Real-Space Imaging of Pentagonal Symmetry Elements by 2-keV Electrons in the Icosahedral Quasicrystal $Al_{70}Mn_9Pd_{21}$

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Pentagonal symmetry elements in an icosahedral quasicrystal are unambiguously observed for the first time in real space using the technique of secondary-electron imaging.

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In this Letter, we report on the successful imaging of contrast details documenting the existence of local pentagonal symmetry axes in real space in the surface layer of an (aperiodic) icosahedral quasicrystal. This has been achieved by applying the method of secondary-electron imaging (SEI) to a fragment of a macroscopic single quasicrystal with composition $Al_{70}Mn_9Pd_{21}$.

Quasicrystals possess specific symmetry elements such as fivefold [1], eightfold [2], tenfold [3], and twelvefold [4] rotation axes which uniquely define the point-group symmetry and the aperiodic nature of the Fourier transform of their structure. In the first publication describing an icosahedral quasicrystal material [1] and in most of the subsequent reports, the presence of local pentagonal symmetry axes required by the point-group symmetry ($\bar{5}\bar{3}m$) of the icosahedron was demonstrated by recording the selected-area electron-diffraction patterns normal to a fivefold, a threefold, and a twofold symmetry axis, respectively. Ordinary diffraction patterns obtained from icosahedral or decagonal quasicrystals using a neutron, an x-ray, or an electron beam do not allow us to distinguish between a fivefold and a tenfold rotation axis because of the inversion symmetry of the reciprocal space. By contrast, electron-channeling patterns, obtained by using a 20–30 keV beam, or convergent-beam electron diffraction patterns (made with the electron beam of a transmission electron microscope with 100–300 keV energy) allow us to differentiate between a fivefold and a tenfold symmetry even for very small regions of aperiodic materials [3].

The SEI technique used in this work was recently introduced, as a method which is complementary to diffraction-based approaches, for obtaining real-space information about the geometric arrangement of atoms in the near-surface region [5]. This method involves the excitation of the surface layer by electrons having an energy near 2000 eV and subsequent two-dimensional spherical recording of the backscattered electrons, i.e., of secondary electrons, with energy losses of up to approximately 5% of the primary-beam energy. In order to explain the processes involved in the image formation in SEI, the following model is used: Primary electrons penetrate the solid and are scattered elastically as well as inelastically by the atoms at and below the surface. These atoms are considered to be point sources for the scattered electrons which are subsequently scattered again by the surrounding atoms. At energies of several keV, elastic forward scattering is the dominant process. Therefore, the electrons which can escape the solid are predominantly those scattered by atoms near the source. Hence, electrons are focused along the atomic rows defined by the source and the adjacent atoms and in this way produce bright spots on the collector screen for particular directions of escape. Consequently, the observed pattern represents a *central projection* of the real-space atomic arrangement around each source, with many sources contributing incoherently to the pattern. Hence, the atom arrangement of the structure producing the SEI pattern must not necessarily possess perfect long-range order as present in crystals. The only requirement is that the local environment must have its atom rows in equal orientation around each emitting source. This is demonstrated by a recent application of the SEI method to a texture consisting of disordered submonolayers of Ag on Al(111) [6]. Here, SEI revealed the presence of local sixfold symmetry due to the arrangement of the Ag atoms, superimposed onto the threefold symmetry of the substrate.

The investigated specimen had the approximate shape of a cube, with sides as long as 3 mm. The composition was determined by wavelength-dispersive x-ray microanalysis on a scanning electron microscope. Before taking the images, the surface was cleaned by Ar^+ (1500 eV, 0.1 $\mu A/mm^2$, 60 sec) in an ultrahigh vacuum apparatus described earlier [5,6]. The electron beam was focused on the specimen to a spot size of 0.5 mm. Since the display screen has the shape of a spherical segment with limited angular size, only a 100° section of the available solid angle 2π could be observed. The SEI pattern was recorded by a charge-coupled device camera with 195×162 picture elements (having thus an angular resolution of 0.5°/picture element), with an integration time of 10 s. In the SEI patterns the central portion is blocked by the shadow of the electron gun used for the excitation.

Figure 1(a) shows the SEI pattern obtained from the $Al_{70}Mn_9Pd_{21}$ quasicrystal. It consists of bright spots arranged in fivefold symmetry around a point slightly below (8.3°) the center of the imaged area. The positions of these spots are found to coincide with the vectors defined by the central point and all vertices of an icosahedral arrangement of twenty acute Kowalewsky-Ammann rhom-

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bohedra [7] which have the central point in common. The presence of icosahedral clusters is strongly suggested by recent experimental investigations on the presently studied specimen [8]. The central projection of the vertices of this cluster with the icosahedral inversion center as its origin is presented in Fig. 1(b), in the *same angular scale* and orientation as the SEI pattern in Fig. 1(a). The central point of Fig. 1(b) corresponds to the center of fivefold symmetry in the SEI pattern. The points in this scheme are arranged on three concentric rings around the central point. The sets of five spots situated on the same ring can be attributed to the same type of symmetry element in an icosahedrally symmetric model cluster centrally projected in Fig. 1(b). In this figure, the innermost ring contains five axes of twofold symmetry, the second ring contains five threefold axes, the third contains five more twofold axes, and the outermost ring contains five fivefold axes. These different types of symmetry elements have been marked by different symbols, i.e., twofold axes by rectangles, threefold axes by triangles, and fivefold axes by pentagons.

A comparison of Fig. 1(a) with 1(b) shows a perfect correspondence between the positions of the observed bright spots in the experimental pattern and those of the symbols in the simulated central projection. We therefore interpret the pattern in Fig. 1(a) as a real-space imaging of the averaged local atomic arrangement and its icosahedral symmetry in the investigated quasicrystal material. The center of the diagram then corresponds to a fivefold axis, and the pentagon of five bright spots corresponds to twofold symmetry axes located on the innermost ring. Similarly, the second ring from the center contains five threefold axial directions. Because of the limited angular size of the display screen, the two outer rings containing more twofold and fivefold symmetry directions can barely be imaged in Fig. 1(a), and they appear around the edge of this limit. However, the SEI technique permits us to observe these spots after a simple tilt of the specimen. In our experiment, this revealed the positions of all the other axial elements indicated in Fig. 1(b). The bright patches situated halfway between pairs of twofold axes may be due to additional decoration atoms of the rhombohedral units in the clusters. Since in SEI a finite region near the surface is imaged, this technique is sensitive not only to the surface atoms, but also to atoms situated beneath the surface [5].

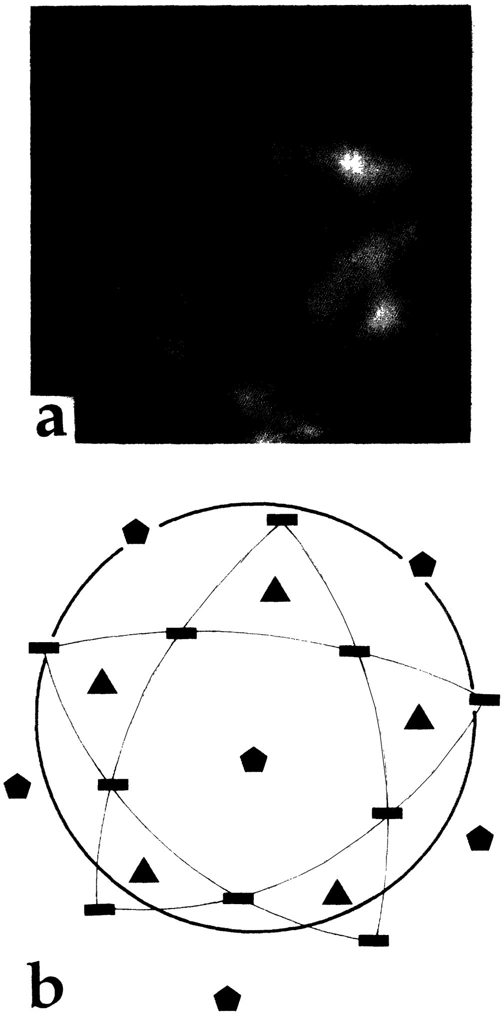

FIG. 1. (a) A secondary-electron pattern obtained from a single quasicrystal of Al$_{70}$Mn$_9$Pd$_{21}$ at a primary-electron energy of 2000 eV. (b) Central projection of the vertices, respectively the symmetry elements of a certain icosahedral cluster, drawn on the same angular scale and the same orientation as the SEI pattern. The circle in bold delimits the maximum angle of observation (100°). The thin lines represent the great circles connecting twofold axes. For details, see text.

Besides proving the existence of the pentagonal symmetry elements, the pattern presented in Fig. 1(a) also renders an observation on the degree of far order in the quasicrystal specimen. A pattern such as that in Fig. 1(a) can only be generated if all or a substantial portion of the icosahedrally symmetric (complete or incomplete) clusters are arranged in parallel rotation orientation. This causes a high degree of long-range orientational order in the structure [1]. If this type of order would not be present in the quasicrystal, a strongly diffuse SEI pattern would have been obtained. On the other hand, according to a recent neutron and x-ray study [8], the surface of an icosahedral quasicrystal contains atomic arrangements of local pentagonal symmetry, which occur in two orientations related to each other by a 180° rotation around the fivefold symmetry axis (cf. Fig. 10 in Ref. [8]). An inspection of this figure by comparing atom positions in different layers parallel to the surface, shows that only one type of pentagons oriented in one and the same direction, contains an atom along the pentagonal axis below the surface. Since in SEI a local symmetry of atoms is imaged by electrons originating from a source located below these atoms (central projection), only those pentagons are imaged that have an atom beneath and consequently only those oriented in the same direction, and not others rotated by 180°. Hence, the present results are not at all in contradiction with the atom positions proposed in Ref. [8].

Since field-ion microscopy of icosahedral Al-Mn-Si has so far given only a rather inconclusive evidence of local fivefold symmetry [9] and since there is no experimental evidence from scanning tunneling microscopy of local pentagonal axes in icosahedral $Al_{65}Cu_{20}Fe_{15}$ [10], the present Letter represents the first unambiguous proof of local pentagonal symmetry in the real-space structure of a quasicrystal. The SEI technique permits us to record three-dimensional views of the atomic structure by a simple rotation of the specimen. By this procedure, a set of patterns for all symmetry directions of the icosahedral point group has been obtained which will be published elsewhere.

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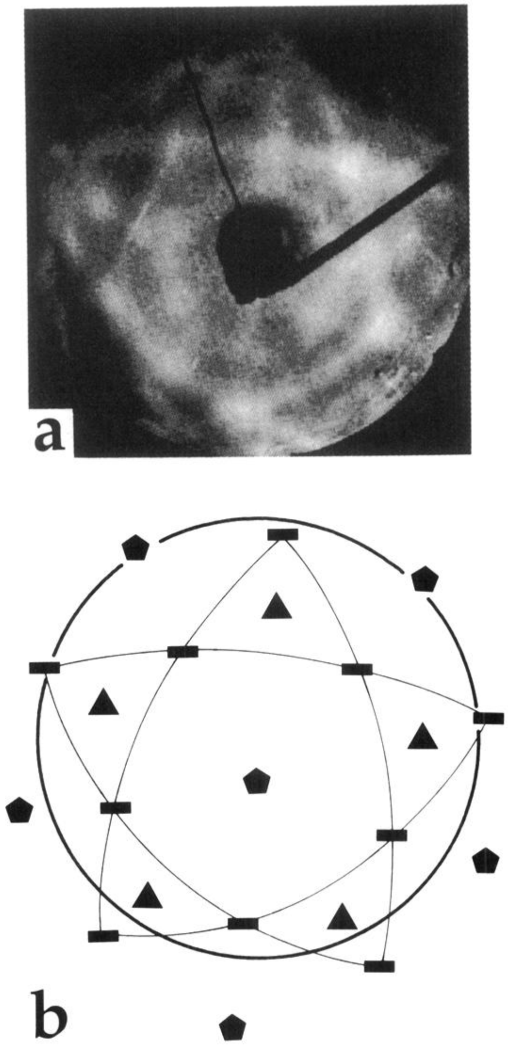

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