns correspond to the X/Y and Z reflections. Irregular domain walls or DCs, similar to those observed in the Mn-Si-Al phases [4], are clearly visible in dark-field images of an X -, Y -, or Z -type reflection of the fourfold pattern.

Regularly spaced DC lines and DC dislocations observed in dark-field images of an X - and a Z -type reflection in an $A2P$ and an $A2D$ pattern, respectively, from the same area of a specimen, are shown in Fig. 2. The density of DCs in the $A2D$ pattern is twice that of the $A2P$ pattern. This is expected as the splitting in an $A2D$ pattern is twice that in an $A2P$ pattern. On the average, the DC lines are aligned perpendicular to the fourfold axis. This is in agreement with the splitting of the reflections. Note that DCs are not visible in images taken with one of the split spots. The separation between the DC lines is the reciprocal of the separation of the splitting of the reflection. Thus the density of DC lines, which is the inverse of separation between DC lines, increases with increasing separation of the splitting of the reflection. Dark-field images and their corresponding selected-area diffraction patterns in Fig. 3 show that the densities of DCs vary by an order of magnitude. When splitting is not observed, the DC lines are not aligned and their separation, which is about 20 nm, is

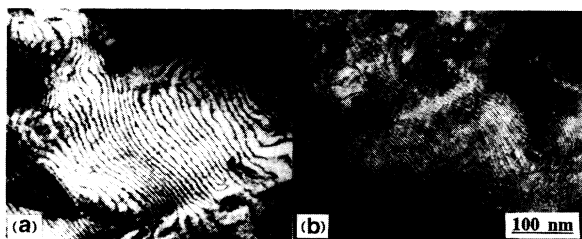


FIG. 2. (a),(b) Dark-field images of split reflections, marked X and Z in Figs. 1(b) and 1(c), from the same region. The spacing of the DC lines in (a) is twice that in (b).

relatively wide [Fig. 3(a)]. When splitting is clearly visible, the DC lines are basically aligned. The separation of the DC lines in Figs. 3(c) and 3(e) are 6 and 2 nm, respectively. The images and diffraction patterns in Fig. 3 have been taken from widely separated regions of a specimen. Adjacent areas with substantially different densities of DCs in the same specimen have also been observed. This is shown in Fig. 4. Three regions with significant differences in the densities of DCs are clearly visible. The separation of the DCs in regions I, II, and III are about 20, 4, and 1.3 nm, respectively. The densities of DCs in regions I and III differ by more than an order of magnitude. The boundaries of the regions are marked by the presence of DC dislocations. The decrease of the DC lines is accomplished by the termination of the lines in DC dislocations. The hierarchy of DC density in Fig. 4 is really quite remarkable. Although the contrast is not very good, it appears that the DC lines terminate in groups of four, just like in Fig. 3(c) and in the previously



FIG. 3. Dark-field images (type X) and the corresponding diffraction patterns from three widely separated regions showing the variation of DC line spacing from about 20 to 6 to 2 nm.

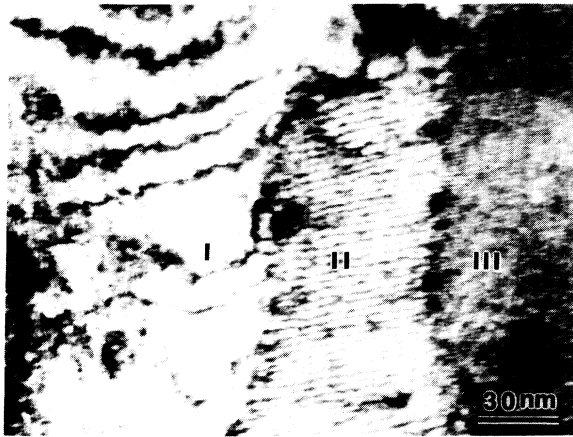


FIG. 4. Dark-field image (type X) showing the variation of DC line spacing by more than 1 order of magnitude in adjacent regions in an inhomogeneous specimen. Note some of the DC lines terminate in DC dislocations at the boundaries between adjacent regions.

reported Mn-Si-Al quasicrystal [3]. Figure 4 is part of an image taken near an $A2P$ axis from a specimen consisting of inhomogeneous regions with different densities and configurations of DCs. Selected-area diffraction patterns taken from different regions show that the various regions share a common orientation while the splitting of the corresponding spots is directly related to the density of DCs. Note that the width of the DCs decreases from region I to region III. The decrease of DC width with decreasing separation of DC lines is also evident in Fig. 3. Comparing diffraction patterns taken from regions with different densities of DCs, the shifting and splitting of particular spots can be followed.

It is clear from the diffraction patterns that the Mo-Cr-Ni quasicrystal is distorted. The distortion is consistent with the presence of phason strain [2]. DCs are observed in some dark fields of certain reflections. As in the case of the Mn-Si-Al quasicrystal, based on the invisibility and visibility of DCs in dark fields, the diffraction spots can be separated into basic and satellite reflections. Unlike the case of DCs arising from periodic lattice distortion or charge-density waves in $TaSe_2$ [14,15], where the change in the density of the DCs is temperature driven, the DCs in Figs. 3 and 4 are interpreted as due to local ordering of atomic species in the distorted quasilattice. It is expected that the local ordered structures would be unstable against a rise in temperature. The diffusion of atomic species would randomize the distribution of atoms so that a more homogeneous structure would result. Such a process would be irreversible. *In situ* heating of a Mo-Cr-Ni specimen in the electron microscope transforms it into an incommensurate crystal with diffraction patterns intermediate between those of the phason-strained quasicrystal and the β -Mn structure.

Based on the hierarchy of the DCs in adjacent regions in Fig. 4, we can rule out temperature in favor of local ordering of atomic species as the origin of the difference in local DC density. It is inconceivable that the temperature of adjacent regions is different. The temperature gradient would be too large to be realistic. The interpretation of ordering of atomic species has previously been put forward to explain the DCs in the Mn-Si-Al quasicrystal. The result inferred from Fig. 4 supports the ordering interpretation. But until the structure of the transformed incommensurate phase is determined, it is not possible to give a model to describe the DCs in the Mo-Cr-Ni phase. We can, however, say a few words about the nature of interaction between the DCs. Notice that the DCs do not cross or intersect except at DC dislocations. When the density of DCs is low, the DC lines are not aligned. This is only consistent with a repulsive interaction between DC lines. At high density, the non-crossing DC lines are forced to align parallel to one another. The presence of DCs and the corresponding splitting of some of the diffraction spots is quite remarkable. This is the first time this has been observed. It is not clear how the splitting is related to the structure of the transformed incommensurate phase. Certainly, the splitting is related to the parallel alignment of dense DCs of the order of nm separation.

The results obtained above can be understood within the framework of the two-dimensional (2D) octagonal random tiling model considered by Li, Park, and Widom [16]. Taking the orientation of the squares and 45° rhombi into account, there are six types of tiles in the 2D quasilattice. Each tile has an associated chemical potential. The geometrical and thermodynamical properties of the octagonal quasicrystal depend on the relative tile concentrations. The ordering of atomic species corresponds to a change in the tiling configuration. Ordering tends to lower the symmetry of the system and results in structures with average phason strain. The possible phases in their model include a phason-strained quasicrystal, incommensurate phases as well as crystal phases. Previous theoretical studies of the octagonal quasicrystal have been limited to the 2D plane normal to the eightfold axis. The diffraction patterns and dark-field images above show that change occurs simultaneously in planes containing and perpendicular to the fourfold axis. More work, both experimental and theoretical, should be done to establish the correlation between the diffraction patterns and the appropriate dark-field images from the $A4$ and $A2P/A2D$ axes.

In conclusion, DCs have been observed in the dark fields of the split reflections of the phason-strained Mo-Cr-Ni quasicrystal. Regions with different densities of DC lines correspond to different incommensurate phases. It is likely that these phases arise from phase separation due to local variation of atomic concentration during rapid solidification. Adjacent regions separated by the pres-

ence of DC dislocations at the boundaries have also been observed. The hierarchy of DC densities in adjacent regions in a specimen gives support to the interpretation that the DCs in the phason-strained Mo-Cr-Ni quasicrystal phases are due to the ordering of atomic species in the quasilattice.

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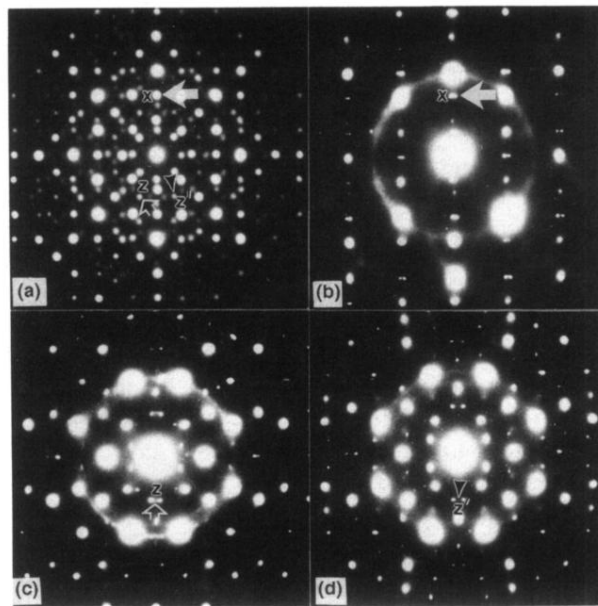


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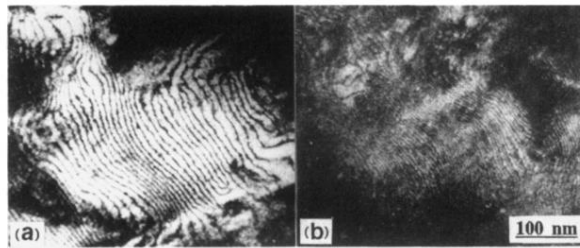


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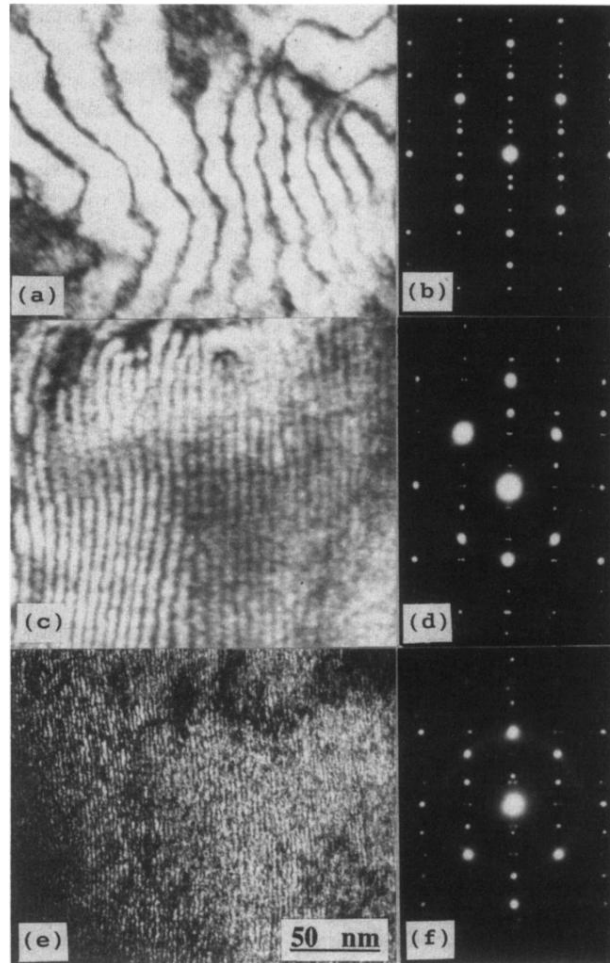


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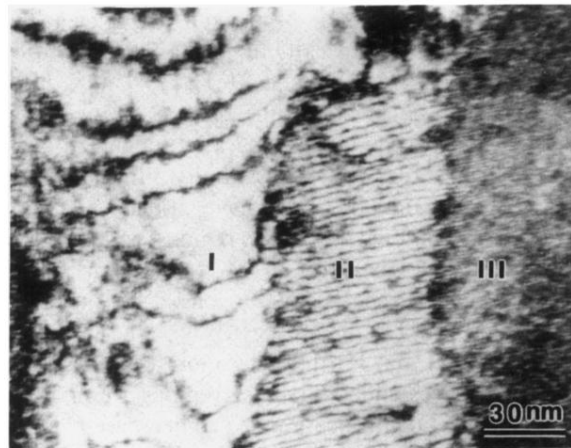


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