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Debye-Waller factors in a quasicrystal

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The mean-square vibrational amplitude $\langle U^2 \rangle$ for five reflections located on a twofold axis of an icosahedral quasicrystal $Al_{71.0}Pd_{20.5}Mn_{8.5}$ have been determined between room temperature (RT) and below 20 K by x-ray diffraction. Their Q vectors ($Q = 2\sin\theta/\lambda$) range from 1.278 Å^{-1} to 2.556 Å^{-1}. For four reflections, the logarithm of the integrated intensity is linear, proportional to temperature, near and below RT, and tends to saturate to a constant value at low temperature (LT), an effect of the zero-point energy. All plots for these four reflections are indeed linear at RT and below, and saturate at LT to values that are different from those predicted by Debye theory. This behavior is reminiscent of that of layered crystals such as graphite or TaS_2, in which the anomaly could be explained by considering the effect of reduced dimensionality and anisotropy, none of which can be applied to icosahedral quasicrystals. The effect may be due to a change of Debye temperature below 100 K. The fifth reflection ($Q = 2.252$ Å^{-1}) displays a temperature dependence that does not lead to a single mean-square vibrational amplitude. The Debye temperature obtained from the first four plots is in the neighborhood of 312 K.

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I. INTRODUCTION

One of the problems discussed in the early days of quasicrystals is the effect of temperature on their diffraction patterns. Since quasicrystals are nonperiodic structures, the first question to ask is whether or not the standard Debye-Waller theory, valid for crystals, can be applied.

The theory, developed by Jarić and Nelson,[1] for an icosahedral crystal, leads to a Debye-Waller factor of the form

$$e^{-2M} = e^{-(q^2 T/K + q_\perp^2 T/K_\perp)}. \tag{1}$$

In Eq. (1), q is the familiar momentum exchanged in the scattering process ($=2\sin\theta/\lambda$). K and $K_\perp$ are derived from the quasicrystal elastic constants, and $q_\perp$ is the wave vector in perpendicular space. The first term of the exponent in Eq. (1) is the familiar Debye-Waller factor in the high-temperature approximation. All phonon modes have the same energy kT, which gives rise to a proportionality to temperature (equipartition). The second term is specific to quasicrystals, and has no counterpart in periodic structures. It owes its existence to a new kind of excitations, called ''phasons,'' which can only exist in quasicrystals.

Both q and $q_\perp$ can be expressed as linear combinations of the six Miller indices associated with a particular Bragg reflection. Expressions for such linear combinations are given in review articles[2] and books.[3] A more detailed explanation on how to calculate q from the six Miller indices is given in Ref. 4. Leaving aside for the moment the second term in the exponent of Eq. (1), associated with phasons, we may want to ask the following question: is Debye theory applicable to describe the phonon part of the Debye-Waller factor in a quasicrystal?

An important step in understanding the physics of quasicrystals would be to test Eq. (1) by experiment. The first and only attempt to do this was performed several years ago by Bancel.[5] He used the best material available at that time: Al-Cu-Fe. A very bizarre behavior was found in the plots of intensity vs temperature. It was later found that Al-Cu-Fe undergoes a series of phase transitions in the temperature range explored in this experiment (25–750 °C), which precluded one from observing the real effect of temperature on Bragg reflections. The other problem with Bancel's experiment was that most reflections had relatively low q values, which meant that the effect of temperature was rather small. For example, the highest q value used in Ref. 5 was 1.31 Å^{-1}, very close to the minimum q value (around 1.28 Å^{-1}) needed for observing a detectable temperature effect in Al-Pd-Mn (between 4.2 and 360 K). All other q values used in Ref. 5 are substantially below 1.31 Å^{-1}. It is important to observe that for this particular reflection of $q = 1.31$ Å^{-1}, the corresponding value of $q_\perp$ is 0.017 Å^{-1}, much smaller than q. The ratio between their squared values is >5500 which makes it practically impossible to evaluate the second term in the exponent of the Debye-Waller factor given by Eq. (1).

We have not been able to find any reflection, in Al-Pd-Mn, located on the twofold axis, or in its neighborhood, with both q and $q_\perp$ big enough so that the temperature effect could be observed over our temperature range (4.2–360 K) and have an appreciable contribution from the $q_\perp^2$ term in Eq. (1).

For this reason the focus of our work has been on the applicability of Debye theory to Bragg reflections.

At the time of Bancel's work[5] the best quasicrystal available was Al-Cu-Fe. Later on an even better material was discovered:[6] Al-Pd-Mn, which is isomorphous with Al-Cu-Fe and has a very similar value for the lattice constant. Al-Pd-Mn quasicrystals yield very sharp rocking curves, close to the resolution limit of synchrotron x-ray beams, and have made it possible to observe dynamical diffraction effects such as the Borrmann effect[7] and standing waves.[8]

The program of this work is to consider a number of Bragg reflections located on the twofold axis, with large q, say, greater than 1.278 Å^{-1}. The choice of twofold reflections was dictated by the way our specimen was cut. In all our cases the $q_\perp$ values were very small, so the second term in the exponent of the Debye-Waller factor [Eq. (1)] was neglected.

II. EXPERIMENT

The crystal was a thin slab of $\mathrm{Al}_{71.0}\mathrm{Pd}_{20.5}\mathrm{Mn}_{8.5}$, cut perpendicular to a twofold axis (within 0.25°), diamond polished on both sides. The thickness was 0.385 mm, as measured with a micrometer. Transmission and reflection topographs revealed a grain structure, with large grains (a few mm^3 each), and strained regions between grains. A perfect region was selected, in which a synchrotron beam from a perfect Si crystal monochromator would produce a sharp diffraction peak with no apparent broadening (about 30 arc sec wide or less). The same crystal region was used for transmission experiments (to be described elsewhere) at 9.0 keV. At this low energy the only mechanism to get a diffracted beam in the Laue geometry is anomalous transmission, which is an indication of the high perfection of the quasicrystal specimen used in these experiments. To make sure that the same crystal region was used in all experiments, the crystal was set against a thick copper plate with a 1.5-mm hole. Three bronze springs were keeping the crystal gently pressed against the copper plate, so that no strain was applied to the crystal as the temperature was cycled between 5 K and room temperature. The hole drilled in the copper plate had conical walls, with an angle of 41.5° between the lateral surface of the cone and its axis.

All measurements were done using the Bragg symmetric case of diffraction at the x-ray energy of 17.4 keV. The copper plate holding the sample was mounted in a Displex cryostat. Synchrotron x rays were used for all reflections except for the profile called QY, at $q = 1.278\,\text{Å}^{-1}$, which was obtained in the laboratory, using a standard helium cryostat, a molybdenum x-ray tube ($\lambda = 0.711\,\text{Å}$), and a curved quartz monochromator. At every temperature, a complete rocking curve was performed by rotating the crystal and keeping the wide open counter stationary. Typically, the angular range covered in every rocking curve would be of the order of 7 times the full width at half maximum. The background was linearly extrapolated from the extreme intensity values to the left and to the right of the Bragg peak and subtracted from the total integrated intensity.

III. METHOD OF ANALYSIS

The Debye theory of thermal vibrations, when applied to interpret temperature effects in diffraction experiments, predicts a linear dependence on temperature at high temperatures, when all phonon modes have the same energy kT (equipartition). The theory was originally developed for monoatomic crystals, so an assumption is needed in dealing with polyatomic crystals.

We will assume that the mean-square vibrational amplitude of atoms projected along a specific direction $\langle U^2\rangle$ is mostly contributed by low-frequency acoustic modes, for which the atoms of Al, Pd, and Mn vibrate together. So we will tentatively disregard possible differences in mean-square vibrational amplitudes for specific atomic species.

At low temperature, equipartition no longer holds, and the zero-point energy contribution becomes important. The plot of $\langle U^2\rangle$ vs T is no longer linear; it bends over with decreasing slope as $T=0$ is approached, and it saturates to a finite value at $T=0$ with horizontal slope.

Specifically, Debye theory predicts for the mean-square vibrational amplitude of an atom in a crystal the following expression:

$$\langle U^2\rangle = \frac{9h^2T}{4\pi^2 mk\Theta^2}\left[\frac{x}{4}+\Phi(x)\right], \tag{2}$$

where $h=$ Planck's constant, $m=$ atomic mass, $k=$ Boltzmann's constant, $x=\Theta/T$, $\Theta=$ Debye temperature, and $\Phi(x)$ is the Debye function. The limiting value for $T\simeq 0$ of $\langle U^2\rangle$ is $9h^2/16\pi^2 mk\Theta$.

Equation (2) gives a straight line for $T\simeq 0.2\,\Theta$. Our strategy consists in fitting the high-temperature points first, in order to determine an approximate value of Θ, and then to fit the whole profile, at high and low temperatures, by trial and error.

From the point of view of diffraction theory, we assume that the effect of thermal vibrations can be introduced by simply multiplying each structure factor by the same Debye-Waller factor e^{-M}, where

$$M=\left(\frac{\sin\theta}{\lambda}\right)^2 8\pi^2\langle U^2\rangle. \tag{3}$$

In order to extract $\langle U^2\rangle$ from integrated intensities (R_H's) of x-ray reflections at various temperatures we need to know how the integrated intensity is related to the structure factor F_H. The problem here is that this relationship depends on crystal quality. For a mosaic crystal, R_H is proportional to F_H^2. We have good reasons to believe that our crystals are essentially perfect, and that dynamical theory must be used in order to extract F_H from R_H. For strong reflections, dominated by extinction, R_H is directly proportional to F_H.[9]

We have indeed verified that dynamical theory gives good agreement between experimental and calculated intensities for strong reflections by measuring a few integrated intensities on an absolute basis.[10] We are therefore justified in assuming that our crystals are perfect and that dynamical theory can be used to extract F_H from R_H. In addition, we have in fact verified by numerical computations that R_H is proportional to F_H for some of the reflections used in our work. We can therefore write

$$R=R_0e^{-M}, \tag{4}$$

where R stands for R_H and M is given by Eqs. (3) and (2).

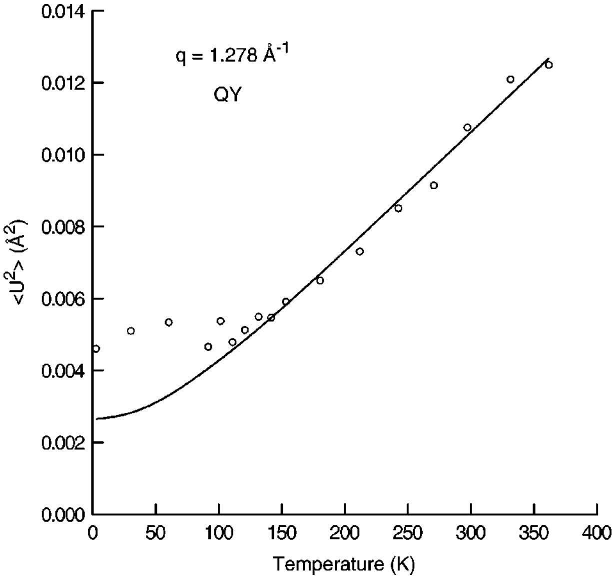

FIG. 1. Mean-square vibrational amplitude vs temperature. $q = 1.278\,\text{Å}^{-1}$, $q_\perp = 0.0168\,\text{Å}^{-1}$, $M = 880$, $N = 544$. $\Theta = 304 \pm 10$ K. Miller indices (0 6 10 0 $\overline{6}$ 10). The parameters M and N are defined in Ref. 3, Eq. (3.24).

The strategy of our method of analysis consists in first fitting the high-temperature region, where equipartition holds, and then to see whether or not the same Debye temperature can be used to fit the low-temperature data. In the high-temperature region, the factor $x/4 + \Phi(x)$ is very close to 1, and we can write

$$\ln R = KT + b, \tag{5}$$

where K and b are determined by least-squares analysis. By comparing Eqs. (5), (4), (3), and (2) we get a preliminary estimate of Θ, the Debye temperature. We can then drop the assumption that $[x/4 + \Phi(x)]$ is close to 1, and calculate $\langle U^2 \rangle$ at low temperature, where the linear dependence is no longer valid.

IV. RESULTS AND DISCUSSION

Figure 1 shows the experimental results and the theoretical fit for the lowest-q reflection for which a temperature effect could be observed ($q = 1.278\,\text{Å}^{-1}$). Earlier attempts to observe temperature effects on a reflection with $q = 0.4882$ failed to show any effect at all.

While the linear temperature dependence is well observable at $T \geqslant 120$ K, there is no question that the low-temperature points depart from the behavior expected from Debye theory. The data of Fig. 1 have been obtained in the laboratory, using a curved quartz-crystal monochromator and Mo $K\alpha$ x rays ($E = 17.435$ eV). The same low-temperature behavior has been observed in a separate synchrotron experiment, at the same x-ray energy. So the effect is noticeable and reproducible.

Similar departures from Debye theory at low temperature have been observed in graphite and layered compounds.[11] In those cases, the experimental points were below rather than above the theoretical profile. This result was interpreted as being due to the strong anisotropy and reduced dimensionality of graphite and TaS_2. Such an explanation would not certainly hold for icosahedral quasicrystals, which are considered to be perfectly isotropic, in the limit of long-wavelength acoustic thermal phonons, when all the atoms vibrate together. In fact, the speed of sound has been measured in Al-Pd-Mn (Ref. 12) and found to be essentially the same in all directions.

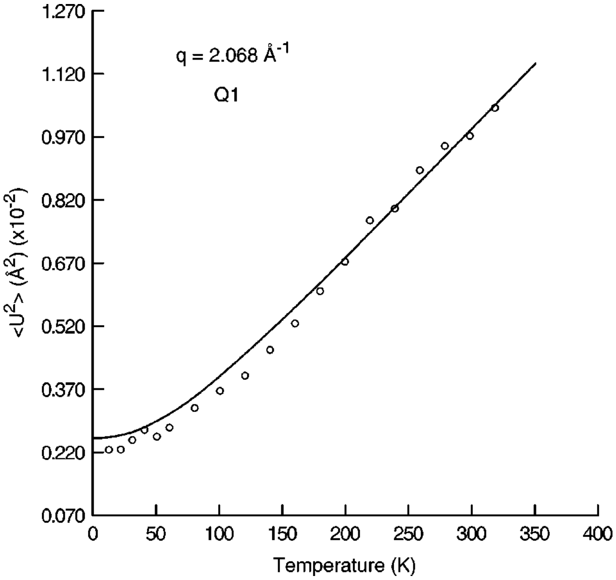

FIG. 2. The same as Fig. 1 except for $q = 2.068\,\text{Å}^{-1}$, $q_\perp = 0.0104\,\text{Å}^{-1}$. $M = 2304$, $N = 1424$. $\Theta = 315 \pm 10$ K. Miller indices (0 10 16 0 $\overline{10}$ 16).

Other reflections have been measured and similarly analyzed. Figures 2, 3, and 4 show the temperature dependence of three Bragg reflections, with higher q values than that

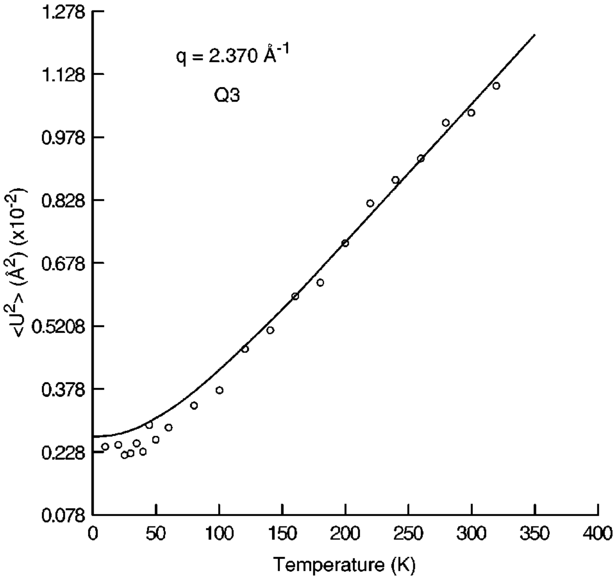

FIG. 3. The same as Fig. 1 except for: $q = 2.370\,\text{Å}^{-1}$, $q_\perp = 0.0816$. $M = 3024$, $N = 1872$. $\Theta = 305 \pm 10$ K. Miller indices (0 12 18 0 $\overline{12}$ 18).

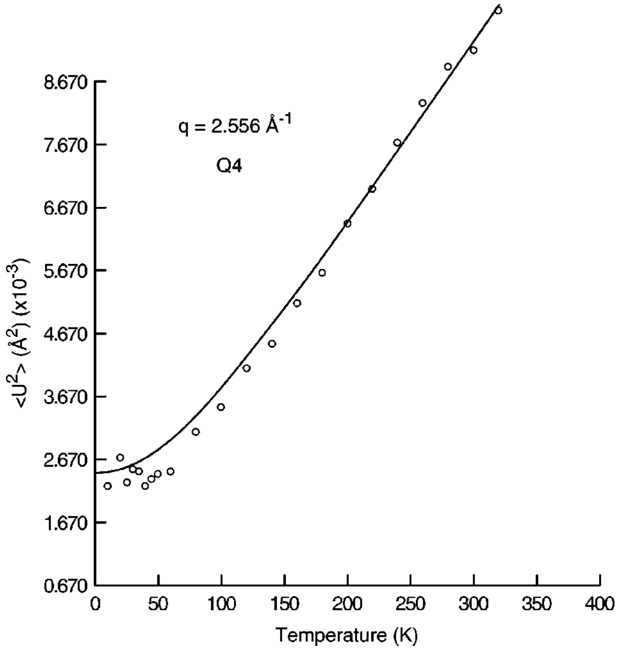

FIG. 4. The same as Fig. 1, except for $q = 2.556\,\text{Å}^{-1}$, $q_\perp = 0.0336\,\text{Å}^{-1}$. $M = 3520$, $N = 2176$. $\Theta = 325 \pm 10$ K. Miller indices (0 12 20 0 $\overline{12}$ 20).

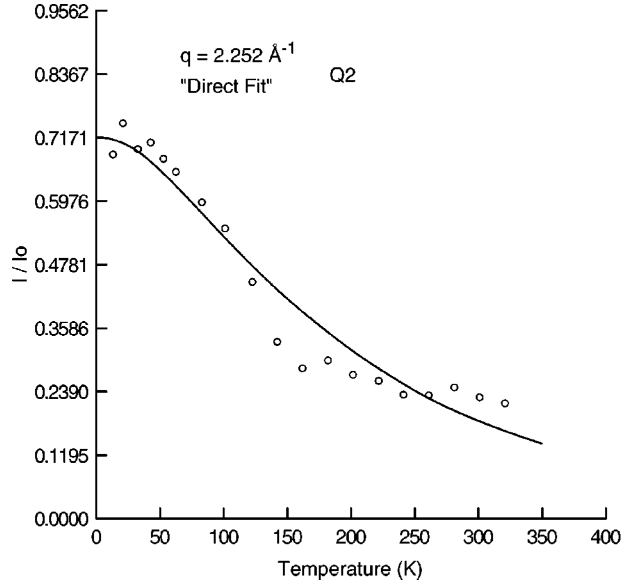

FIG. 5. Intensity vs temperature for the following reflection: $q = 2.252$, $q_\perp = 0.1049$, $M = 2376$, $N = 1696$. Miller indices (0 10 18 0 $\overline{10}$ 18). A single Debye temperature cannot be extracted from this plot. The solid line is the best fit that could be obtained using Debye theory for a monoatomic crystal. It is not a good fit.

used in Fig. 1, ranging between 2.068 Å^{-1} and 2.556 Å^{-1}. In all these cases the linear behavior at high temperatures is well confirmed. At the same time, it is also clear that there is a trend at low temperatures (say, below 100 K) to depart from Debye theory. For these reflections the experimental points tend to stay below the theoretical profile, similarly to what has been observed in graphite and layered structures.[11]

The departure from Debye theory in Figs. 1–4 could be interpreted as due to a change in Θ at low temperature. In fact, the limiting value of $\langle U^2\rangle$ for $T \rightarrow 0$ is

$$\langle U^2\rangle = \frac{9h^2}{16\pi^2 mk\Theta}. \qquad (6)$$

Such a phenomenon has indeed been observed in Ge.[13]

The reason that the change in Θ present in Fig. 1 is opposite in sign to that present in Figs. 2–4 could be due to the fact that different atomic species might have greater weights in the reflection of Fig. 1 as compared with those of the other reflections. One of the key assumptions of Debye theory is that Θ is independent of temperature. When this is not true, we have a breakdown of Debye theory.

One of the reflections we measured (called $Q2$, at $q = 2.252$) could not be analyzed like all the other reflections. Figure 5 shows the intensity points (in arbitrary units) as a function of temperature. The solid line is obtained by fitting with a Debye-Waller factor e^{-M} in which the Debye temperature is an adjustable parameter. We shall call this kind of plot a ‘‘direct fit.’’ Figure 5 shows the best fit that could be obtained, with $\Theta = 240$ K, but it is clear that the calculated profile is not capable of reproducing the sharp bending over of the experimental points at 150 K. It is instructive to see the same kind of plot (‘‘direct fit’’) for $Q4$ (Fig. 6), which could be easily analyzed using the method described in Sec. III. The fit is very good indeed. $Q2$ is the weakest reflection we measured. Its $q_\perp$ value is 0.1049 Å^{-1}, whereas for the other reflections $q_\perp$ range between 0.0104 Å^{-1} and 0.0816 (for $Q3$). Yet its q value (2.252) is smaller than that of $Q4\,(=2.556)$. Therefore, the reason this reflection is so weak is because there is a strong negative interference between the atoms. In this situation it is no longer permissible to talk about a single ‘‘global’’ Debye-Waller factor, corre-

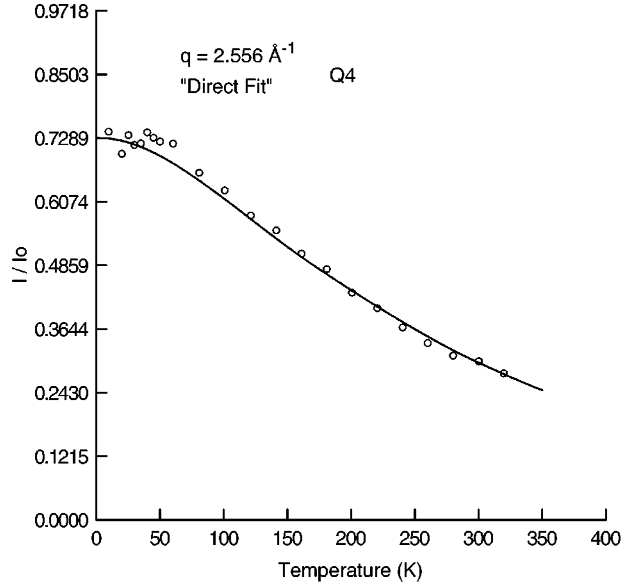

FIG. 6. The same as Fig. 5 except for $q = 2.556\,\text{Å}^{-1}$, $q_\perp = 0.0336\,\text{Å}^{-1}$. $M = 3520$, $N = 2176$. Miller indices (0 12 20 0 $\overline{12}$ 20). The solid line is a fit using Debye theory for a monoatomic crystal, a good fit indeed.

sponding to a single vibrating mass, equal to the sum of the Al, Pd, and Mn atomic masses. In other words, there is more than one Debye-Waller factor, and the total amplitude is the sum of more than one term of the form $A=A_0\exp(-M)$. In this situation it is not possible analyze the data in terms of a single $\langle U^2\rangle$. It is more convenient to try to fit the raw experimental data directly. Clearly, a single Θ cannot be extracted from the plot of Fig. 5.

V. CONCLUSIONS

It is shown in this paper how Debye-Waller factors in a quasicrystal can be reliably extracted from Bragg reflections measured at different temperatures. The quasicrystal used in this work, Al-Pd-Mn, is perfect, so that dynamical theory must be used to correlated Bragg intensities with structure factors. We know that dynamical diffraction theory holds even when phonons are present, provided that thermal vibrations are taken into account in calculating all structure factors F_H.[14]

To observe the effect of temperature between room temperature and 10 K high q reflections have been used, with q values greater or equal to 1.278 Å^{-1}. These reflections, all located along a twofold axis, were quite strong, despite their high q values, with $q_\perp$ never exceeding 0.0816 Å^{-1}. For thermal vibrations along the twofold axis, a Debye temperature of 312 ± 10 K could be estimated. It is shown that Debye theory breaks down at low temperatures, below 120 K.

Similar effects have been observed in layered crystals, in which an explanation could be given in terms of anisotropy. Such an explanation would not hold for icosahedral quasicrystals, which are considered to be perfectly isotropic.

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