PHYSICAL REVIEW B VOLUME 38, NUMBER 3 15 JULY 1988-II

Patterson Fourier analysis of the icosahedral (Al,Si)-Mn alloy

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(Received 3 February 1988)

Neutron and absolute x-ray diffraction data obtained from single-phase icosahedral powder $Al_{73}Mn_{21}Si_6$ are analyzed using a generalized Patterson autocorrelation function in three dimensions. The icosahedral pattern is quasiperiodic. The local atomic arrangements match those encountered in the prototypic crystalline α phase. Extra peaks in the local icosahedral pattern match those of an icosahedrally rotated α pattern.

We present here a Patterson analysis of an (Al,Si)-Mn icosahedral quasicrystal, using neutron and x-ray diffraction data obtained from powdered rapidly solidified alloys. We compare this Patterson analysis with an equivalent analysis performed on the periodic cubic α phase[1] of the same elements in order to test the hypothesis that the local arrangements in the quasicrystal match those encountered in the crystal. Using powder data which has inherent spherical averaging instead of single- (quasi) crystal data presents no serious problem since the quasicrystal powder patterns are easily indexed. Our indexing method for powders supplies the directional information that is usually obtained from single-crystal data.

Patterson analyses are based entirely on measured integrated intensities. A Patterson function (PF) is a convolution of the scatterer density distribution in the specimen with itself, a real three-dimensional (3D) autocorrelation function. It is obtained by Fourier-transforming the observed intensities and is useful because it yields a graphical representation of the interatomic distance vectors. The way the PF is calculated implicitly erases the natural disorder of the specimen since it assumes that all the reflections are δ functions. The resulting interatomic distance distribution is an average distribution on a *perfect* quasicrystal which would diffract the same integrated intensities. As a consequence, the PF has no actual physical significance for distances larger than the correlation length given by the average peak width, at least 30 nm in our case. The PF technique is, in that respect, different from the usual radial inverse Fourier transform,[2] used mainly for isotropic materials, of all the intensity and yields a radial distribution function (RDF) which loses all the directional information of the PF but includes the intrinsic radial disorder and therefore is not a spherical average of the PF.

X-ray and neutron powder diffraction spectra showed that the finely powdered rapidly solidified $Al_{73}Mn_{21}Si_6$ alloys were almost entirely icosahedral phase with only a trace of the hexagonal crystalline β phase[3] and no detectable fcc Al. Diffraction data[4-6] as a function of angle were obtained and were corrected for background, sample holder, thermal factor, and Lorentz factor. Peak positions and integrated intensities (absolute x-ray intensities for the icosahedral phase[6]) were obtained from Gaussian fits to the peak shapes.[4-6] The positions of the reflections are fitted with a relative accuracy better than 5×10^{-3} using a six-integer indexing in three dimensions related to a 6D icosahedral primitive lattice of parameter $A=0.6497$ nm.[7] The average width of the peaks as measured both by x-ray and neutron diffraction leads to a correlation length greater than 30 nm. The widths hardly depend on the perpendicular components of the **k** vectors in six dimensions.[4-14] Upon heating at 30 °C/h, the alloy transforms entirely into the β hexagonal phase at 700 °C. A fine-powder specimen of α-cubic-phase $Al_{73}Si_{11}Mn_{16}$ has also been prepared and studied by both x-ray and neutron diffraction. Detailed experimental procedures and extensive discussions of the data treatment will be presented in forthcoming papers.[4-6]

The six-integer indexing method[7,12-14] to index the powder peak positions has the advantage that the sequence of ordered peak positions is related to two integers; one index N increases monotonically, similar to that for crystalline powders. Peak positional data are converted to 3D diffraction vectors, thereby regaining directional information lost in the powder data. Most of the powder pattern reflections can be uniquely identified with a specific reciprocal quasilattice vector **k** in three dimensions. For the occasional overlaps where two or more nonequivalent **k** vectors have the same magnitude, e.g., $N=12$, $M=16$,[14] the total integrated intensity has been split proportional to the corresponding multiplicities. Associated with the reciprocal quasilattice is a direct quasilattice whose translations are also described by six indices.[7] Unlike a crystalline translation, a quasi-crystalline translation has only a fraction of the structure superimposed upon itself.

A crystalline PF is defined by the 3D Fourier transform

$$P(\mathbf{r})=\sum_{\mathbf{k}} I(\mathbf{k})\exp(2i\pi\mathbf{k}\cdot\mathbf{r}) \, , \tag{1}$$

where **k** runs over the reciprocal-lattice nodes. The generalization to quasiperiodic structures is to sum over those indexed peaks having intensity. Note, that in practice only those few peaks having significant intensity contribute to the sum. Only a small number of x-ray powder lines are observed; the inverse Fourier transformation has been performed using these 38 orbits for x rays (because of the high multiplicities encountered in the icosahedral group, even these 38 orbits contain 2159 reflections) and 47 orbits for the neutron spectra. A table of these data is appended to the following paper.[15] Convergence for the neutron Patterson sum was forced by multiplying the intensity with a Gaussian in **k**, analogous to the Debye-Waller factor.

Figure 1 shows x-ray and neutron PF's for the twofold plane in the physical space for both the cubic α crystal and the icosahedral quasicrystal. This plane of the quasicrystal is a mirror plane and contains the twofold, threefold, and fivefold rotation axes. The close similarity between the periodic and quasiperiodic phases in the powder x-ray results and the single-crystal results[1] verifies both the applicability of our powder method and the hypothesis that atoms in these two phases have quite

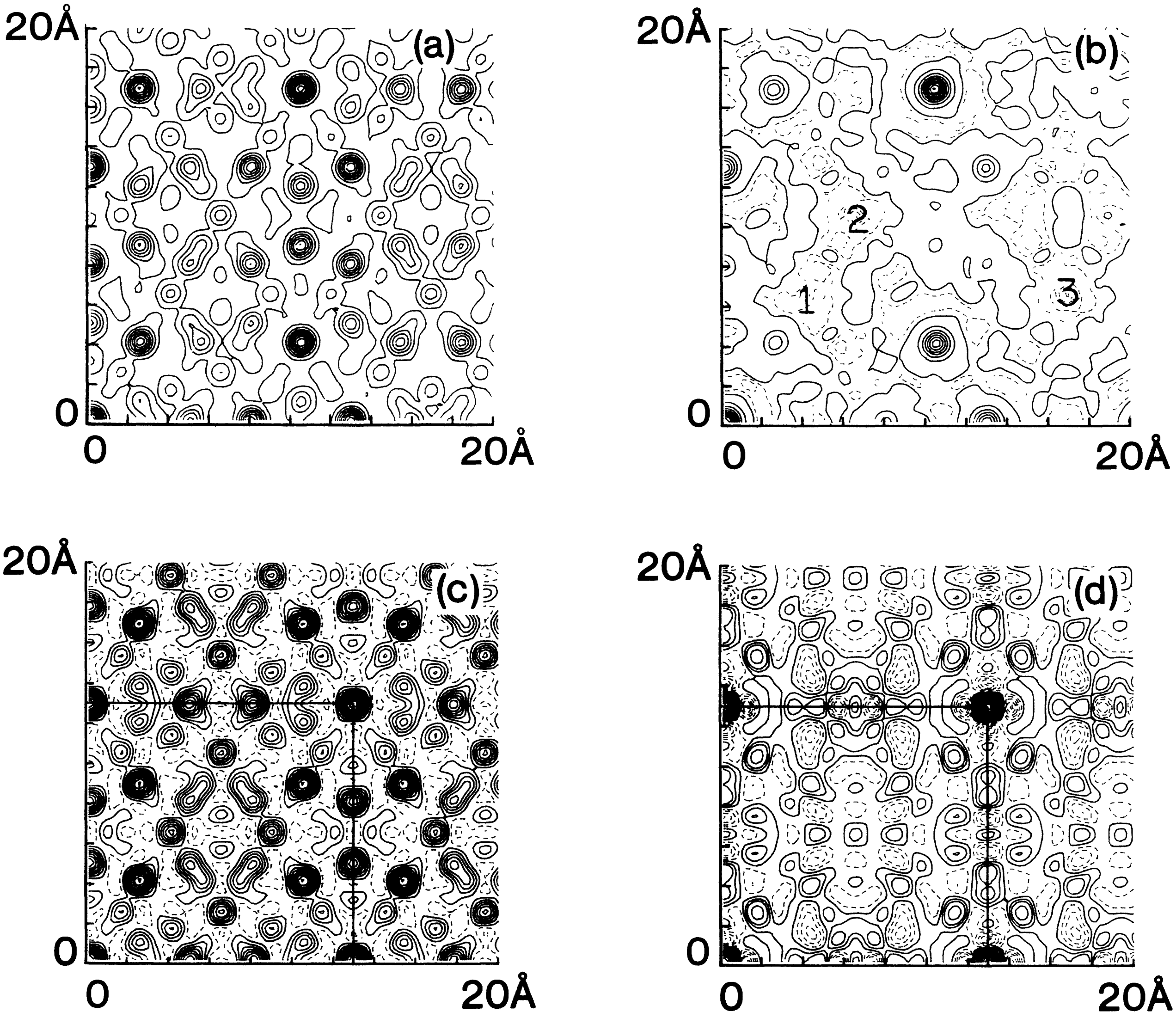

FIG. 1. (a) X-ray and (b) neutron PF's in the twofold orientation of the icosahedral phase compared to (c) x-ray and (d) neutron PF's of the α structure for the same orientation; the α unit cell is drawn in sold lines. Positive contours are solid and separated by 0.1. Negative contours are dashed and separated by 0.03. The fivefold axes in (a) and (b) have slope τ, the threefold axes slope $2-\tau$, and the twofold axes are the ordinates and abscissae. Negative peaks indicated by numbers 1, 2 and 3 in (b) are referred to in the text.

similar local environments.[16–20] (Note that one must interchange x and y in Ref. 1 to make their results consistent with ours.) Even the mirror symmetry in the pattern of the α phase along the planes x (or y)$=a/2$ ($a=1.268$ nm, lattice parameter of the α phase) is approximately present as a pseudomirror in the icosahedral pattern. Since Al and Mn atoms have neutron scattering lengths of opposite sign and almost the same magnitude, the positive (homoatomic distances) and negative (heteroatomic distances) regions of the PF are clearly identified in the neutron patterns. Comparison of neutron with x-ray peaks shows that several of the peaks are close pairs of opposite atomic character. Comparing the two neutron patterns shows striking differences. The pseudomirror at $a/2$ has disappeared in the quasicrystal pattern: Some neighbor distances along the twofold axis happen to be heteroatomic pairs, contrary to what is observed in the α phase where all these distances correspond to homoatomic pairs.[1] This difference can be understood by examining Fig. 2, which is the PF of the irrational crystal plane $(\tau\ 1\ \tau-1)$ ($\tau=1.618\,033\,9\ldots$), which would be a twofold plane in icosahedral symmetry. The quasicrystal PF's for both x rays and neutron are similar to a *linear combination* of the PF's for these two crystal planes. The strong peak missing from the crystal twofold orientation is the $(\bar{1}11)$ peak actually observed in the pseudo-twofold plane. Also shown in Fig. 3 are the fivefold plane and pseudo-fivefold plane $(1\tau 0)$ for both structures and both radiations. Again there are striking similarities which strongly enforce the hypothesis that the α crystal and the quasicrystal in (Al,Si)-Mn have quite similar local environments both in distances (as already noted in extended x-ray-absorption fine-structure experiments[21–23]) and orientations. Strong positive neutron peaks correspond to quasilattice translations. Note that the quasilattice translation of 0.46 nm along the fivefold axis, which is the edge in many of the proposed 3D tilings, is strong for x rays but quite weak for neutrons, and thus must essentially be a heteronuclear distance of the structure. All of the strong positive neutron peaks are translations that can be shown to be vector additions of 1.09-nm vectors along the threefold axes. In the α crystal this corresponds to a body-centering distance with a high PF, since it leads to superpositioning of the inner shells of the Mackay icosahedra.

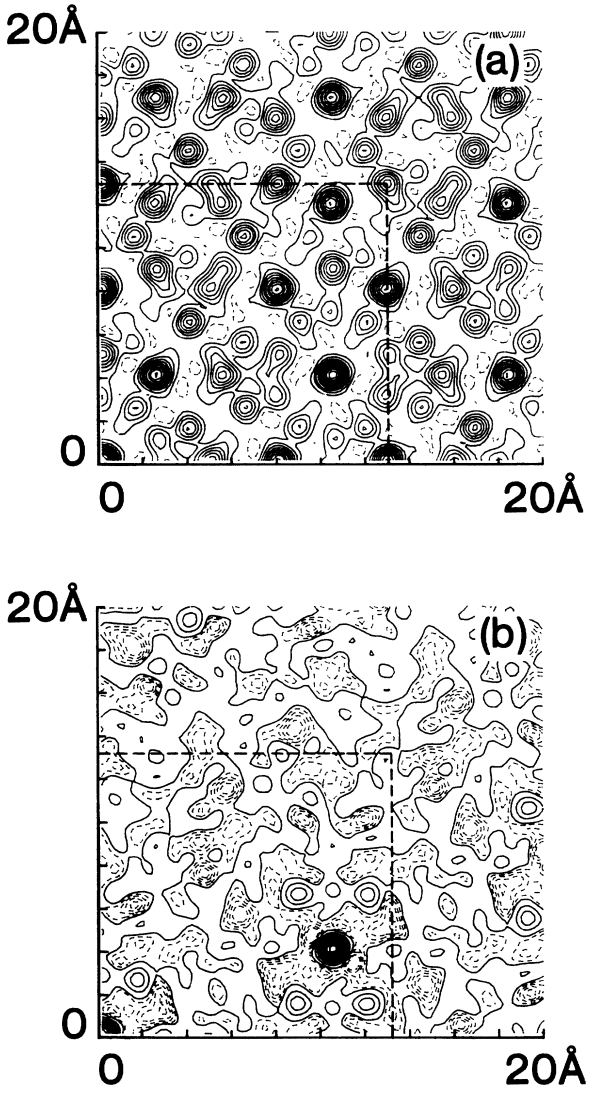

FIG. 2. PF in pseudo twofold orientation of the α phase for (a) x rays and (b) neutrons. The base of the cubic unit cell is superimposed in dashed lines. Note that the negative peak 3 of Fig. 1(b) has no counterpart here.

Figure 4 compares the neutron and x-ray PF's along the fivefold direction. Important distances show up as peaks at 0.46, 1.49, and 1.9 nm. Comparing x rays with neutrons shows that the two shortest distance peaks have a large heteroatomic component; in fact, both peaks are superpositions of homoatomic and heteroatomic distances of slightly different lengths. The longer quasilattice translations, e.g., at 1.9 nm along the fivefold axis, give quite large positive peaks for both x rays and neutrons, indicating that much but not all of the structure superimposes on itself, characteristic of quasilattices.

In the α crystal, the 1.268-nm peak along the twofold axis is the lattice translation. All other peaks in the unit cell in Figs. 1(c) and 1(d) are motif translations depending on the positions of the atoms in the unit cell and incommensurate with the lattice parameter. These strong crystal motif peaks become quasilattice translations in the quasicrystal with minor shifts. This experimentally confirms the hypothesis proposed by Guyot and Audier[17] and by Elser and Henley[18] that the quasicrystal could have a chemical short-range ordering close to that encountered in the α phase.

Of interest are several strong peaks in Figs. 1(a) and 1(b) in symmetric positions *not identifiable* with a simple quasilattice translation. For instance, along the fivefold axis, there is a geometric series of lengths differing by a factor of τ in which every third peak is a quasilattice translation of ever increasing peak height asymptotically reaching a limit of 1 as in Fig. 4. In between for neutrons, there are two negative peaks indicated by the numbers 1 and 2 on Fig. 1(b). A similar negative peak labeled

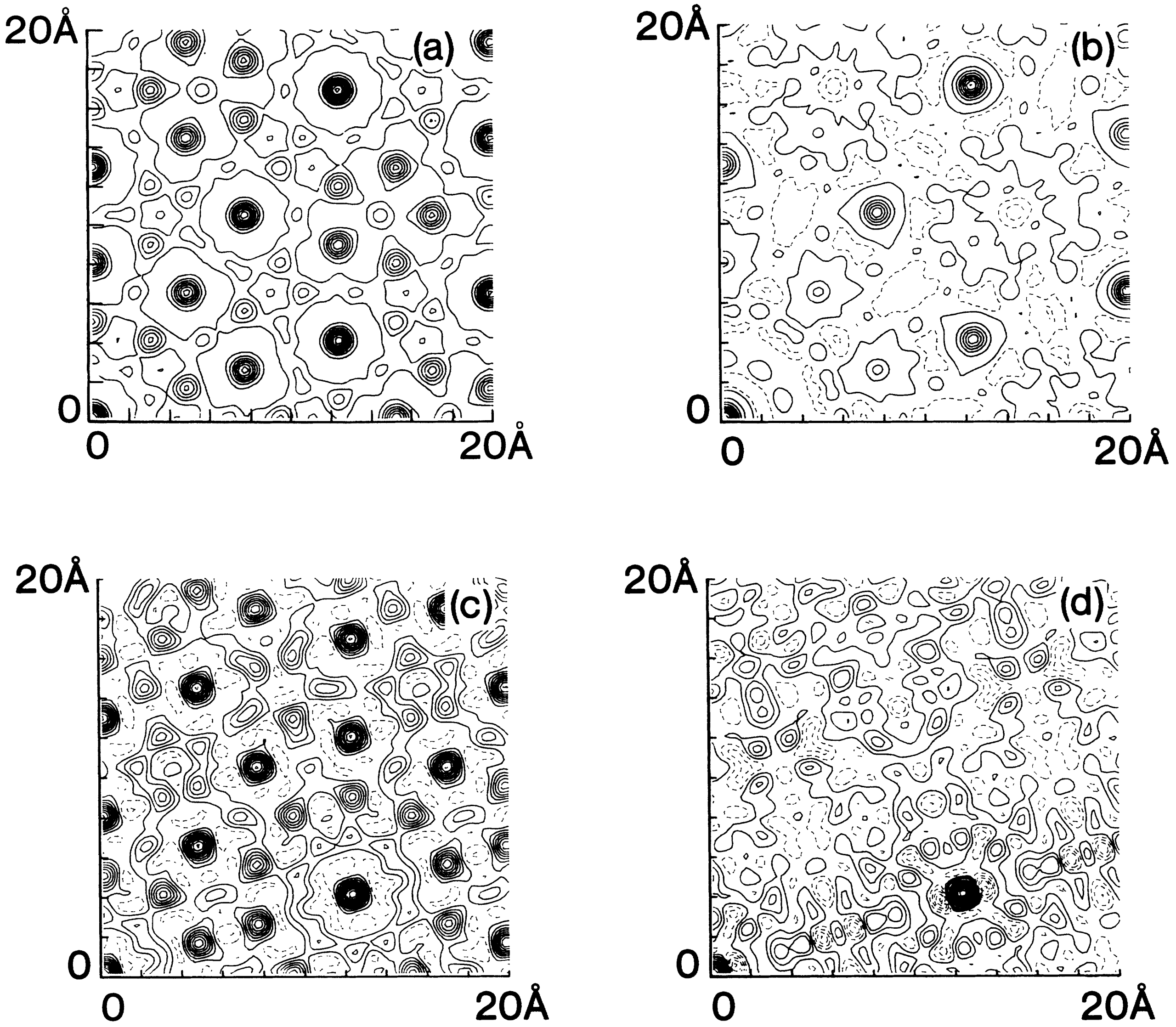

FIG. 3. Fivefold (a) x ray and (b) neutron and pseudo fivefold (c) x ray and (d) neutron for the icosahedral and the cubic phases. In (a) and (b) the twofold axes begin at a slope of 18° and recur every 36° thereafter.

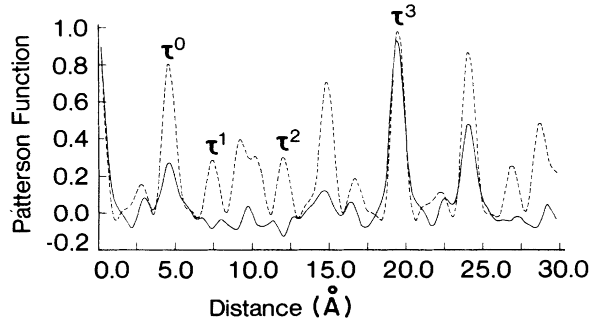

FIG. 4. X-ray (dashed line) and neutron (solid line) PF's along the fivefold axis, indicating that, except for the 1.9-nm distance, most of the vectors along this axis have a large heteroatomic component.

3 occurs along the threefold axis in Fig. 1(b). At larger distances of the PF there are additional negative peaks whose magnitudes approach -0.2. This is close to the maximum negative value that can be attained in these alloys and indicates a high degree of chemical order for distances that do not belong to the fundamental quasilattice, but which can be shown to come from special symmetry points attached to it. Such τ and τ^2 multiples of quasilattice translations violate, along the threefold and fivefold axes, the parity rules of the indexing method[7] and therefore cannot themselves be a quasilattice translation. Since they occur at intersections of planes in the direct quasilattice, they are associated with points having special symmetry in the quasilattice.[15]

We have constructed PF's from experimental data for the (Al,Si)-Mn quasicrystal and examined some of its features. The way the PF was obtained guaranteed that it would be quasiperiodic with a 6D arithmetic basis. It can therefore also be obtained as a 3D cut of a strictly periodic 6D PF.[24–27] In a subsequent paper, we will show how to construct this 6D function from the same data and use the 6D periodic function to demonstrate additional relationships among positions and peak intensities in the quasiperiodic 3D pattern.

Special thanks are due to A. Rabinkin and J. Bigot for preparing two specimens that proved to have identical spectra.

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