Neutron-Diffraction Approach to the Atomic Decoration of the Al-Mn Icosahedral Quasicrystal

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Neutron-diffraction data were obtained from single-phase icosahedral powder of the system $Al_{74}Si_5Mn_{21}$ and its modification by isomorphous substitution on the Mn sites. Amplitudes and phase differences of the partial structure factors (F_{Al}, F_{Mn}) were determined. From their $Q_\perp$ dependences, and within a strip-projection approach, phases were reconstructed. Atomic densities calculated in the physical 3D space show that Mackay icosahedra, the structural units usually invoked for quasicrystal models, do not emerge as the basic ingredients of the atomic arrangements.

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The discovery of systems with diffraction patterns exhibiting the icosahedral symmetry[1] forbidden in classical crystallography has recently been a challenge for theoreticians and experimentalists who have tried to find models explaining the observed features. In fact, mathematicians had introduced, early in the century, quasiperiodic and almost periodic functions and it is easy to show that these families of functions Fourier transform into dense sets of sharp Dirac-type peaks. Moreover, incommensurate phases were at the time an already known example of nonperiodic structures showing sharp diffraction peaks. MacKay[2,3] had also drawn attention to two- and three-dimensional Penrose tilings (3DPT) and their diffraction patterns which were qualitatively similar to that observed by Shechtman *et al.*[1] Since then, numerous examples of metallic alloys have been discovered, the atomic structures of which display "forbidden" symmetries.[4] The debate has resulted in a wealth of published papers. A bibliography of quasicrystals,[5] a collection of significant reprints,[6] and a recent workshop[7] have updated the state of knowledge on the subject. Basically, successful descriptions of quasiperiodic geometrical networks have been achieved with use of a variety of different schemes for generating them: space tiling by two rhombohedral cells with matching rules, inflation-deflation procedure, multigrid or dual methods, and strip-projection[8] or cut-projection approaches.[9] The latter in particular shows that any quasiperiodic network has actually hidden periodic translations which can be recovered if the structure is properly described in a higher-dimensional space. This is a simple consequence of the fact that icosahedral point-group symmetries $m\bar{3}\bar{5}$ are compatible with a six-dimensional space group but not a three-dimensional one. Once generated by one of the above methods, a long-range-ordered quasilattice without periodicity is not the end of it. We still have to describe where the atoms are located to specify completely the structure. Experimental approaches and modeling have both contributed to the point which has been extensively reviewed.[4,10] The 6D approaches of atomic decoration are probably the most generic and global and are, actually, a direct extrapolation of conventional crystallography methods. Following this scheme, a 6D periodic model has recently been proposed[11] for the Al-Mn-Si icosahedral quasiperiodic crystal, resulting from an embedding of the cubic α structure into 6D. However, the large number of geometrical parameters to be determined and folding effects due to the presence of several chemical species (Al, Mn, Si), presumably sitting in different atomic positions, make the comparison of the model to diffraction data a little doubtful. Moreover, the hexagonal μ-$MnAl_4$ phase[12] should have been better used as a related crystalline structure.

The purpose of the present paper is to show that sophisticated techniques, namely contrast variation effects with neutron diffraction, are a requisite for deciphering raw data in the framework of a N-dimensional space.

Quasicrystalline phases of the Al-Mn system can be produced by melt-spinning techniques,[1] as described in detail in previously published papers.[13] Finely powdered rapidly solidified $Al_{74}Si_5Mn_{21}$ alloys, and their modifications resulting from Fe and/or Cr substitutions to Mn, were obtained almost as single icosahedral phases. Only a trace of a hexagonal phase was detected in the unsubstituted alloy.

High-resolution neutron-diffraction data have been measured in the same conditions as reported elsewhere[14,15] for other quasicrystalline alloys. Peak positions and integrated intensities were obtained from Gaussian fits to the peak shapes.[13-15] The positions $Q_\parallel$ of the reflections are in an ordered sequence of peaks related to two integers N and M by the expression $Q_\parallel(\text{Å}^{-1}) = 0.359(N+\tau M)^{1/2}$ within a relative accuracy better than 3×10^{-3}; N and M are defined in Ref. 16 and τ is the golden mean. Such a sequence of positions is equivalent to a six-integer indexing in 3D [16] related to a 6D icosahedral primitive lattice with parameter equal to

6.497 Å. Intensities were carefully corrected for absorption, for Debye-Waller thermal effects, and for Lorentz factor. Peak positional powder data can be reconverted into 3D diffraction $\mathbf{Q}_\parallel$ vectors by distributing the total integrated intensity over the corresponding set of equivalent reflections[14,15] (indexing and multiplicity being accounted for). The $I(\mathbf{Q}_\parallel)$ intensities may be written as

$$I(\mathbf{Q}_\parallel)=|b_{\mathrm{Al}}F_{\mathrm{Al}}+b_T F_T|^2, \tag{1}$$

where the b's stand for the neutron-scattering lengths of aluminum and transition metal atoms, respectively, and the F's are the partial structure factors defined by

$$F_{\mathrm{Al}}=\sum_{\mathrm{Al}}\exp(i\mathbf{Q}_\parallel\cdot\mathbf{r}_{\mathrm{Al}}),\quad F_T=\sum_T\exp(i\mathbf{Q}_\parallel\cdot\mathbf{r}_T). \tag{2}$$

An equivalent expression for $I(\mathbf{Q}_\parallel)$ is then

$$I(\mathbf{Q}_\parallel)=b_{\mathrm{Al}}^2|F_{\mathrm{Al}}|^2+b_T^2|F_T|^2 +2b_{\mathrm{Al}}b_T|F_{\mathrm{Al}}||F_T|\cos\Delta\phi, \tag{3}$$

in which $\Delta\phi$ is the phase difference between F_{Al} and F_T. Obviously, Eq. (3) contains $|F_{\mathrm{Al}}|$, $|F_T|$, and $|\Delta\phi|$ as three unknown quantities which can be determined, for each $\mathbf{Q}_\parallel$ reflection, by one measuring three independent intensities $I(\mathbf{Q}_\parallel,b_T)$ with three samples strictly identical but for their neutron-scattering contrast b_T on the transition-metal sites. Rescaling procedure and self-consistency tests using actually more than three contrasted samples have been extensively described and probed in previously reported works.[14,15,17,18]

The raw product of the neutron-diffraction data and contrast variation is then the triple set $|F_{\mathrm{Al}}(\mathbf{Q}_\parallel)|$, $|F_T(\mathbf{Q}_\parallel)|$, and $|\Delta\phi(\mathbf{Q}_\parallel)|$. As already observed with other icosahedral alloys,[14] the phase differences $\Delta\phi$ measured in the present work happened to be all equal to 0 or π within experimental accuracy. As a consequence, the measured partial structure factors F_{Al} and F_T of the icosahedral phase can be expressed by pairs of real numbers, either of same or opposite signs, multiplied by a common phase factor $\exp(i\Phi)$. For a given pair, however, the sign of F_{Al} and F_T and their common phase $\Phi(\mathbf{Q}_\parallel)$ cannot be deduced from diffraction data and a phase-reconstruction procedure must be discovered if one wishes to proceed beyond the usual Patterson function analysis.[11] This can be obtained as a consequence of quasiperiodic structures having hidden translational symmetries in a higher-dimensional space.

In the formulation of the strip projection method[8] one starts with a 6D primitive cubic lattice in R_6 which is projected onto two orthogonal well chosen 3D subspaces $R_{3\parallel}$ and $R_{3\perp}$. The quasiperiodic crystal consists in projection onto $R_{3\parallel}$ of those points of the cubic lattice which are within a strip S_6 extending infinitely parallel to $R_{3\parallel}$ but having a finite cross section $A_{3\perp}$ in $R_{3\perp}$ called the acceptance function. The 6D diffraction pattern of the infinite real 6D cubic lattice would be a 6D cubic distribution of Dirac functions at vectors $\mathbf{Q}_6$. The 6D diffraction pattern of the strip S_6 would also be a 6D distribution of extended spots centered at $\mathbf{Q}_6$, still Dirac-like when scanned at $\mathbf{Q}_\parallel$ vectors in the 3D reciprocal space associated with $R_{3\parallel}$, but broadened in the orthogonal 3D reciprocal subspace associated with $R_{3\perp}$ because of convolution with the Fourier transform $G(\mathbf{Q}_\perp)$ of the acceptance function $A_{3\perp}$ ($\mathbf{Q}_\perp$ and $\mathbf{Q}_\parallel$ are the projections of $\mathbf{Q}_6$ in the two 3D reciprocal subspaces associated with $R_{3\perp}$ and $R_{3\parallel}$, respectively). In such a formation the partial structure factors F_{Al} and F_T actually determined in 3D can be expressed, for each Al or T site, as

$$F_{\mathrm{Al}}(\mathbf{Q}_\parallel)=f_{\mathrm{Al}}(\mathbf{Q}_6)G_{\mathrm{Al}}(\mathbf{Q}_\perp),$$
$$F_T(\mathbf{Q}_\parallel)=f_T(\mathbf{Q}_6)G_T(\mathbf{Q}_\perp), \tag{4}$$

in which f and G stand for the structure factors of the infinite periodic structure in R_6 and the Fourier transform of the pertinent partial acceptance functions in $R_{3\perp}$, respectively. Let us first analyze the data corresponding to $F_T(\mathbf{Q}_\parallel)=f_T(\mathbf{Q}_6)G_T(\mathbf{Q}_\perp)$, i.e., the partial structure factor of the transition-metal atom subnetwork. The measured amplitudes $|F_T|$ of this partial structure factor, as a function of $Q_\perp=[\tau(N\tau-M)/2(2+\tau)]^{1/2}$, go to zero for $Q_\perp$ values of about 0.7 (with $2\pi/a$ taken as unit length where $a=6.497$ Å is the lattice parameter of the 6D cubic lattice). With the assumption that the acceptance function $A_{3\perp}$ can be approximated by a sphere of radius, R_c would give the expression

$$G(Q_\perp)\propto 3R_c^3\left[\frac{\sin(2\pi Q_\perp R_c)}{(2\pi Q_\perp R_c)^3}-\frac{\cos(2\pi Q_\perp R_c)}{(2\pi Q_\perp R_c)^2}\right], \tag{5}$$

which turns from positive to negative for $Q_\perp=0.7$ if $R_c=102a$. This radius is not very far from the one sphere ($1.013a$) having the same volume as the rhombic triacontahedral acceptance function corresponding to the unit cell of the 6D cubic lattice, when the immersion of $R_{3\parallel}$ into R_6 generates the six fivefold directions by projection of the six cube edges. This is a very strong indication that the manganese (or T) subnetwork in $R_{3\parallel}$ can be generated by projection of those lattice points of a 6D primitive cubic lattice which are within a strip having the same cross section as the 6D cubic unit cell in $R_{3\perp}$. The consequences are twofold.

First, the projected points into $R_{3\parallel}$ are then the vertices of a 3DPT[19] which defines completely the Mn atom subnetwork. Second, in the expression $F_T(\mathbf{Q}_\parallel)=f_T(\mathbf{Q}_6)G_T(\mathbf{Q}_\perp)$, the factor $f_T(\mathbf{Q}_6)$ becomes simply the structure factor of a 6D primitive undecorated cubic periodic lattice and, thus, is a set of constant real numbers. As the Fourier transform of a cut function, $G_T(\mathbf{Q}_\perp)$ is also a real number. The very important conclusion is that $F_T(\mathbf{Q}_\parallel)$ can only be real numbers and so the $F_{\mathrm{Al}}(\mathbf{Q}_\parallel)$ are also since it has been deduced from diffraction data that phase differences between F_T and F_{Al} can be only 0 or π. At this stage, F_T and F_{Al} are

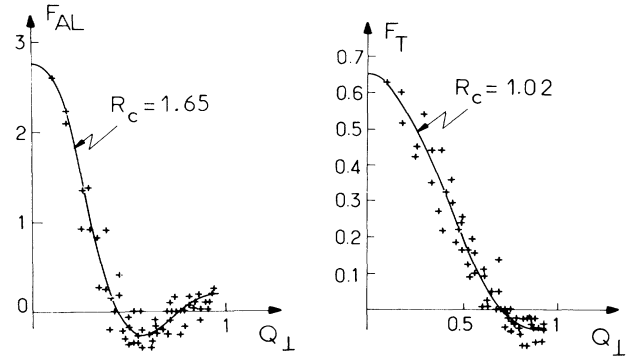

FIG. 1. $Q_\perp$ dependences of the Al and Mn partial structure factors of the quasicrystalline structure: data (+) and the sphere approximation (full line). Phases have been "reconstructed" as explained in the text. Radii R_c of the spherical acceptance functions are given. $R_c(\mathrm{Al})$ and $R_c(T)$ are in a ratio roughly equal to τ.

then real numbers whose relative sign is known from diffraction data for each measured reflection. But if $F_T(\mathbf{Q}_\perp)$ is compared to a $G_T(\mathbf{Q}_\perp)$ as given by Eq. (5), it has to be positive for $Q<0.7$ and negative for $0.7<Q<1.2$ which, combined with the F_T/F_{Al} relative sign, removes the remaining underdetermination. The resulting $F_{\mathrm{Al}}(Q_\perp)$ and $F_T(Q_\perp)$ with their "reconstructed"[20] phases are represented in Fig. 1 and compared to $G(\mathbf{Q}_\perp)$ functions of the type described by Eq. (5).

An obvious procedure to generate the real atomic structure is to Fourier transform the partial structure factors according to

$$\rho_T(\mathbf{r})=\sum_{\mathbf{Q}_\parallel}F_T(\mathbf{Q}_\parallel)\exp(i\mathbf{Q}_\parallel\cdot\mathbf{r}),$$
$$\rho_{\mathrm{Al}}(\mathbf{r})=\sum_{\mathbf{Q}_\parallel}F_{\mathrm{Al}}(\mathbf{Q}_\parallel)\exp(i\mathbf{Q}_\parallel\cdot\mathbf{r}), \tag{6}$$

in which ρ_T and ρ_{Al} are the partial 3D atomic densities at $\mathbf{r}$. Then, the resulting atomic coordinates, occupation

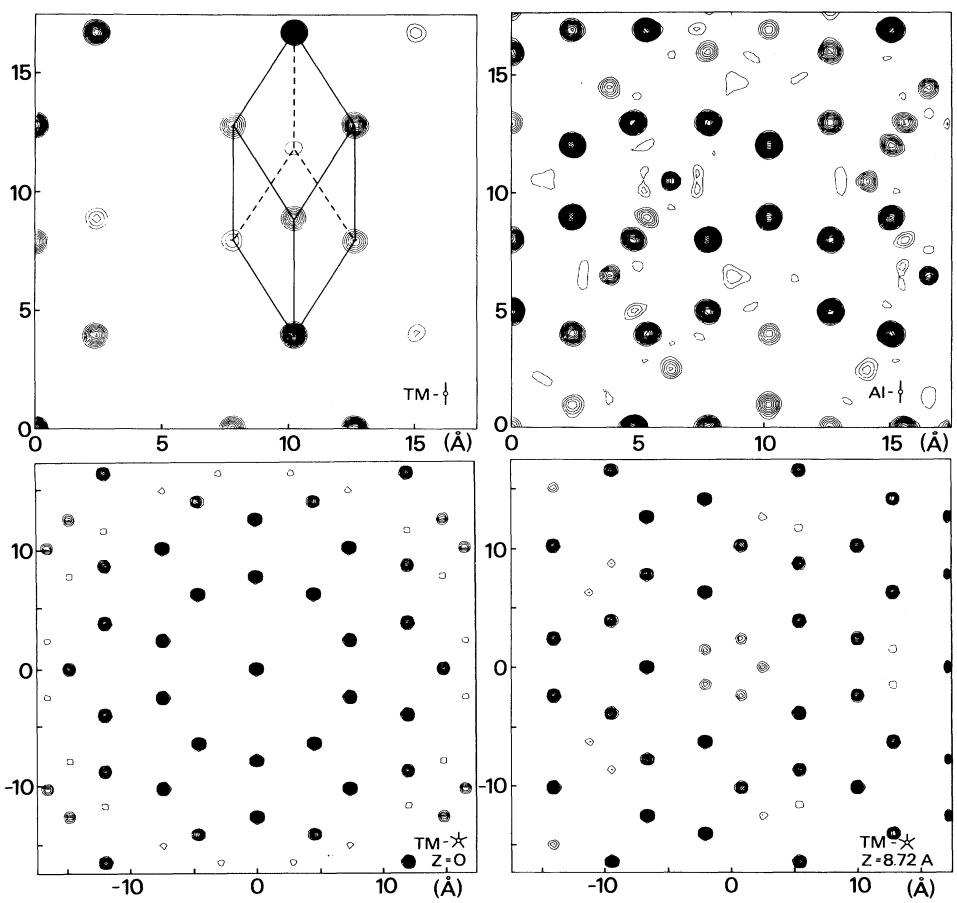

FIG. 2. Samples of density maps obtained by direct Fourier transforms of the measured partial structure factors (with phases reconstructed). These maps are 2D cuts of 3D atomic density, perpendicular to fivefold (*) and twofold axis (ϕ), of the 3D partial atomic densities for Al and Mn as indicated. (Level Z of the cut is given when relevant for comparison.) A perspective view of one prolate rhombohedron has been drawn for the sake of illustrating the transition-metal subnetwork.

fractions within each subnetwork, and distances from the origin can be calculated.[21] Typical atomic density maps representing 2D cuts of $\rho_T(\mathbf{r})$ are shown in Fig. 2. A careful examination of these results allows interesting conclusions to be drawn regarding the atomic structure. The manganese atoms are obviously at the vertices of a 3DPT with 4.6-Å edges. But occupation fractions for some positions are smaller than 1. For instance, the two vertices at the short diagonals of the oblate rhombohedra, separated by 2.59 Å, are scarcely occupied simultaneously by Mn atoms. The aluminum atoms seem to be more poorly located. However, it appears that the major Al sites are

(i) at a few vertex positions, shared with Mn atoms;

(ii) near positions situated at 2.57 and 6.78 Å from the vertices on the triad axis of the prolate rhombohedra (10.96 Å for this triad axis and 13.55 Å if an oblate rhombohedron is aligned properly); and

(iii) near positions on the faces of the prolate and oblate rhombohedra, dividing the long diagonals of the rhombi into segments of 2.98 and 4.83 Å (7.81 Å for the diagonal).

These different Al sites are never simultaneously occupied in a given rhombohedron of the 3DPT. This is fortunate for obvious steric constraints and introduces a "chemical modulation" of the structure which may be welcomed to allow stability of the whole architecture.[22] Moreover, it can be demonstrated that "natural" matching rules result also from this occupancy modulation.

The structure obtained in the present work is not a "model": The atomic positions have been *deduced* from diffraction data without any of the crystallochemistry assumptions which are usually used to build "reasonable" structures. It differs quite deeply from the so far accepted schemes which have also vertex sites for Mn but have mid-edge sites instead of face sites for Al.[23] Thus, the MacKay icosahedron does not appear any more as the basic structural unit of the quasicrystal structure and some atomic arrangements are introduced which cannot be found in related crystalline compounds. Some similarities may, however, be found in models proposed by Henley[24] or Sachdev and Nelson.[25]

The next step in the structural specification is now to find a refinement method derived from the conventional Fourier-difference technique. This is actually in progress and will be published, along with tables of atom coordinates, in a forthcoming paper.

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