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Determination of Quasicrystalline Structures: a Refinement Program using Symmetry-Adapted Parameters

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(*Received 29 March 1993; accepted 3 August 1993*)

Abstract

A general program for the refinement of quasicrystalline structures using diffraction data is presented. The program can be used for both icosahedral and polygonal quasicrystals. The refinement process is based on the fitting of the structural model to experimental diffraction data and observed density and chemical composition. Superspace formalism is used for the structure description and the hypersurfaces in superspace describing the atomic positions are assumed to be parallel to the internal space. No additional *a priori* assumption on the form of the atomic hypersurfaces is necessary except that the deviations of the atomic-surface contours from a spherical shape do not contain very short wave components in a significant amount. The contours of each symmetry-independent atomic hypersurface in internal space are parametrized in terms of linear combinations of radial functions (surface harmonic) invariant for the hypersurface point group in internal space. This allows a continuous refinement of the structure in terms of symmetry-adapted parameters consistent with the symmetry restrictions resulting from the postulated superspace symmetry. The program requires an initial very approximate guess of the structure in terms of 'spherical' hypersurfaces of which only the symmetry centres are known with confidence. The continuous parametrization of the hypersurfaces does not *a priori* restrict their form, except in its degree of complexity or fine detail, which is limited by the number of terms considered in the linear expansion of the surface contours. In general, the number of surface harmonics considered should be consistent with the accuracy allowed by the experimental data set. The refinement process can be performed either by a full least-squares method or by means of a simplex algorithm. The physical consistency of the refined hypersurfaces with respect to the predicted density, chemical composition and interatomic distances is controlled by including additional 'penalty functions' in the parameter to be minimized.

1. Introduction

Accurate determination of the structures of quasicrystals (QCs) is still an open problem. The introduction of superspace formalism (Bak, 1985; Janssen, 1986) represented important progress towards achieving a *quasicrystallography* comparable with ordinary crystallography. Under the superspace approach, the field has developed rather quickly and methods of structural analysis of QCs have greatly improved (Janot, de Boissieu, Dubois & Pannetier, 1989; de Boissieu, Janot & Dubois, 1990; Cahn, Gratias & Mozer, 1988*a*,*b*; van Smaalen, 1989; Cornier-Quiquandon, Quivy, Lefebvre, Elkaim, Heger, Katz & Gratias, 1991; Steurer, 1990, 1991; Jaric & Qiu, 1991); however, important difficulties in attaining accuracies comparable with those of ordinary structural crystallography have been pointed out (de Boissieu, Janot, Dubois, Audier & Dubois, 1991; Cornier-Quiquandon, Gratias & Katz, 1991). In the superspace description, the structure-solution problem is translated into the determination of a periodic scalar function of n variables within its unit cell (superspace density); n being the rank of the diffraction diagram. Such a task is practically impossible without a previous hypothesis of the form of the function to be determined. Part of this modelling consists of the assumption that the superspace density is a set of $(n-3)$-dimensional hypersurfaces or atomic surfaces (ASs), essentially perpendicular to the *real* space in the superspace and weighted by the corresponding atomic scattering densities (electronic density for X-ray diffraction) along the *real* space. The structure analysis is then basically reduced to the determination of the imposition and shape of these ASs in the n-dimensional superspace. The centres of the ASs (usually at high-symmetrical points) and their approximate sizes can normally be determined from Patterson analysis (Cahn, Gratias & Mozer, 1988*b*; Steurer, 1989). Any further resolution of the structure is usually done by means of further modelling, *i.e.* the introduction of additional hypotheses on the shapes of the ASs. Typically, the ASs are considered to have specific polyhedral shapes with only one or two adjustable parameters. There are various arguments leading to the hypothesis of polyhedral or other specific forms for the ASs: steric requirements (de Boissieu, Janot, Dubois, Audier & Dubois, 1991); physical plausibility of atomic displacements corresponding to movements of the superspace density along directions perpendicular to real space (Frenkel, Henley & Siggia, 1986; Cornier-Quiquandon, Gratias & Katz, 1991); restriction to tiling models (van Smaalen, 1989); experimental evidence from Patterson or Fourier analysis *etc.*

On the other hand, the possibilities of a general approach based on the parametrization of the ASs with continuous parameters and their subsequent refinement, analogous to the methods of standard crystallography, have been scarcely investigated. We have proposed (Elcoro, Pérez-Mato & Madariaga, 1992) the use of truncated series of symmetry-adapted functions for a continuous parametrization of the ASs under the assumption that they are perpendicular to the *real* space. It was shown that a few parameters could be, in general, sufficient for a description of the ASs consistent with the expected experimental accuracy and that the use of a continuous parametrization of the ASs does not exclude the resulting fitted ASs conforming (within experimental resolution) to polyhedra. In the following, we present a general least-squares refinement program for polygonal and icosahedral QCs, named *QUASI*, based on this approach. The paper is organized as follows: in §§ 2 and 3, the superspace description of a QC and its superspace symmetry are briefly reviewed and some of the structural parameters used in the program computations are defined; § 4 is devoted to describing the parametrization of the AS in a general case; in §§ 5 and 6, this parametrization is applied to the polygonal and icosahedral cases and the symmetry-adapted functions used by the program are given; in § 7, the general structure of the program *QUASI* and its possibilities are discussed. The results of the structure refinement of the icosahedral QC $Al_{57}Cu_{11}Li_{32}$ using *QUASI* and previously published data sets (de Boissieu, Janot, Dubois, Audier & Dubois, 1991) are presented in a subsequent paper.

2. Superspace description of quasicrystals

We summarize here the superspace formalism from an applied viewpoint, as required for the development of a refinement program. Following Bak (1985, 1986), we introduce the superspace as the space of the phases of a minimal set of fundamental modulations in the structure and, accordingly, we stress the adimensional character of the superspace and its lack of predetermined metric.

Let us consider a QC with a diffraction diagram of rank $n > 3$, where a minimal basis of wave vectors $\{\mathbf{k}_1, \ldots \mathbf{k}_n\}$ has been chosen such that any diffraction vector, $\mathbf{H}$, is indexed in the form

$$\mathbf{H} = \sum_{i=1}^{n} h_i \mathbf{k}_i \qquad (1)$$

with h_i integers. The structure of the QC is then described by a scattering density $\rho(\mathbf{r})$ given by

$$\rho(\mathbf{r}) = \sum_{\mathbf{H}} F(\mathbf{H}) \exp\left(-2\pi i \sum_{i=1}^{n} h_i \mathbf{k}_i \cdot \mathbf{r}\right), \qquad (2)$$

where $F(\mathbf{H})$ is the structure factor of the three-dimensional QC structure for each diffraction vector $\mathbf{H}$. A scalar function of n variables, the so-called superspace density $\rho_s(\theta_1, \ldots, \theta_n)$, can then be defined by the expression

$$\rho_s(\hat{\theta}) = \rho_s(\theta_1, \ldots, \theta_n) = \sum_{\mathbf{H}} F(\mathbf{H}) \exp\left(-2\pi i \sum_{i=1}^{n} h_i \theta_i\right). \qquad (3)$$

By definition, the superspace density is periodic for all the variables θ_i, with period 1, and may also have additional centring periodicities depending on the possible systematic absences of the structure factor. According to (3), $F(\mathbf{H})$ is also the structure factor of the superspace density:

$$F(\mathbf{H}) = \int_0^1 \mathrm{d}\theta_1 \ldots \int_0^1 \mathrm{d}\theta_n \, \rho_s(\theta_1, \ldots, \theta_n) \exp\left(2\pi i \sum_{i=1}^{n} h_i\theta_i\right)$$
$$\equiv \int_c \mathrm{d}\hat{\boldsymbol{\theta}} \rho_s(\hat{\boldsymbol{\theta}}) \exp 2\pi i \hat{\mathbf{h}} \cdot \hat{\boldsymbol{\theta}}, \qquad (4)$$

where we use the symbols $\hat{\boldsymbol{\theta}}$ and $\hat{\mathbf{h}}$ for the set of parameters $(\theta_1, \theta_2, \ldots, \theta_n)$ and $(h_1, h_2, \ldots, h_n)$, respectively, and we represent the summation in $h_i\theta_i$ by $\hat{\mathbf{h}} \cdot \hat{\boldsymbol{\theta}}$.

Rigorously, the variables θ_i are adimensional and can be interpreted as the phases of the modulation waves associated with the wave vectors chosen for the basis in (1) (Bak, 1985, 1986). The n-dimensional space corresponding to these n phases can be identified with what is usually called 'superspace'. Thus interpreted, this is in fact a space of n scalar 'phases' and has no predetermined metric, which can be introduced arbitrarily. Usually, the superspace formalism is formulated with a particular implicit or explicit choice for this metric, which allows a simple geometrical picture of the superspace density. For instance, in the case of icosahedral quasicrystals, the superspace lattice is usually given under a 'hypercubic' representation (the set of vectors $\mathbf{k}_i$ having been adequately chosen), so that the variables θ_i are associated with an orthonormal basis.

It should be noted that the definition of the superspace density (3) is still meaningful (but trivial) in the case of a normal crystal, where the rank n coincides with the dimension of the real space; in this particular case, the three phases θ_i, $i = 1, 2, 3$, can be interpreted as the relative coordinates, x_i, with respect to three vectors in direct space reciprocal to the $\mathbf{k}_i$ vectors used in the indexing (1); the superspace density $\rho_s(x_1, x_2, x_3)$ reduces simply to a mapping of the scattering density on the space of relative coordinates for the chosen unit-cell parameters.

Comparison of definition (3) and equation (2) shows that the real-space QC scattering density, $\rho(\mathbf{r})$, is given by the section of the superspace density defined by

$$\rho(\mathbf{r}) = \rho_s(\theta_1 = \mathbf{k}_1 \cdot \mathbf{r}, \ldots, \theta_n = \mathbf{k}_n \cdot \mathbf{r}). \qquad (5)$$

Hence, the superspace density restricted to the subspace carrying this section represents a map of the scattering density in real space; we call this subspace 'parallel space', being different from real (physical) space.

The rational independence of the wave vectors $\{\mathbf{k}_i\}$ and the periodicity of the superspace ensure that any value of the superspace density in a unit cell will be realized at some point on the section defined by (5); conversely, the value of the scattering density at any point $\mathbf{r}$ of real space, given by (5), is equal to the value of the scattering density at some point inside one unit cell of the superspace density. There is, therefore, a one-to-one mapping between the superspace density in one unit cell and the aperiodic scattering density in real space. From this viewpoint, the superspace density is just a form of 'book-keeping' all the atomic positions in real space. Thus, for point-like atoms and a finite sample, the superspace density in a unit cell would consist of a set of about 10^{23} points, corresponding to all atomic positions in real space. The introduction of the superspace description would be of no use if we had to determine the positions of all these points! What makes the superspace approach really useful is that, in real quasicrystalline materials, the set of these points in the superspace unit cell typically forms a few closed domains (dense in the idealized case of an infinite sample) that can be described by a few parameters. This property of the superspace density is directly seen, for instance, in superspace Patterson analysis of experimental data. Indeed, the possibility of describing the superspace density by means of a small number of parameters seems to be directly related to the hierarchy of diffraction intensities observed experimentally that allows in practice the indexing of a diffraction diagram that is mathematically dense.

We can introduce in the superspace a variable transformation $(\mathbf{x}, \mathbf{x}_I) = \mathbf{A}^{-1}\hat{\boldsymbol{\theta}}$ such that $\mathbf{x}$ belongs to the parallel space and $\mathbf{x}_I$ to a complementary 'internal space'. First, we choose an arbitrary vector basis in real space, $\{\mathbf{a}_j\}$, to be used in the description of any generic vector in real space:

$$\mathbf{r} = \sum_{j=1}^{3} x_j\mathbf{a}_j. \qquad (6)$$

The wave vectors $\{\mathbf{k}_i\}$ of the basis in (1) can be expressed in terms of the corresponding reciprocal basis $\{\mathbf{a}_j^*\}$:

$$\mathbf{k}_i = \sum_{j=1}^{3} \alpha_{ij}\mathbf{a}_j^*, \quad i = 1, \ldots, n. \qquad (7)$$

According to (5), a generic point $\hat{\boldsymbol{\theta}} = (\theta_1, \ldots, \theta_n)$ can then be related to the coordinates x_i by an equation of the form

$$\theta_i = \sum_{j=1}^{3} \alpha_{ij}x_j + \sum_{j=1}^{n-3} \gamma_{ij}x_{Ij}, \quad i = 1, \ldots, n, \qquad (8)$$

so that a vector in real space given by the coordinates x_i in (6) corresponds to the superspace point given by (8) with $x_{Ij} = 0$. The superspace density at this point represents the scattering density at the corresponding point in the real space. Symbolically, we can rewrite (8) as

$$\hat{\boldsymbol{\theta}} = \mathbf{A}\,\hat{\mathbf{x}} = \mathbf{A}\begin{pmatrix}\mathbf{x}\\ \mathbf{x}_I\end{pmatrix}, \qquad (9)$$

with **A** given by

$$\mathbf{A} = \begin{pmatrix} \alpha_{11} & \cdots & \alpha_{13} & \gamma_{11} & \cdots & \gamma_{1\,n-3} \\ \vdots & \cdots & \vdots & \vdots & \cdots & \vdots \\ \alpha_{n1} & \cdots & \alpha_{n3} & \gamma_{n1} & \cdots & \gamma_{n\,n-3} \end{pmatrix}. \quad (10)$$

It should be stressed that, while the parameters α_{ij} are determined by the set of wave vectors $\{\mathbf{k}_i\}$ used in the indexing and the vector basis $\{\mathbf{a}_i\}$, chosen in real space, the values of γ_{ij} are arbitrary, except for the condition that the determinant of **A** is nonzero. The choice made defines the internal space, given by $x_i = 0$, $i = 1, \ldots, 3$.

If we call $\{\hat{\mathbf{e}}_i\}$ the basis in the superspace corresponding to the coordinates θ_i, the matrix **A** represents a transformation to a new basis $\{\hat{\boldsymbol{\varepsilon}}_i\}$ so that

$$\hat{\boldsymbol{\varepsilon}}_i = \mathbf{A}_{ji}\hat{\mathbf{e}}_j. \quad (11)$$

Note that, although the parallel space generated by the subset $\{\hat{\boldsymbol{\varepsilon}}_1, \hat{\boldsymbol{\varepsilon}}_2, \hat{\boldsymbol{\varepsilon}}_3\}$ is isomorphous to real space, its metric is at this point undetermined.

As mentioned above, the essential assumption in the superspace description, confirmed by experiment, is that the superspace density defined by (3) can be described by a small set of closed domains where the superspace density is different from zero, *i.e.* the superspace density can be described in the new coordinates as

$$\rho_s(\mathbf{x}, \mathbf{x}_I) = \sum_\mu \rho_{m(\mu)}(\mathbf{x} - \mathbf{x}_\mu(\mathbf{x}_I)) \cdot \eta_\mu(\mathbf{x}_I), \quad (12)$$

with $\eta_\mu(\mathbf{x}_I) = 1$ if $\mathbf{x}_I$ belongs to a certain closed domain in the internal space, W_μ, and $\eta_\mu(\mathbf{x}_I) = 0$ otherwise. The function $\rho_{m(\mu)}$ is the atomic scattering density of a certain atom of kind m associated with the domain μ; in the case of disorder, it can be an effective density given by the relevant occupation probabilities. The sum in (12) extends over all the existing closed domains W_μ in the superspace density. The structure in real space is then given by the function $\rho_s(\mathbf{x}, 0)$, where $\mathbf{x} = (x_1, x_2, x_3)$ represents a real-space vector given by (6). The form (12) ensures that the section corresponding to parallel space is given by a set of individual atoms located at the positions $\mathbf{x}_\mu(0)$ associated with those domains W_μ that intersect parallel space. The *atomic surfaces* (AS) defined by the domains W_μ and the functions $\mathbf{x}_\mu(\mathbf{x}_I)$ and the atom kind associated with each describe completely the superspace density. The number of independent ASs is limited because of the symmetry properties (periodic and rotational) of the superspace density ρ_s, as described by a certain superspace group (see § 3).

As a consequence of the lattice periodicity of the superspace density and the incommensurate orientation of the parallel section, any point of any AS within a superspace unit cell represents an atom in parallel space, situated at the position where a translational equivalent AS intersects parallel space through this point. Accordingly, the average concentration in real space (number of atoms per unit volume) of an atom type m, as the result of a certain AS in the superspace unit cell 'occupied' by this atom m, is given by

$$C_m = |\mathbf{A}| V_\mu / V(\mathbf{a}_i), \quad (13)$$

where V_μ is the volume of the domain W_μ, $|\mathbf{A}|$ is the determinant of the transformation matrix **A** in (9) and $V(\mathbf{a}_i)$ is the volume of the cell in real space defined by the vectors $\{\mathbf{a}_i\}$. In a more general case, if atom m is 'present' in a set of ASs within the unit cell, with some 'occupation' probabilities $p_m(\mu)$, the total average concentration of atom m is

$$C_m = [|\mathbf{A}|/V(\mathbf{a}_i)] \sum_\mu p_m(\mu) V_\mu, \quad (14)$$

where the sum extends to all ASs μ in a superspace unit cell for which $p_m(\mu)$ is different from zero. The average density and composition corresponding to the structural model can be derived directly from (14), when considered for each atomic species present in the material.

From (4), the structure factor of a QC described by the superspace density (12), for a (real-space) diffraction vector **H**, can be written in the form

$$\begin{aligned} F(\mathbf{H}) = {} & [|\mathbf{A}|/V(\mathbf{a}_i)] \sum_\mu \sum_m p_m(\mu) f_m(\mathbf{H}) \\ & \times \int_{W_\mu} \mathrm{d}\mathbf{x}_I \exp\{2\pi i[\mathbf{H}\cdot\mathbf{r}_\mu(\mathbf{x}_I) + \mathbf{h}_I\cdot\mathbf{x}_I]\} \\ & \times \exp[-\tilde{\mathbf{H}}\beta^m_\mu(\mathbf{x}_I)\mathbf{H}], \end{aligned} \quad (15)$$

where the sums extend to all ASs μ in a superspace unit cell and to all atom types m within each AS, $f_m(\mathbf{H})$ is the scattering factor of atom m, $p_m(\mu)$ is the occupation probability of atom m within the AS μ, while $\mathbf{r}_\mu(\mathbf{x}_I)$ is the real-space vector associated by (6) with the parallel-space vector $\mathbf{x}_\mu(\mathbf{x}_I)$ and $\mathbf{h}_I\cdot\mathbf{x}_I$ represents $\sum h_{Ii}x_{Ii}$, where the $(n-3)$ components of h_I are given by the transformation **A**:

$$h_{Ii} = \sum_{j=1}^{n} A_{j(i+3)}h_j = \sum_{j=1}^{n} \gamma_{ji}h_j \quad i = 1, \ldots, n-3, \quad (16)$$

with h_i being the indices in (1). Only standard thermal factors have been introduced in (15); physical arguments against including additional thermal factors for the 'internal part', $\mathbf{h}_I$, of the diffraction vector can be found in Pérez-Mato, Madariaga & Elcoro (1991). Each atom represented by a point within an AS μ is physically inequivalent to any other one; therefore, thermal factors need not be constant throughout an AS. Hence, in (15), thermal factors have been assumed to be dependent on $\mathbf{x}_I$; however, this variation is expected to be weak with consequences on the experiment that are rather subtle and essentially negligible in standard experimental data.

Let us suppose now that the ASs are all parallel to an $(n-3)$-dimensional subspace and the transformation $\mathbf{A}$ is chosen such that the internal space coincides with it. In this case, the functions $\mathbf{x}_\mu(\mathbf{x}_I) = \mathbf{x}_\mu$ are independent of $\mathbf{x}_I$, for all μ, and the structure factor can be expressed as

$$\begin{aligned} F(\mathbf{H}) = {} & [|\mathbf{A}|/V(\mathbf{a}_i)]\sum_\mu \sum_m p_m(\mu) f_m(\mathbf{H}) \\ & \times \exp(-\tilde{\mathbf{H}}\beta^m_\mu \mathbf{H}) \exp(2\pi i \hat{\mathbf{h}} \cdot \hat{\boldsymbol{\theta}}_\mu) \\ & \times \int_{W_\mu} \mathrm{d}\mathbf{x}_I \exp[2\pi i \mathbf{h}_I \cdot (\mathbf{x}_I - \mathbf{x}_{I\mu})], \end{aligned} \qquad (17)$$

where, in general, we have considered a different thermal factor for each atom type associated with a single AS, and $\hat{\boldsymbol{\theta}}_\mu = \mathbf{A}(\mathbf{x}_\mu, \mathbf{x}_{I\mu})$ is some 'centred point' chosen in the AS μ, with $\mathbf{x}_{I\mu}$ being its internal coordinate.

3. Rotational symmetry and superspace groups

The symmetry of the quasicrystalline structure (2), the so-called superspace group of the QC, will be given by the set of rotations in real space and translations in the superspace, $\{\mathbf{R}|\hat{\mathbf{t}}\}$, such that the structure factor in (2) satisfies, for any $\mathbf{H}$,

$$F(\tilde{\mathbf{R}}\mathbf{H}) = F(\mathbf{H}) \exp(-2\pi i \hat{\mathbf{h}} \cdot \hat{\mathbf{t}}). \qquad (18)$$

This relation directly implies that the diffraction diagram should have the rotational symmetry corresponding to the set of rotations $\{\mathbf{R}\}$. The observed extinction rules are to be related to the nonprimitive translations $\hat{\mathbf{t}}$ of some superspace-group elements by the usual method of considering (18) in the case that $\tilde{\mathbf{R}}\mathbf{H} = \mathbf{H}$. Relation (18) is trivially fulfilled for the superspace lattice translations $\{\mathbf{E}|m_1, \ldots, m_n\}$ (m_i integers), already considered in the preceding section. The symmetry relation (18) is difficult to visualize in direct space; it means that the rotation $\mathbf{R}$ transforms the structure $\rho(\mathbf{r})$ in a new atomic configuration that is physically undistinguishable from the original one and energetically equivalent (Rokhsar, Wright & Mermin, 1988; Mermin, 1991). After the rotation, the original structure can be 'recuperated' by a translation $\hat{\mathbf{t}}$ of the n independent phases corresponding to the set of rationally independent wave vectors $\{\mathbf{k}_i\}$ chosen for the indexing (1). In the superspace density (3), however, a superspace group operation $\{\mathbf{R}|\hat{\mathbf{t}}\}$ has a simple interpretation if an $n \times n$ matrix $\hat{\mathbf{R}}$ is introduced that has as coefficients the integers r_{ij} that describe the transformation of the basis vectors $\mathbf{k}_i$ with $\mathbf{R}$:

$$\tilde{\mathbf{R}}\mathbf{k}_i = \sum_{j=1}^{n} r_{ij}\mathbf{k}_j, \quad r_{ij} = \text{integers}. \qquad (19)$$

From (3), (18) and (19), it is straightforward to demonstrate that the superspace density defined in (3) satisfies

$$\rho_s(\hat{\mathbf{R}}\hat{\boldsymbol{\theta}} + \hat{\mathbf{t}}) = \rho_s(\hat{\boldsymbol{\theta}}), \qquad (20)$$

where we use the obvious notation $\hat{\mathbf{R}}\hat{\boldsymbol{\theta}}$ for the point in superspace given by the coordinates $\sum r_{ij}\theta_j$. According to (20), $\{\hat{\mathbf{R}}|\hat{\mathbf{t}}\}$ can be considered a symmetry operation of the superspace density. From (18) or (20), it is obvious that the usual composition law between space-group operations is satisfied:

$$\{\hat{\mathbf{R}}_1|\hat{\mathbf{t}}_1\}\{\hat{\mathbf{R}}_2|\hat{\mathbf{t}}_2\} = \{\hat{\mathbf{R}}_1\hat{\mathbf{R}}_2|\hat{\mathbf{R}}_1\hat{\mathbf{t}}_2 + \hat{\mathbf{t}}_1\}. \qquad (21)$$

From its definition, it can be easily seen that the parallel subspace is invariant for any superspace transformation $\hat{\mathbf{R}}$ included in the superspace group and the vectors $\hat{\boldsymbol{\varepsilon}}_i$ ($i = 1, 2, 3$) transform in the same way as the vectors $\{\mathbf{a}_i\}$ for the corresponding three-dimensional transformation $\mathbf{R}$. On the other hand, the choice of the coefficients γ_{ij} in the matrix $\mathbf{A}$ can always be made in such a way that the internal space is also invariant, so that

$$\mathbf{A}^{-1}\hat{\mathbf{R}}\mathbf{A} = \begin{bmatrix} \mathbf{R} & 0 \\ 0 & \mathbf{R}_I \end{bmatrix}, \qquad (22)$$

where $\mathbf{R}$ is the 3×3 matrix associated with the corresponding three-dimensional rotation in the basis $\{\mathbf{a}_i\}$ and $\mathbf{R}_I$ is an $(n-3)$-dimensional matrix. In the rest of the paper, we assume that the transformation $\mathbf{A}$ has been chosen so that (22) is fulfilled and that, within this choice, the ASs are parallel to the defined internal space.

4. Parametrization of the atomic surfaces

According to (20), analogous to what happens in ordinary crystallography for the actual atoms, the set of ASs in the superspace unit cell that describe the superspace density will be symmetry related. As discussed above, in general, an AS μ in the unit cell can be described by some 'centre', $\hat{\boldsymbol{\theta}}_\mu$, a closed domain (relative to $\hat{\boldsymbol{\theta}}_\mu$) in internal space, W_μ, and the atomic occupation probabilities, $p_m(\mu)$; if $\{\mathbf{R}|\hat{\mathbf{t}}\}$ is an operation of the superspace group of the structure, there will also exist an AS ν in the unit cell, with the same occupation probabilities, centred at $\hat{\boldsymbol{\theta}}_\nu = \hat{\mathbf{R}}\hat{\boldsymbol{\theta}}_\mu + \hat{\mathbf{t}} + \hat{\mathbf{l}}$ (with $\hat{\mathbf{l}}$ being some superspace lattice translation), and its domain, W_ν (with respect to $\hat{\boldsymbol{\theta}}_\nu$), related to W_μ by the internal-space rotation $\mathbf{R}_I$ associated with $\mathbf{R}$ ($W_\nu = \mathbf{R}_I W_\mu$).

When the AS occupies a special position for some superspace-group operation, the symmetry-related AS coincides with the original one. In this case, the centre $\hat{\boldsymbol{\theta}}_\mu$ can be chosen so that $\hat{\boldsymbol{\theta}}_\nu = \hat{\boldsymbol{\theta}}_\mu$ and $W_\mu = \mathbf{R}_I W_\mu$. In general, the domain W_μ will conform to the point-group symmetry P_μ defined by the set of operations $\mathbf{R}_I$, associated by (22) with the operations

$\hat{\mathbf{R}}$ that describe the point-group symmetry in superspace of its centre $\hat{\boldsymbol{\theta}}_\mu$.

Given this rotational symmetry, the structure factor of the QC can be expressed as

$$F(\mathbf{H}) = [|\mathbf{A}|/V(\mathbf{a}_i)] \sum_{\mu,m} p_m(\mu) f_m(\mathbf{H})$$
$$\times \sum_{\mathbf{R}} \exp(-\widetilde{\mathbf{RH}}\,\beta_\mu^m \mathbf{RH}) \exp[2\pi i \hat{\mathbf{h}} \cdot (\hat{\mathbf{R}}\hat{\boldsymbol{\theta}}_\mu + \hat{\mathbf{t}})]$$
$$\times \int_{\mathbf{R}_I W_\mu} \mathrm{d}\mathbf{x}_I \exp(2\pi i \mathbf{h}_I \cdot \mathbf{x}_I), \tag{23}$$

where the sum in μ extends to all symmetry-independent ASs in the unit cell and, for each independent AS, the sum in $\{\mathbf{R}|\hat{\mathbf{t}}\}$ is restricted to a minimal set of operations capable of generating the orbit of the symmetry-related AS within the superspace unit cell.

From the viewpoint of optimization of numerical calculations, it is more convenient to express (23) in the form

$$F(\mathbf{H}) = [|\mathbf{A}|/V(\mathbf{a}_i)] \sum_{\mu,m} p_m(\mu) f_m(\mathbf{H})$$
$$\times \sum_{R} \exp(-\widetilde{\mathbf{RH}}\,\beta_\mu^m \mathbf{RH}) \exp[2\pi i \hat{\mathbf{h}} \cdot (\hat{\mathbf{R}}\hat{\boldsymbol{\theta}}_\mu + \hat{\mathbf{t}})]$$
$$\times \int_{W_\mu} \mathrm{d}\mathbf{x}_I \exp[2\pi i (\tilde{\mathbf{R}}_I \mathbf{h}_I) \cdot \mathbf{x}_I]. \tag{24}$$

The domain W_μ of any AS μ is described by its boundaries in internal space. The set of ASs describing a QC can in general be chosen such that their boundaries can be given by two radial functions, $r^\mu_{\rm in}(\varphi_1, \varphi_2, \ldots, \varphi_{n-4})$ and $r^\mu_{\rm ex}(\varphi_1, \varphi_2, \ldots, \varphi_{n-4})$, which define the limits (internal and external, respectively) of the volume occupied by the domain for any direction in the internal space specified by the $n-4$ angles φ_i. These radial functions are defined with respect to the centre of the AS whose position in the superspace unit cell determines the point-group symmetry to which the AS should conform.

The rotational relation $W_\nu = \mathbf{R}_I W_\mu$, between the domains of two symmetry-related ASs, implies the following relation between their boundary radial functions:

$$r^\nu_j(\varphi_1, \ldots, \varphi_{n-4}) = r^\mu_j[\mathbf{R}_I^{-1}(\varphi_1, \ldots, \varphi_{n-4})], \quad j = \text{in., ex.,} \tag{25}$$

where $\mathbf{R}_I^{-1}(\varphi_1, \ldots, \varphi_{n-4})$ represents the set of angles that define the direction in the internal space obtained by the action of the internal-space rotation $\mathbf{R}_I^{-1}$ over the one given by $(\varphi_1, \ldots, \varphi_{n-4})$.

For superspace-group operations keeping invariant the AS ($\nu = \mu$), the symmetry relation (25) becomes an invariance equation for the radial function and, therefore, a symmetry restriction on the form of the AS boundaries in internal space. If P_μ is the point group of the AS in internal space, as defined above, the boundary radial functions should be P_μ invariant. The obvious choice for a continuous parametrization of these radial functions are the so-called invariant 'surface harmonics' (Bradley & Cracknell, 1972), *i.e.* symmetry-adapted radial functions that transform according to the identity representation of the point group P_μ. If $\{Z_i(\varphi_1, \ldots, \varphi_{n-4})\}$ is a complete set of orthonormalized P_μ-invariant surface harmonics, the radial functions can then be expressed in terms of a linear combination of them:

$$r^\mu_j(\varphi_1, \ldots, \varphi_{n-4}) = \sum_{i=1}^{\infty} a_i^{\mu,j} Z_i(\varphi_1, \ldots, \varphi_{n-4}), \quad j = \text{in., ex.} \tag{26}$$

In general, the set of functions $Z_i(\varphi_1, \ldots, \varphi_{n-4})$ can be chosen such that they are ordered according to an increasing degree of complexity. In most of the QC, the ASs are centred at points of the superspace unit cell with very high symmetry; this means, in general, that the point-group symmetry of the AS in internal space P_μ is also equally high. This situation guarantees that, in most cases, the number of invariant surface harmonics up to a high order of complexity is quite small and a truncated expansion (26) with a few terms can be enough to describe the AS surface boundaries with sufficient accuracy.

The thermal tensors $\boldsymbol{\beta}_\mu^m$ in (24) are also symmetry-restricted by the condition

$$\tilde{\mathbf{R}}\boldsymbol{\beta}_\mu^m \mathbf{R} = \boldsymbol{\beta}_\mu^m \tag{27}$$

for all transformations $\mathbf{R}$ belonging to the AS point-group symmetry.

For all relevant AS point-groups in every QC type (icosahedral or polygonal), the program *QUASI* either contains or builds normalized surface harmonics Z_i (up to some order). For each point group, the function variables refer to an orthogonal coordinate system with a fixed chosen orientation with respect to the point-group operations. The orientations chosen in each case are indicated in § 5. The actual orientation in internal space of the point-group of each symmetry-independent AS must be taken into account in the calculations by introducing a matrix $\boldsymbol{\Gamma}$ that relates the internal coordinates $\mathbf{x}_I$, defined by the transformation $\mathbf{A}$, with a coordinate system having the required standard orientation (with respect to the AS point-group symmetry operations). In other words, for each symmetry independent AS μ, an orthogonal $(n-3) \times (n-3)$ matrix, $\boldsymbol{\Gamma}_\mu$, must be introduced, such that the set of matrices $\boldsymbol{\Gamma}_\mu \mathbf{R}_I \boldsymbol{\Gamma}_\mu^{-1}$, for the operations $\mathbf{R}_I$ [see (22)] belonging to P_μ, have the matricial form associated with the point-group operations in the standard coordinate system chosen in the program for describing the functions Z_i.

The general expression for the structure factor used in the program is, then,

$$\begin{aligned} F(\mathbf{H}) = {} & [|\mathbf{A}|/V(\mathbf{a}_i)] \sum_{\mu,m} p_m(\mu) f_m(\mathbf{H}) \\ & \times \sum_R \exp(-\widetilde{\mathbf{RH}}\,\boldsymbol{\beta}_\mu^m \mathbf{RH}) \\ & \times \exp[2\pi i\hat{\mathbf{h}} \cdot (\hat{\mathbf{R}}\hat{\boldsymbol{\theta}}_\mu + \hat{\mathbf{t}})] \int_\Omega \mathrm{d}\varphi_1 \ldots \mathrm{d}\varphi_{n-4} \\ & \times \int \Big\{ \sum_i a_i^{\mu,\mathrm{ex}} Z_i(\varphi_1,\ldots,\varphi_{n-4}) \mathrm{d}r\, J(r,\varphi_1,\ldots,\varphi_{n-4}) \\ & \times \exp[2\pi i(\tilde{\boldsymbol{\Gamma}}_\mu{}^{-1}\tilde{\mathbf{R}}_I\mathbf{h}_I)\cdot \mathbf{x}_I] \\ & \times \sum_i a_i^{\mu,\mathrm{in}} Z_i(\varphi_1,\ldots,\varphi_{n-4}) \Big\}, \end{aligned} \quad (28)$$

where $J(r, \varphi_1,\ldots,\varphi_{n-4})$ is the Jacobian of the transformation to generalized spherical variables.

The structural parameters that specify the model are then the wavevectors $\{\mathbf{k}_i\}$, the centres of the independent AS $\boldsymbol{\theta}_\mu$, the occupation probabilities $p_m(\mu)$ in each AS, the thermal tensors $\boldsymbol{\beta}_\mu^m$, and the coefficients $a_i^{\mu,\mathrm{in}}$ and $a_i^{\mu,\mathrm{ex}}$.

5. Polygonal quasicrystals

Polygonal QCs are those for which the set of modulation wave vectors $\mathbf{k}_i$ in the indexing (1) can be chosen in such a form that $(n-1)$ vectors lie on a plane and are related by a p-fold rotational axis, while the nth vector is directed along this axis, perpendicular to the plane. Up to now, octagonal, decagonal and dodecagonal quasicrystals ($p = 8$, 10 and 12, respectively) have been obtained. In each of these cases, the rank n of the diffraction diagram is 5.

In the following, possible convenient choices (Steurer, 1990) of the indexing wave vectors $\{\mathbf{k}_i\}$ and matrix $\mathbf{A}$ for the three types of polygonal QC when the refinement program is used are listed (the wave vectors are referred to a Cartesian coordinate system with unit vectors $|\mathbf{a}_1^*| = |\mathbf{a}_2^*|$ and $|\mathbf{a}_3^*| \neq |\mathbf{a}_1^*|$).

(*a*) *Octagonal case*

$$\mathbf{k}_i = (\cos(2\pi i/8), \sin(2\pi i/8), 0), \quad i = 1, \ldots, 4,$$
$$\mathbf{k}_5 = (0, 0, 1).$$

The rows of the matrix $\mathbf{A}$ are the five-dimensional vectors

$$\mathbf{d}_i = (\cos(2\pi i/8), \sin(2\pi i/8), 0, \cos(6\pi i/8), \sin(6\pi i/8)), \quad i = 1, \ldots, 4,$$
$$\mathbf{d}_5 = (0, 0, 1, 0, 0).$$

So the simplified expression for the matrix is

$$\mathbf{A} = \begin{bmatrix} 2^{-1/2} & 2^{-1/2} & 0 & -2^{-1/2} & 2^{-1/2} \\ 0 & 1 & 0 & 0 & -1 \\ -2^{-1/2} & 2^{-1/2} & 0 & 2^{-1/2} & 2^{-1/2} \\ -1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}.$$

(*b*) *Decagonal case*

$$\mathbf{k}_i = (\cos(2\pi i/5), \sin(2\pi i/5), 0), \quad i = 1, \ldots, 4,$$
$$\mathbf{k}_5 = (0, 0, 1).$$

The rows of the matrix $\mathbf{A}$ are

$$\mathbf{d}_i = (\cos(2\pi i/5), \sin(2\pi i/5), 0, \cos(6\pi i/5), \sin(6\pi i/5)), \quad i = 1, \ldots, 4,$$
$$\mathbf{d}_5 = (0, 0, 1, 0, 0),$$

therefore,

$$\mathbf{A} = \begin{bmatrix} (\tau-1)/2 & (2+\tau)^{1/2}/2 & 0 & -\tau/2 & -[(\tau-1)(2+\tau)^{1/2}]/2 \\ -\tau/2 & [(\tau-1)(2+\tau)^{1/2}]/2 & 0 & (\tau-1)/2 & (2+\tau)^{1/2}/2 \\ -\tau/2 & -[(\tau-1)(2+\tau)^{1/2}]/2 & 0 & (\tau-1)/2 & -(2+\tau)^{1/2}/2 \\ (\tau-1)/2 & -(2+\tau)^{1/2}/2 & 0 & -\tau/2 & [(\tau-1)(2+\tau)^{1/2}]/2 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix},$$

τ being the 'golden mean', $(1 + 5^{1/2})/2$.

(*c*) *Dodecagonal case*

$$\mathbf{k}_i = (\cos(2\pi i/12), \sin(2\pi i/12), 0), \quad i = 1, \ldots, 4,$$
$$\mathbf{k}_5 = (0, 0, 1).$$

The rows of the matrix $\mathbf{A}$ are

$$\mathbf{d}_i = (\cos(2\pi i/12), \sin(2\pi i/12), 0, \cos(10\pi i/12), \sin(10\pi i/12)), \quad i = 1, \ldots, 4,$$
$$\mathbf{d}_5 = (0, 0, 1, 0, 0),$$

therefore,

$$\mathbf{A} = \begin{bmatrix} 3^{1/2}/2 & 1/2 & 0 & -3^{1/2}/2 & 1/2 \\ 1/2 & 3^{1/2}/2 & 0 & 1/2 & -3^{1/2}/2 \\ 0 & 1 & 0 & 0 & 1 \\ -1/2 & 3^{1/2}/2 & 0 & -1/2 & -3^{1/2}/2 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}.$$

The above choices for the indexing wave vectors and matrix $\mathbf{A}$ are recommended, for with them the resulting matrices $\mathbf{R}_I$ are orthogonal, but the program allows any other choice compatible with condition (22) for all point-group operations in the QC superspace group, provided that the input matrices $\boldsymbol{\Gamma}$ are in accordance with this choice.

In the case of a polygonal QC of rank 5, such as octagonal, decagonal and dodecagonal QCs, the point-group symmetry of the two-dimensional AS in internal space is either a rotational symmetry of a certain order (N), a symmetry line (m) or both (Nm). For instance, in a decagonal QC, ASs may have point-group symmetries like 1, 5, 10, m, $5m$ or $10m$. In this case, the 'surface harmonics' $Z_j(\varphi)$ can be simply chosen as the successive normalized cosine and sine functions in a symmetry-restricted Fourier series:

$$r(\varphi) = [a_0/(2\pi)^{1/2}] + \sum_{j=1}^{\infty} a_j\pi^{-1/2}\cos(N_j\varphi)$$
$$+ \sum_{j=1}^{\infty} b_j\pi^{-1/2}\sin(N_j\varphi). \qquad (29)$$

If the point group of an AS contains one or more symmetry lines, the orientation of the standard coordinate system is oriented so that the angle φ is relative to one of the symmetry lines and therefore the sine functions in (29) are dropped; the actual orientation of this reference symmetry line with respect to the basis in internal space defined by the transformation **A** is taken into account through the matrix **Γ**, as explained in the previous section.

6. Icosahedral quasicrystals

In the case of an icosahedral QC, the rank of the diffraction diagram is 6. A possible choice for the indexing wave vector [described in a cubic (orthogonal) vector basis with a_3^* and a_2^* directed along a fivefold axis and a twofold axis, respectively, of the diffraction diagram] is

$$\mathbf{k}_1 = 2^{-1/2}(0,0,1)$$
$$\mathbf{k}_i = 2^{-1/2}((2/5^{1/2})\cos(2\pi i/5), (2/5^{1/2})\sin(2\pi i/5), (1/5^{1/2})), \quad i = 2,...,6.$$

The rows of the matrix **A** can then be chosen as,

$$\mathbf{d}_1 = 2^{-1/2}(0,0,1,0,0,1)$$
$$\mathbf{d}_i = 2^{-1/2}((2/5^{1/2})\cos(2\pi i/5), (2/5^{1/2})\sin(2\pi i/5), (1/5^{1/2}), -(2/5^{1/2})\cos(4\pi i/5), -(1/5^{1/2})\sin(4\pi i/5), (-1/5^{1/2})), \quad i = 2,...,6.$$

Therefore,

$$\mathbf{A} = 10^{-1/2}\begin{bmatrix} 0 & 0 & 2\tau-1 & 0 & 0 & 2\tau-1 \\ -\tau & (\tau-1)(2+\tau)^{1/2} & 1 & -(\tau-1) & (2+\tau)^{1/2} & -1 \\ -\tau & -(\tau-1)(2+\tau)^{1/2} & 1 & -(\tau-1) & -(2+\tau)^{1/2} & -1 \\ \tau-1 & -(2+\tau)^{1/2} & 1 & \tau & (\tau-1)(2+\tau)^{1/2} & -1 \\ 2 & 0 & 1 & -2 & 0 & -1 \\ \tau-1 & (2+\tau)^{1/2} & 1 & \tau & -(\tau-1)(2+\tau)^{1/2} & -1 \end{bmatrix}.$$

As in the case of a polygonal QC, any other choice of wave vectors and matrix **A** compatible with condition (22) is possible.

The internal space is three-dimensional; the spherical harmonics referred to an orthogonal basis are then a natural choice to express any radial function:

$$r(\theta,\varphi) = \sum_{l,m} C_{lm}Y_l^m(\theta,\varphi). \qquad (30)$$

The subspaces of functions associated with a given index l are invariant for any proper or improper rotation $\mathbf{R}_l$. Hence, the set of symmetry-adapted orthonormalized functions (invariant for the point-group symmetry of the AS) can be chosen conforming to this previous decomposition:

$$r(\theta,\varphi) = \sum_{l,i} a_{li}Z_{li}(\theta,\varphi), \qquad (31)$$

with

$$Z_{li}(\theta,\varphi) = \sum_{m=-l}^{l} z_{lm}(i)Y_l^m(\theta,\varphi). \qquad (32)$$

The coefficients a_{li} constitute the continuous parameters to be determined and fitted in the structural diffraction analysis, while the coefficients $z_{lm}(i)$ are determined by the point-group symmetry of the AS and the normalization condition of the functions Z_{li}. The index i allows for the eventual existence of several orthogonal invariant functions within the same subspace l. Obviously, the zeroth-order term in (31) is, in any case, the spherical harmonic $Y_0^0(\theta,\varphi)$, corresponding to a spherical surface. If the point group is large enough, there will be many subspaces l where no invariant function exists. For instance, if the site point-group symmetry of the AS is $\bar{5}\bar{3}m$, up to $l = 15$ only a single invariant function exists for $l = 0$, 6, 10 and 12 (Cohan, 1958; Laporte, 1948).

The possible AS point groups that can be considered by the program are listed in Table 1. The number of invariant surface harmonics up to $l = 16$ for each point group and the orientation of the chosen coordinate system are indicated in the same table; their analytical expressions in terms of the spherical harmonics are listed in Tables 2 and 3. For the higher symmetries, the harmonics were calculated using the method proposed in another context by Michel (1992). The lowest-order functions were checked by comparison with the results of Cohan

Table 1. *Point groups that, in the program QUASI, can be associated with the symmetry of the atomic surfaces of icosahedral quasicrystals*

The second column indicates the generators for each possible point group in the standard coordinate system to which the spherical coordinates of the radial functions refer. In the last column, the limitations on the number of invariant surface harmonics for each point group are summarized; the lowest subspaces *l* that contain invariant surface harmonics and their numbers (in brackets) are listed.

Point group	Generators	Harmonic surfaces
$\bar{5}\bar{3}m$	$\bar{C}_5=\begin{bmatrix}-\cos(2\pi/5) & \sin(2\pi/5) & 0\\ -\sin(2\pi/5) & -\cos(2\pi/5) & 0\\ 0 & 0 & -1\end{bmatrix}, \quad C_2=\begin{bmatrix}-1/5^{1/2} & 0 & 2/5^{1/2}\\ 0 & -1 & 0\\ 2/5^{1/2} & 0 & 1/5^{1/2}\end{bmatrix}$	0(1), 6(1), 12(1), 16(1)
532	$C_5=\begin{bmatrix}\cos(2\pi/5) & -\sin(2\pi/5) & 0\\ \sin(2\pi/5) & \cos(2\pi/5) & 0\\ 0 & 0 & 1\end{bmatrix}, \quad C_2=\begin{bmatrix}-1/5^{1/2} & 0 & 2/5^{1/2}\\ 0 & -1 & 0\\ 2/5^{1/2} & 0 & 1/5^{1/2}\end{bmatrix}$	0(1), 6(1), 12(1), 15(1), 16(1)
$\bar{5}m$	$\bar{C}_5=\begin{bmatrix}-\cos(2\pi/5) & \sin(2\pi/5) & 0\\ -\sin(2\pi/5) & -\cos(2\pi/5) & 0\\ 0 & 0 & -1\end{bmatrix}, \quad m=\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$	0(1), 2(1), 4(1), 6(2), 8(2), 10(3), 12(3), ...
$5m$	$C_5=\begin{bmatrix}\cos(2\pi/5) & -\sin(2\pi/5) & 0\\ \sin(2\pi/5) & \cos(2\pi/5) & 0\\ 0 & 0 & 1\end{bmatrix}, \quad m=\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$	0(1), 1(1), 2(1), 3(1), 4(1), 5(2), 6(2), 7(2), 8(2), 9(2), 10(3), ...
$\bar{3}m$	$\bar{C}_3=\begin{bmatrix}-\cos(2\pi/3) & \sin(2\pi/3) & 0\\ -\sin(2\pi/3) & -\cos(2\pi/3) & 0\\ 0 & 0 & -1\end{bmatrix}, \quad m=\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$	0(1), 2(1), 4(2), 6(3), 8(3), 10(4), 12(5), ...
$3m$	$C_3=\begin{bmatrix}\cos(2\pi/3) & -\sin(2\pi/3) & 0\\ \sin(2\pi/3) & \cos(2\pi/3) & 0\\ 0 & 0 & 1\end{bmatrix}, \quad m=\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$	0(1), 1(1), 2(1), 3(2), 4(2), 5(2), 6(3), 7(3), 8(3), 9(4), 10(4), ...

(1958) and Laporte (1948). A graphical representation of the lowest three surface harmonics (besides the sphere) for the point-group symmetry $\bar{5}\bar{3}m$ is given in Figs. 1 and 2, where a section of each harmonic (of arbitrary amplitude) superposed on a sphere is shown. A three-dimensional representation of the second harmonic is also shown in Fig. 3. It can be seen that these three lowest surface harmonics already contain 'short-wavelength' components and their combination can be expected to be enough to reproduce the contour of the AS up to an accuracy consistent with the experimental resolution. Significant fluctuations of much higher order on the surfaces limiting the AS domains are not expected, as they would imply quite intense Bragg reflections for high values of $\mathbf{h}_\perp$ and this is not observed experimentally.

7. The program *QUASI*

The program *QUASI* minimizes the quantity χ^2, defined as

$$\begin{aligned}\chi^2 = {} & \left\{\sum_{\mathbf{H}} w_{\mathbf{H}}[F_o(\mathbf{H}) - k|F_c(\mathbf{H})|]^2 \Big/ \sum_{\mathbf{H}} w_{\mathbf{H}} F_o^2(\mathbf{H})\right\}\\ & + w_c\left[\sum_m (C_o^m - C_c^m)^2 \Big/ \sum_m (C_o^m)^2\right]\\ & + w_\rho[(\rho_o - \rho_c)^2/\rho_o^2], \qquad (33)\end{aligned}$$

which measures the deviation of the structural model with respect to the experimental evidence. $w_{\mathbf{H}}$ represents the weight of each experimental structure-

Table 2. *Invariant surface harmonics for the point groups 5m and 3m for any subspace l*

The functions $Y_l^{m,c}(\theta,\varphi)$ and $Y_l^{m,s}(\theta,\varphi)$ are connected with the spherical harmonics by the relations

$$Y_l^{m,c}(\theta,\varphi) = 2^{-1/2}[Y_l^m(\theta,\varphi) + Y_l^{-m}(\theta,\varphi)]$$

$$Y_l^{m,s}(\theta,\varphi) = i2^{-1/2}[Y_l^m(\theta,\varphi) - Y_l^{-m}(\theta,\varphi)].$$

The spherical harmonics are normalized and chosen in such a way that they are positive when both arguments are infinitesimal and positive. The surface harmonics for the point groups $\bar{5}m$ and $\bar{3}m$ coincide with those of the corresponding noncentred group for *l* even and do not exist for *l* odd. [*x*] means the integer part of *x*.

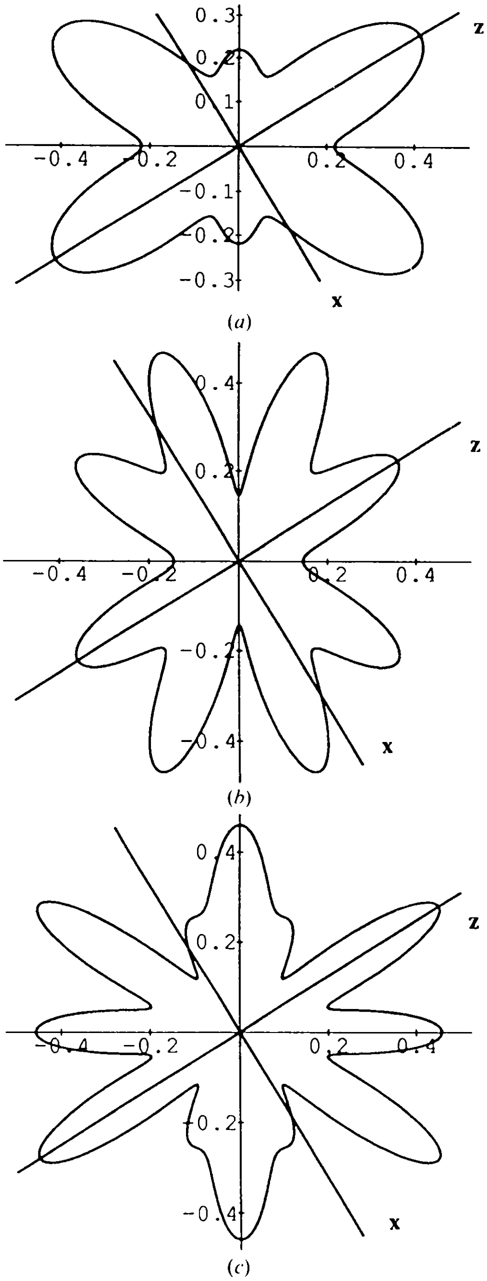
Point group	Harmonic surfaces
$5m$	$Y_l^0(\theta,\varphi),\ Y_l^{5i,c}(\theta,\varphi) \quad i = 1, \ldots, [l/5]$
$3m$	$Y_l^0(\theta,\varphi),\ Y_l^{3i,c}(\theta,\varphi) \quad i = 1, \ldots, [l/3]$

Table 3. *Surface harmonics for the point group* 532 *up to* $l = 16$

The functions $Y_l^{m,c}(\theta,\varphi)$ and $Y_l^{m,s}(\theta,\varphi)$ are defined in Table 2 The spherical harmonics are chosen with the same criterion as in Table 2. The surface harmonics for the centred group $\bar{5}\bar{3}m$ are the same except for those with *l* odd that are forbidden.

1	$l=0$	$Y_0^0(\theta,\varphi)$
2	$l=6$	$(11^{1/2}/5)Y_6^0(\theta,\varphi)+(14^{1/2}/5)Y_6^{5,c}(\theta,\varphi)$
3	$l=10$	$[247^{1/2}/25(3^{1/2})]Y_{10}^0(\theta,\varphi)-(418^{1/2}/25)Y_{10}^{5,c}(\theta,\varphi)$ $+[374^{1/2}/25(3^{1/2})]Y_{10}^{10,c}(\theta,\varphi)$
4	$l=12$	$[3(119^{1/2})/25(5^{1/2})]Y_{12}^0(\theta,\varphi)+[2(143^{1/2})/25(5^{1/2})]Y_{12}^{5,c}(\theta,\varphi)$ $+[1482^{1/2}/25(5^{1/2})]Y_{12}^{10,c}(\theta,\varphi)$
5	$l=15$	$[-10(3335^{1/2})/871028^{1/2}]Y_{15}^{5,s}(\theta,\varphi)+(1914^{1/2}/871028^{1/2})Y_{15}^{10,s}(\theta,\varphi)$ $+[10(1001^{1/2})/871028^{1/2}]Y_{15}^{15,s}(\theta,\varphi)$
6	$l=16$	$[4(5890^{1/2})/125(30^{1/2})]Y_{16}^0(\theta,\varphi)-[102765^{1/2}/125(30^{1/2})]Y_{16}^{5,c}(\theta,\varphi)$ $-[169694^{1/2}/125(30^{1/2})]Y_{16}^{10,c}(\theta,\varphi)$ $+[102051^{1/2}/125(30^{1/2})]Y_{16}^{15,c}(\theta,\varphi)$

factor modulus (F_o); k is a global scale factor; ρ_o and ρ_c are, respectively, the experimental and calculated mass densities in g cm^{-3}; C_o^m and C_c^m are the experimental and calculated relative weights of atom type m in the QC composition ($\sum C^m = 1$). Therefore, the refinement of the structural model consists of the minimization of a weighted R factor (wR) for the moduli of the structure factors, corrected by some penalty functions that control the goodness of the structural model with respect to the QC density and

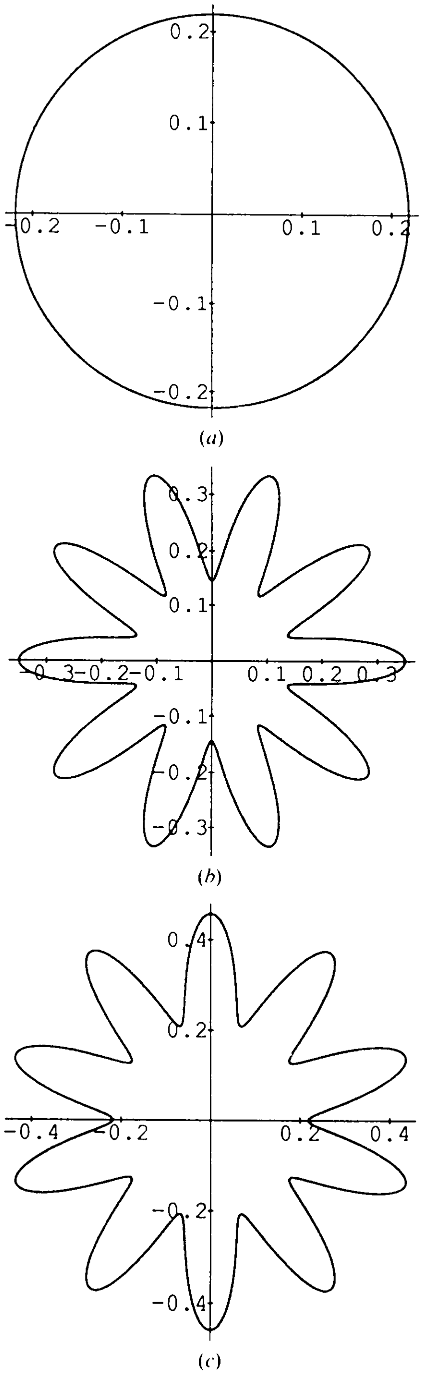


(a)

(b)

(c)

Fig. 1. Sections parallel to two fivefold axes of the (a) first, (b) second and (c) third surface harmonics of $\bar{5}\bar{3}m$ symmetry described in Table 3 and corresponding to $l = 6$, 10 and 12, respectively. The harmonics are given with an arbitrary amplitude and are superposed on a sphere of arbitrary radius. The axes are parallel to two twofold axes and the x and z axes are those corresponding to the standard coordinate system to which the spherical coordinates of Table 3 refer.



(a)

(b)

(c)

Fig. 2. Sections perpendicular to a fivefold axis of the same surface harmonics as in Fig. 1. The axes are the x and y axes of the standard coordinate system to which the spherical coordinates in Table 3 refer.

its chemical composition. The weights of these density and composition restraints on the structural model are controlled by the input parameters w_ρ and w_c. Although a pure minimization of wR is possible by simply setting w_ρ and w_c to zero, this is usually inadequate because, in contrast to normal crystals, in the QC case the chemical composition and density of the structure depend on the structural parameters to be adjusted. The structure-factor formula used for calculating the structure-factor values F_c is (28). The integrals in internal space of the radial coordinate are computed by the Gauss method.

Apart from the global scale factor k, adjustable structural parameters in the refinement can be the occupation probabilities $p_m(\mu)$ for each independent AS μ, the amplitudes $a_i^{\rm in}$ and $a_i^{\rm ex}$ of the harmonic surfaces Z_i in the superpositions of type (26) that describe the internal and external contours of each AS domain and the symmetry-restricted thermal tensors $\boldsymbol{\beta}_\mu^m$. The AS centres, $\boldsymbol{\theta}_m$, are supposed in any case to be fully restricted by symmetry and are not susceptible to being refined.

The minimization process can be done either by a full least-squares process, or by use of a simplex algorithm (Nelder & Mead, 1965); this last method is more satisfactory when the number of observations is particularly low. In both cases, some constraints can be introduced in the refinement parameters. For instance, the external contour of an AS can be forced to coincide with the internal contour of another AS centred at the same point, as seems to happen for several ASs in the icosahedral AlPdMn system (Boudard *et al.*, 1992). Typically, thermal tensors $\boldsymbol{\beta}_\mu^m$ are constrained to be equal for all atom types within each AS (independent of m); however, a more general case can be introduced in the refinement where thermal tensors for each atom type within an AS are constrained to be proportional with fixed proportionality factors different from 1. Thus, expected differences of thermal displacement parameters owing to strong mass differences among atom types can be taken into account. The program allows refinement using several independent data sets simultaneously, for instance X-ray and neutron data.

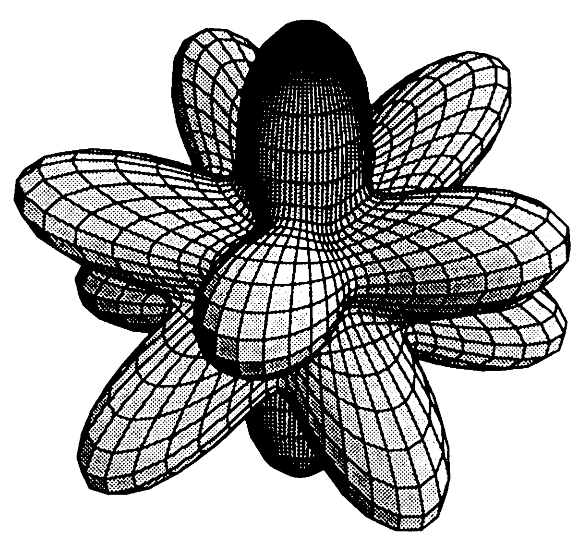


Fig. 3. Three-dimensional representation of the first ($l = 6$) surface harmonic of symmetry $\bar{5}\bar{3}m$ superposed with arbitrary amplitude on a sphere.

The essential data input includes the vector system $\{\mathbf{a}_i^*\}$ defined in (7), the transformation matrix $\mathbf{A}$ described in (9) and (10), the matrices $\hat{\mathbf{R}}$ and translations $\hat{\mathbf{t}}$ corresponding to the generators of the QC superspace group, the number of symmetry-independent ASs, their point-group symmetry and positions of their centres, $\boldsymbol{\Gamma}$ matrices describing the orientation of each point group in internal space with respect to the standard coordinate system chosen by the program, the atom types present in each AS, the number of surface harmonics to describe the inner and outer limits of each AS, and the number of points to be used in the numerical integrations.

If the minimization procedure is done using the simplex algorithm, the simplicity of the method allows additional terms in the function to be minimized without much effort. For instance, an additional penalty function that controls the goodness of the structural model with respect to unphysical interatomic distances can be optionally included in (33). This function is defined as

$$f = \sum_{\mu} \sum_{\nu} w_{\mu\nu} \int_{W_\mu} {\rm d}\mathbf{x}_l \xi_\nu(\mathbf{X}_l), \qquad (34)$$

where the first sum extends to all independent ASs and the second one refers to all ASs in superspace that have their centres (relative to the centre of AS μ) situated at distances in internal space shorter than a certain input parameter and in parallel space shorter than a value equivalent to a minimal physically reasonable distance $d_{\mu\nu}$, for each pair of ASs ν,μ. The function ξ_ν is 1 when $\mathbf{x}_l$ belongs to the domain W_ν of AS ν and zero otherwise. $w_{\mu\nu}$ is an input weight for each relevant pair of ASs. Therefore, the parameter f is different from zero if the projections in internal space of two ASs, whose point projections in parallel space are situated at unphysical distances, superpose. The value of f increases with the amount of this superposition (number of atom pairs at unphysical distances). This additional control parameter can be useful in cases where realistic atomic distances clearly should limit the forms of ASs that are very close (de Boissieu, Janot, Dubois, Audier & Dubois, 1991).

In summary, the program *QUASI* allows the refinement of the contours defining the ASs that describe in the superspace a QC structure with continuous symmetry-adapted parameters. The refinement is based on a fitting of the structural model to experimental diffraction data and observed density and chemical composition, under the condition that the ASs are parallel to the internal space. No additional *a priori* assumption on the form of the ASs is used, except that the deviations of the AS contours from a spherical shape do not include significant very short wave components. The parametrization of the ASs does not restrict *a priori* their form, except in its degree of complexity or fine detail, which is limited by the number of terms considered in expansion (26). This limit should be consistent with the resolution power of the experiment, and in each case can be decided from the comparison of tentative fittings with different numbers of surface harmonics for the AS radial functions. The program requires an initial very approximate guess of the structure in terms of spherical ASs of which only the symmetry centres must be known with confidence. The fitting process can refine the structural model if the experimental accuracy is enough for resolving the form of the AS surfaces up to the detail assumed by the number of harmonics considered. The important point from this fitting procedure is that it yields the standard deviations of the structural parameters adjusted and therefore a clear picture of the degree of experimental accuracy and ambiguities of the refined model is obtained. If the description of the QC structure is wanted in terms of ASs with their shapes more or less fixed by physical or geometrical arguments, a previous 'free' refinement following the method of the program *QUASI* can also be very useful. In general, the resulting standard deviations for the adjusted parameters describing the AS contours will be a good guide to the limits of any further idealization of the AS shapes.

The program *QUASI* has been successfully applied to the determination of the structure of icosahedral $Al_{57}Li_{32}Cu_{11}$, using published X-ray and neutron data (de Boissieu, Janot, Dubois, Audier & Dubois, 1991; van Smaalen & de Boer, 1991) and the results will be published in a subsequent paper. The program is available from the authors upon request.

This work has been partially supported by the UPV (project UPV 063.310-E081-91) and the DGICYT (project PB92-0446). LE is indebted to the Basque Government for financial support.

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