Local anisotropy of icosahedral quasicrystals

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A local anisotropy of the dielectric susceptibility of a quasicrystal can radically change the extinction rules and polarization properties of the observable Bragg reflections, particularly for quasicrystals with nonsymmorphic symmetry space groups.

The high symmetry of icosahedral quasicrystals (point symmetry 532 or $\overline{53}(2/m)$; Refs. 1–4) makes their average dielectric susceptibility isotropic. In the x-ray wavelength region, however, the local properties of quasicrystals may be manifested. At least three physical quantities pertinent to the interaction of x radiation and Mössbauer radiation with matter are sensitive to a local anisotropy: the dielectric susceptibility,[5,6] the anisotropy of the Debye–Waller factor (or Lamb–Mössbauer factor), and the gradient of the electric field at a Mössbauer nucleus.[7] The symmetry of these quantities and their spatial distribution are determined not by the point symmetry group but by the space symmetry group. The physical reason for their anisotropy is an asymmetry of the local surroundings of the atoms. A study of these surroundings is very important for reaching an understanding of the structure of quasicrystals. In the present letter we are concerned primarily with the dielectric susceptibility,[1)] which varies quasiperiodically in space and which gives rise to Bragg reflections.

In ordinary crystals, the existence of a local anisotropy of the susceptibility (LSA) eliminates extinctions from certain reflections which are associated with helical axes and/or grazing-reflection planes. It also leads to a change in the polarization properties of reflections.[5–8] The general form of the LSA tensor can be found for any of the 230 crystallographic groups. The arrangement of atoms in quasicrystals and the corresponding space groups are not yet known exactly. To find the form of the LSA tensor, we will use one possible model of a quasicrystal: a projection from a six-dimensional space.[1,2] We assume that we have a six-dimensional periodic structure which corresponds to one of the icosahedral symmetry groups listed in Refs. 1–4. The LSA tensor of such a structure is a six-dimensional periodic second-rank tensor which is invariant under all symmetry operations of the given group. This tensor is then projected, in the standard way for quasicrystals, onto a three-dimensional space, in which a *quasiperiodic* distribution of a tensor quantity arises. In this manner we find that form of the LSA tensor of the quasicrystal which is the most general form for the given model. Its Fourier harmonics determine the intensity and polarization properties of the reflections, which are extremely unusual, as we will see below.

The tensor $\hat{\chi}(\mathbf{R})$, which is perioidic in the six-dimensional space and which is invariant under the given symmetry group, is constructed in precisely the same way as in the three-dimensional case.[6,8] Below we will discuss only icosahedral groups which

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contain the fivefold, threefold, and twofold rotation operations $\hat{A}_5$, $\hat{A}_3$, and $\hat{A}_2$ and also, in the case of centrally symmetric groups, the inversion operation $\hat{I}$ (we are using the notation of Ref. 2). In nonsymmorphic groups, the rotation $\hat{A}_5$ is accompanied by a translation with a vector a_5. For an arbitrary reciprocal-lattice vector $\mathbf{H} = 2\pi(n_1,n_2,n_3,n_4,n_5,n_6)$, where n_i are the six-dimensional Miller indices, the Fourier harmonic $\hat{\chi}_{\mathbf{H}}$ of the tensor $\hat{\chi}(\mathbf{R})$ is an arbitrary complex symmetric tensor. For any equivalent vector $\mathbf{H}'$, which is related to $\mathbf{H}$ by symmetry operation $\hat{A}(\mathbf{H}' = \hat{A}\,\mathbf{H})$, the tensor $\hat{\chi}_{\mathbf{H}'}$ is no longer arbitrary and is instead expressed in terms of $\hat{\chi}_{\mathbf{H}}$:

$$\hat{\chi}_{\mathbf{H}'} = \hat{A}\hat{\chi}_{\mathbf{H}}\hat{A}^{T}\exp(i\mathbf{H}\,\mathbf{a}_{A}), \tag{1}$$

where a_A is the translation vector which corresponds to the operation $\hat{A}$, and the superscript T means transposition.[2] If the vector $\mathbf{H}$ is invariant under operation $\hat{A}$, then we have $\mathbf{H}' = \mathbf{H}$, and relation (1) imposes restrictions on the tensor form of $\hat{\chi}_{\mathbf{H}}$. Consequently, by specifying $\hat{\chi}_{\mathbf{H}}$ only for nonequivalent $\mathbf{H}$ and determining the other harmonics from (1), we find the most general form of the tensor $\hat{\chi}(\mathbf{R})$ which is invariant under the given space group.

What restrictions on the form of $\hat{\chi}_{\mathbf{H}}$ are imposed for reflections directed along fivefold axes? Selecting the (100000) axis, we easily find from (1) that for $\mathbf{H} = 2\pi(n,l,l,l,l,l)$ the tensor $\hat{\chi}_{\mathbf{H}}$ is

$$\hat{\chi}_{\mathbf{H}} = \begin{pmatrix} b_1^H\delta_{m0} & b_2^H & b_2^H s_m & b_2^H s_m^2 & b_2^H s_m^3 & b_2^H s_m^4 \\ b_2^H & b_3^H & b_4^H s_m^3 & b_5^H s_m & b_5^H s_m^4 & b_4^H s_m^2 \\ b_2^H s_m & b_4^H s_m^3 & b_3^H s_m & b_4^H s_m^4 & b_5^H s_m^2 & b_5^H \\ b_2^H s_m^2 & b_5^H s_m & b_4^H s_m^4 & b_3^H s_m^2 & b_4^H & b_5^H s_m^3 \\ b_2^H s_m^3 & b_5^H s_m^4 & b_5^H s_m^2 & b_4^H & b_3^H s_m^3 & b_4^H s_m \\ b_2^H s_m^4 & b_4^H s_m^2 & b_5^H & b_5^H s_m^3 & b_4^H s_m & b_3^H s_m^4 \end{pmatrix}, \tag{2}$$

where $b_1^H,\ldots,b_5^H$ are arbitrary complex numbers; δ_{ik} is the Kronecker delta; and $s_m = \exp(2\pi i m/5)$, where $m = 0, \pm 1, \pm 2$.

The rotation operation $\hat{A}_5$ sends the tensor $\hat{\chi}_{\mathbf{H}}$ into $s_{-m}\hat{\chi}_{\mathbf{H}}$. If the group is symmorphic ($a_5 = 0$), we find from condition (1) that we have $m = 0$ for all reflections $\mathbf{H} = 2\pi(n,l,l,l,l,l)$. If the group is instead nonsymmorphic then by choosing $a_5 = (1/5,2/5,2/5,-1/5,2/5,-1/5)$, we find from (1) and (2) that the allowed value of the parameter m depends on the first index of the reflection:

$$m = n \pmod 5. \tag{3}$$

If follows from (3) that in the case $n = 5k$ (where k is an integer) we have $m = 0$ and $\mathrm{Sp}(\hat{\chi}_{\mathbf{H}}) \neq 0$. In other words, such reflections can exist even in the absence of an anisotropy of the susceptibility.[2,3] Reflections with $n \neq 5k$ can be exited only by virtue of an anisotropy.

We now wish to find the tensor form of $\hat{\chi}_{\mathbf{h}}$ in three-dimensional space. For this purpose we project from a six-dimensional space: $\hat{\chi}_{\mathbf{h}} = \hat{P}\hat{\chi}_{\mathbf{H}}\hat{P}^T$ and $\mathrm{h} = \hat{P}\mathbf{H}$, where $\mathbf{h}$ is a three-dimensional projection of the vector $\mathbf{H}$, and $\hat{P}$ is the projection matrix. From (2) we find the following expressions for the tensor Fourier harmonics $\hat{\chi}_{\mathbf{h}}$ in the three-dimensional space (the z axis runs parallel to $\mathbf{h}$):

$$\hat{\chi}_{\mathbf{h}} = \begin{cases} b_1^H \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + (b_3^H + \tau^{-1} b_4^H - \tau b_5^H) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, & \text{if} \quad m = 0 \\ (\sqrt{5} b_2^H + b_3^H - \tau b_4^H + \tau b_5^H) \begin{pmatrix} 0 & 0 & \pm i \\ 0 & 0 & 1 \\ \pm i & 1 & 0 \end{pmatrix}, & \text{if} \quad m = \mp 1 \\ (b_3^H + 2b_4^H + 2b_5^H) \begin{pmatrix} -1 & \pm i & 0 \\ \pm i & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, & \text{if} \quad m = \mp 2, \end{cases} \tag{4}$$

where $\tau = (1+\sqrt{5})/2$. Consequently, again in the three-dimensional space $\hat{\chi}_{\mathbf{h}}$ is sent into $\hat{\chi}_{\mathbf{h}} e^{im\varphi}$ upon a rotation through an angle φ around $\mathbf{h}$. By analogy with nonsymmorphic crystals,[6,8] we could say that the tensor form of $\hat{\chi}_{\mathbf{h}}$ is as it would be if there were a 5_1 axis, but with different (and generally incommensurate) translation vectors for the different $\mathbf{h}$ (or, equivalently, each of the axes 5_2, 5_3, 5_4). The tensors $\hat{\chi}_{\mathbf{h}}$ for reflections forbidden (in the case of an isotropic susceptibility) by the existence of grazing-reflection planes could be derived in a similar way.[2,3]

The tensor form of $\hat{\chi}_{\mathbf{h}}$ has a radical effect on the polarization properties of the reflections. In the case $m = 0$, as in the isotropic case, an incident wave with a linear $\sigma(\pi)$ polarization, whose vector is perpendicular to (parallel to) the scattering plane, gives rise to a diffracted wave which also has the $\sigma(\pi)$ polarization. For $m = \pm 1$, a wave with a σ polarization gives rise to a diffracted wave with a π polarization, and vice versa. With $m = \pm 2$, only a wave with a certain elliptical polarization will undergo diffraction (in back diffraction, this elliptical polarization degenerates to a circular polarization: right-handed if $m = -2$ and left-handed if $m = 2$). It is thus possible to distinguish enantiomorphic pairs of quasicrystals on the basis of their polarization properties. The polarization properties of such reflections, which have already been observed in crystals,[5] are discussed in Refs. 6 and 8.

The quasicrystals which have been studied to date are apparently symmorphic. The tensor form of $\hat{\chi}_{\mathbf{h}}$ in such quasicrystals is quite natural: If the vector $\mathbf{h}$ runs parallel to fivefold and threefold axes, then $\hat{\chi}_{\mathbf{h}}$ is a uniaxial tensor. If $\mathbf{h}$ runs parallel to a twofold axis through which a mirror-reflection plane passes, then $\hat{\chi}_{\mathbf{h}}$ is a biaxial diagonal tensor with axes directed along $\mathbf{h}$ and two twofold axes orthogonal to $\mathbf{h}$. Because of the biaxial nature of $\hat{\chi}_{\mathbf{h}}$, the intensities and polarization properties of the reflections depend on the azimuthal angle (φ) of the rotation around $\mathbf{h}$. In the case of polycrystalline materials, an average is taken over the azimuthal angle. This circumstance may lead to a partial depolarization of the diffracted radiation (for uniaxial $\hat{\chi}_{\mathbf{h}}$, there is no such depolarization). Note also that in imperfect quasicrystals the coherence length for the anisotropic part of $\hat{\chi}_{\mathbf{h}}$ may not be the same as the coherence length for the density. The relation between these lengths will depend on the model of the quasicrystal and the nature of the imperfections.

It can also be shown that the anisotropy of the Debye-Waller factor does not alter the general extinction rules in quasicrystals, while an anisotropy of the Lamb-Mössbauer factor and graidents of the electric field at Mössbauer nuclei (which have already been observed in quasicrystals) should lead to changes in the extinction rules, the intensities of reflections, and the polarization properties of reflections (if there are electric-field gradients, the anisotropic part of the tensor $\hat{\chi}_{\mathbf{h}}$ may be comparable to the isotropic part). The restrictions on the tensor form of the Fourier harmonics found above may also prove useful in a study of icosahedral phases in liquid crystals.[9-11]

[1)]Although the symmetry analysis used here also applies to two other quantities.

[2)]Relation (1) could also have been written for three-dimensional $\hat{\chi}_{H}$ and $\hat{\mathbf{A}}$, but the exponential factor would remain six-dimensional.

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