Elastic Isotropy and Anisotropy in Quasicrystalline and Cubic AlCuLi

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Unlike conventional crystals, quasicrystals are predicted to be elastically isotropic. To confirm this prediction experimentally, one must distinguish the quasicrystal from nearly isotropic crystals, which requires a high degree of precision. We report the use of resonant ultrasound spectroscopy to determine that the AlCuLi quasicrystal is isotropic within 0.07%, significantly more isotropic than any conventional crystal (by 10 standard deviations). By contrast, we find that a closely related cubic phase of AlCuLi is slightly, but measurably, anisotropic.

One of the fascinating properties of quasicrystals [1], or materials which give fivefold diffraction patterns, is that, unlike conventional crystals, such materials are elastically isotropic [2]. For conventional crystals with high symmetries (e.g., cubic crystals), many physical properties are isotropic, but the property of linear elasticity is fundamentally anisotropic [3]; that is, the velocity of sound may be different in different directions. Thus it is interesting that materials with diffraction spots in fivefold patterns, having long-range order like conventional crystals, must be isotropic in sound propagation. Quasicrystals are further interesting in that by attaining an appropriate amount of a unique strain (phason strain) [2], they may be transformed into conventional crystals (referred to as "periodic approximants") [4], thereby becoming elastically anisotropic. Measuring these properties experimentally has been challenging [5–8], because while conventional crystals are fundamentally anisotropic, their elastic constants may be numerically very close to those of an isotropic material, so that it is difficult to distinguish between intrinsically isotropic and anisotropic behavior in a measurement. Indeed, nearly isotropic behavior might be expected in the periodic approximants, because they are structurally very similar to the isotropic quasicrystals [9]. In this Letter we report the use of resonant ultrasound spectroscopy [10,11] to obtain high precision measurements of the elastic constants of both the quasicrystalline and a periodic approximant phase of AlCuLi, and find, with a significant level of confidence, that the quasicrystalline phase is isotropic (differing from the most nearly isotropic conventional crystal by 10 standard deviations), while the periodic approximant is not.

Before presenting the details of our measurement, it is worthwhile to quantify the difficulty of determining whether or not a material is elastically isotropic. For this purpose, we consider cubic tungsten, which has the smallest anisotropy for a conventional crystal to be found in the literature [12,13]. The sound velocity in tungsten varies with direction by 0.0% to 0.5%, depending on the orientation used in a particular experiment. To show that a quasicrystal is isotropic and, hence, unlike classical crystals, a conventional sound velocity measurement would have to probe all principal directions (which would require remounting transducers, resulting in a loss of accuracy), then calculate the isotropy (which magnifies the inaccuracies), and finally show that the isotropy is significantly smaller than that for tungsten. This is especially challenging considering the small size of many high-quality samples. Previous studies of quasicrystals [5–8] have found no evidence for elastic anisotropy in sound propagation, but only at a resolution of approximately 1%; considering the properties of tungsten and the possibilities for periodic approximants, it is apparent that more precise measurements are necessary. As will be discussed below, resonant ultrasound spectroscopy probes all principal directions in one measurement, while achieving precision sufficient both to show that the AlCuLi quasicrystal is at least an order of magnitude more isotropic than tungsten and to quantify the anisotropy of a periodic approximant. First, we shall discuss the notion of elastic anisotropy in terms of the elements of the elastic tensor.

The elastic tensor c_{ij} for an isotropic solid has only two independent elements, related to a shear and a bulk modulus. By contrast, the simplest elastic tensor for a conventional crystal (cubic) has three independent constants, c_{11}, c_{12}, and c_{44}, using conventional notation [3]. However, the form for the isotropic and cubic tensors are identical, except that for an isotropic solid, $2c_{44} = c_{11} - c_{12}$ [3]. It is therefore convenient to define an anisotropy parameter ϵ as

$$\epsilon = 1 - \frac{2c_{44}}{c_{11} - c_{12}}, \qquad (1)$$

so that ϵ is zero for an isotropic solid. For tungsten, ϵ is only 0.007 ± 0.002 [12,13].

Verifying small values of ϵ not only requires a precise measurement of the elastic constants, but also requires single crystal (or quasicrystal) samples, since multiple

crystallites could give rise to systematic errors, resulting in a spurious anisotropy result. For our measurement we used the AlCuLi system, because single crystals of both the quasicrystal and a periodic (cubic) approximant can be grown to millimeter size [14]. The cubic approximant, referred to as R phase, is a bcc lattice of essentially icosahedral units, and is similar in structure, composition, and density to the quasicrystalline phase [9,15]. A 1 mm thick disk of AlCuLi cut from an ingot of approximately 1 cm diameter, containing R phase and quasicrystalline phase, was prepared at AT&T Bell Laboratories. Two specimens, one of each phase, were cut from this disk with a diamond wire saw and polished into rectangular parallelepipeds. At first, a few features (possibly fissures or grain boundaries) were observed on the sample surfaces. As a consequence, the specimens were painstakingly polished, examined, and repolished until no surface features were visible. Care was taken to ensure that the sample faces were flat, smooth, and perpendicular to within $0.5°$. The finished parallelepipeds of cubic and quasicrystalline AlCuLi were approximately $1.0 \times 0.7 \times 0.4$ and $0.6 \times 0.4 \times 0.4$ mm, respectively. The finished samples were each small enough to be placed entirely within a 1 mm^2 x-ray beam, and transmission Laue diffraction revealed that they were both single crystals with clear fivefold and classical diffraction patterns. A third parallelepiped, $0.4 \times 0.2 \times 0.3$ mm, with a mass of only ~ 70 μg, was prepared from a separate sample of quasicrystalline AlCuLi for comparison. Laue photographs of this third specimen, however, showed that more than one grain may have been present. Henceforth, these samples shall be referred to as R (R-phase cubic approximant), QX1 (high-quality quasicrystal), and QX2 (lesser quality quasicrystal). The quasicrystal samples may have had some amount of phason strain, but for QX1 the transmission diffraction showed clear fivefold symmetry, as opposed to the classical symmetry of the R-phase sample, and hence the three samples were sufficient to show the correlation of symmetry and sample quality with isotropy. The isotropies of all three samples were determined using resonant ultrasound spectroscopy.

In resonant ultrasound spectroscopy [10,11], a specimen's normal mode frequencies of free vibration are used along with its shape and mass to determine its elastic properties. In the present measurement, a rectangular parallelepiped sample is held lightly at opposing corners between two broadband transducers, one a driver and the other a receiver, as shown in Fig. 1. Since the quasicrystal samples are brittle and may have a mass as small as 70 μg, we employ a polyvinylidene fluoride (PVDF) piezoelectric film transducer [10], with a thickness of only 9 μm, which minimizes contact force and damage to fragile sample corners. The driver frequency is swept and the response at the receiver is monitored with a phase-sensitive detector and digitized. The quality factors of the sample resonances are relatively high, typically 10^3
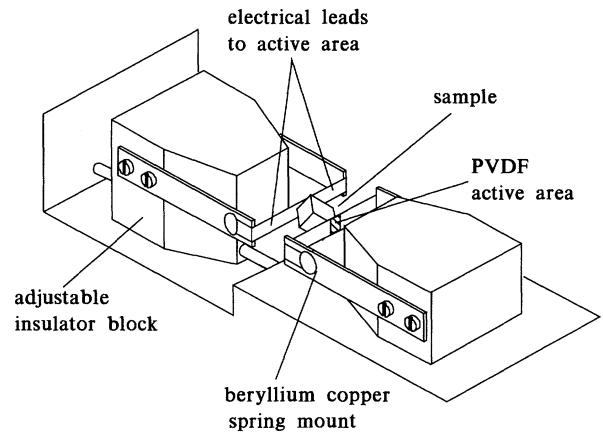

FIG. 1. A resonant ultrasound cell, showing a sample held at its corners between two thin piezoelectric film (PVDF) transducers. The strips are ~ 0.5 mm wide, and aluminum evaporated on either side has a 0.5 mm overlap, creating a 0.5 mm^2 active area (see Ref. [11]).

to 10^5. An initial scan to locate the peaks is followed by a finer scan of each peak; each peak is then fit with a Lorentzian, allowing 10^{-4} to 10^{-6} precision in frequency determination, even for weak signals. The lowest 31 resonances of QX1 were recorded, with somewhat fewer recorded for QX2 and R. Since individual normal modes may involve torsion, shear, dilatation, or a combination, along any axis, all principal directions are investigated in several ways with a single spectrum, if enough modes are used. Once a spectrum of N observed resonance frequencies f_i^o ($i = 1, N$) has been obtained, a Levenberg-Marquart algorithm [16] is used to fit the data by varying the free parameters, such as elastic constants, until a figure-of-merit F is minimized. Following Ref. [11], we minimize

$$F = \sum_{i=1}^{N} \left(\frac{f_i^o - f_i^t}{f_i^o} \right)^2, \qquad (2)$$

where the f_i^t are theoretical frequencies calculated according to the variational method used by Demarest [17] and improved by Ohno [18] and Visscher et al. [19]. Once F has been minimized, the goodness of the fit can be specified by the rms error $(F/N)^{1/2}$, which is approximately equal to the average error in fitting each frequency.

We assume in our fitting procedure that all of our samples have at least cubic symmetry, so that there are at most three independent elastic constants. If the quasicrystal is isotropic and has only two independent constants, the value of ϵ from Eq. (1) will be correspondingly small. The frequencies in the measurement are determined with good precision and accuracy, so that the accuracy of the calculated elastic constants is limited by the accuracy with which the geometry of the sample is determined. The size of the sample may be taken as one physical dimension and

two aspect ratios. Since we measure many more frequencies than elastic constants, the problem is overdetermined and the aspect ratios can be included as free parameters in the fit. Only a single dimension is required to determine the elastic constants, but in calculating the anisotropy parameter with a ratio of elastic constants, the dimension, as well as the mass of the sample, cancels out. Error can occur if the actual shape of the sample differs in a systematic way from that assumed in the fitting program, nominally a rectangular parallelepiped. An inexact shape may result from the limits of our polishing technique and the small size of the samples, and shape anisotropy may appear as elastic anisotropy in the results of a fitting procedure that assumes an ideal shape. For a carefully shaped sample, the sides may differ from being mutually perpendicular by a few tenths of a degree, and the errors in c_{ij} may be a few tenths of a percent [11], sufficiently small for most purposes. However, the present measurement requires as little systematic error as possible, so we measured the actual shape of QX1 by first mounting the sample on a goniometer, and used a laser beam reflecting from the polished sample faces to determine the angles between each side. A second-order frequency perturbation calculation using this more accurate shape is included when fitting the data from QX1. For the R sample, the shape was sufficiently rectangular and the anisotropy was sufficiently large that such fine tuning was unnecessary.

The resulting elastic constants c_{11}, c_{12}, and c_{44}, anisotropy ϵ, and rms error for all three samples are given in Table I, and the anisotropy results are further summarized in Fig. 2, which shows the rms error and the anisotropy, with the standard deviations indicated with error bars. The rms errors for all three data sets are $\leq 0.1\%$, indicating an excellent agreement between observed and predicted resonance frequencies, and a high degree of confidence in the overall fits. The standard deviations for ϵ were obtained by a Monte Carlo method, with the width of the scatter in the synthetic data sets based on the residuals $\mid f_i^o - f_i^t \mid$ in the fit to the actual

data. The standard deviations (and the error bars in Fig. 2) reflect to some degree the sample quality and the number of data points; the error for the high-quality quasicrystal (QX1) is concomitantly the smallest of the three, while the error for QX2 (suspected to be more than one grain) is the greatest. It is apparent that the R phase is measurably anisotropic, while the quasicrystal samples are not. The anisotropy of the R phase is seen to be comparable to that of tungsten, and differs from zero by seven standard deviations. The anisotropy of the high-quality quasicrystal, with $\epsilon = 0.0002 \pm 0.0007$, is 10 standard deviations, or about a factor of 10, smaller than the anisotropy of tungsten. Hence the quasicrystal is significantly more isotropic than the most nearly isotropic conventional crystal to be found in the literature.

An additional test for isotropy can be performed by presuming various crystal orientations, other than the one initially assumed, in the theoretical frequency calculations [11]; i.e., one uses an elastic tensor that has been rotated relative to the axes of the crystal lattice. In this way, one can test whether crystal misorientation affects how well the data are fit by the model. If a crystal is anisotropic, one should notice a minimum in the fit error when the elastic tensor is correctly aligned with the lattice. Plots of the figure-of-merit F versus rotation of the elastic tensor in two of the three Euler angles show that the cubic phase has a clear dependence on orientation, while the quasicrystal shows none. The minimum in F for the cubic phase is along a principal direction, important evidence that its anisotropy is due to its crystal structure and is not an artifact of sample quality.

In conclusion, we have shown the AlCuLi quasicrystal to be isotropic with $\epsilon = 0.0002 \pm 0.0007$, significantly more isotropic than conventional crystals, in accordance
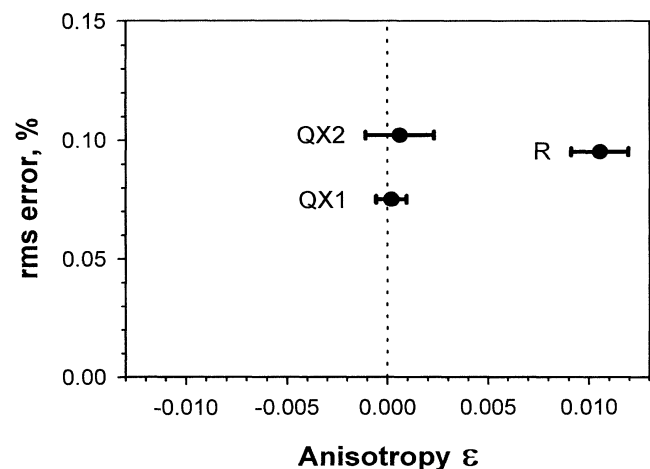
TABLE I. The elastic constants (in Mbar) and anisotropy ϵ for R-phase cubic approximant, high-quality quasicrystalline, and lesser quality quasicrystalline AlCuLi. The analysis of normal-mode frequency data for each sample assumes cubic symmetry and three independent elastic constants; a small value for ϵ indicates that only two constants are independent. The standard deviations are from Monte Carlo simulations; the absolute accuracy of the elastic constant determination is limited by the errors in dimensions and mass (about 1%).

Sample	c_{11}	c_{12}	c_{44}	ϵ [a]	rms error[b] (%)
R	1.112	0.311	0.396	0.0105 ± 0.0014	0.09
QX1	1.122	0.304	0.409	0.0002 ± 0.0007	0.07
QX2	1.152	0.314	0.419	0.0006 ± 0.0017	0.10

[a]Anisotropy, from Eq. (1).
[b]See Eq. (2).

FIG. 2. The anisotropies of quasicrystalline and R-cubic AlCuLi. The vertical coordinate shows the rms error in fitting the frequency data for each sample. QX1 is a single quasicrystal; in QX2 more than one grain may be present.

with theoretical predictions. The R phase periodic approximant has been shown to possess an anisotropy which is very small, but readily measured with resonant ultrasound spectroscopy. For future research it would be of interest to study a sequence of quasicrystal samples, each with a different amount of phason strain; some data on the effects of phason strain on acoustic attenuation have already been obtained [8].

However, as discussed in the text, this does not mean that the isotropy was less than 0.002. Unfortunately, in this paper c_{12} was not determined, so that the true isotropy could not be calculated.

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