

Elastic properties of icosahedral and decagonal quasicrystals

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Abstract. Problems associated with determining the symmetry properties of the elastic constant tensor of icosahedral and decagonal quasicrystals are reviewed. Notions of elastic isotropy and anisotropy are considered, and their relation to the components of the elastic constant tensor is discussed. The question is addressed of how to determine experimentally whether a system under study is elastically isotropic. Experimental results produced by resonant ultrasound spectroscopy of icosahedral Al–Li–Cu and decagonal Al–Ni–Co single quasicrystals are discussed in detail.

1. Introduction

The discovery of a quasicrystalline phase with icosahedral symmetry in the binary Al–Mn system by Shechtman, Blech, Gratias, and Cahn [1] has demonstrated that periodicity does not constitute an indispensable condition for the formation of long-range order in solids and led to a radical revision of concepts about the nature of the crystalline state. Quasicrystals possess many properties characteristic of periodically structured solids, e.g., faceting and sharp-peaked diffractograms. The correlation length of the quasicrystal structure determined by X-ray diffraction analysis can be as large as several micrometers; due to this, quasicrystals rank among the most perfect periodically ordered crystals in terms of structural quality. At the same time, quasicrystals are essentially different from periodically ordered crystals in that they are lacking in translational symmetry. Quasicrystals are characterized by a peculiar type of aperiodic long-range order and may exhibit rotational symmetry incompatible with periodicity. Such quasicrystals include, besides icosahedral phases, axial phases with octagonal, decagonal, and dodecagonal structures.

Elastic isotropy constitutes one of the remarkable properties of icosahedral quasicrystals — that is, phases with long-range coordination order and a class of icosahedral diffraction symmetry [2–5]. None of the periodically ordered crystals possesses this property (even in cubic crystals, the velocity of sound depends on the direction of propagation of the acoustic waves). It should be noted that experimental studies designed to elucidate whether a given medium is elastically isotropic may prove nontrivial. The point is that the relationship between the components of the elastic constant tensor may be very similar to the corresponding relationship for isotropic media even though the elastic properties of periodically ordered crystals are always anisotropic. A well-known example is provided by tungsten having the smallest elastic anisotropy of all periodically ordered crystals (the velocity of acoustic waves in a tungsten single crystal varies with the direction of their propagation by no more than 0.5%) [6]. This emphasizes the importance of highly precise measurements in experimental investigations of weakly anisotropic media.

Icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ became the first object of detailed studies on the elastic properties of quasicrystals. It turned out to be thermodynamically stable, which made it possible to grow single crystals by classical methods. Unlike the thermodynamically stable icosahedral phases with a perfect structure discovered later, e.g., Al–Mn–Pd, the structure of icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ is distorted by the so-called phason strains representing extended static defects characteristic of quasicrystals. The structural quality of quasicrystals having phason strains can be substantially improved by annealing. The equilibrium phase diagram of the ternary Al–Li–Cu system [7] permits the growing of single crystals of both the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ phase and the $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ *R*-phase formed by triacontahedral clusters located at the nodes of the body-centered cubic lattice with a large constant $a = 13.9 \text{ \AA}$ (space group *Im*3) [8]. The $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ *R*-phase is the so-called approximant of icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$, i.e., a periodically ordered crystal with a unit cell in which the component atoms are arranged in a pattern reminiscent of the local atomic structure of a quasicrystal. Of great interest is the possibility of comparing elastic properties of the two phases similar in terms of composition and local structure, one of which

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(icosahedral) is assumed to be elastically isotropic and the other (cubic) of necessity is pronouncedly anisotropic. Detailed studies of elastic properties have also included quasicrystals with a face-centered icosahedral (fci) lattice in the ternary Al–Mn–Pd system, whose Bragg peaks are not broadened by structural defects even in the absence of annealing. The highly perfect structure of fci Al–Mn–Pd single crystals was confirmed by observations of the anomalous transmission of X-rays, i.e., the Borrmann effect [9, 10].

Equally interesting are the elastic properties of decagonal quasicrystals periodically ordered along the axis of tenfold symmetry and quasiperiodically in the plane perpendicular to this axis — that is, displaying the structural properties of both periodic crystals and quasicrystals. On the one hand, deformation of decagonal quasicrystals in the plane perpendicular to the axis of tenfold symmetry is assumed to be isotropic [11]. On the other hand, calculations of the lattice excitation spectrum predict, in the low-frequency region, a significant difference between the dispersion relations along the periodic decagonal axis and along the direction in the quasiperiodic plane [12]. Today, there are several decagonal phases available as single crystals, the sizes of which make them suitable candidates for acoustic experiments. Decagonal quasicrystals in the ternary Al–Ni–Co system have been studied most extensively.

In recent years, a variety of reviews on different aspects of quasicrystal physics have been published [13–16]. However, these publications do not specially consider studies on elastic properties, barring brief notes on the subject, despite a large number of original papers devoted to this issue. Hence, it is opportune to systematize and bring order to the data obtained thus far on the elastic properties of quasicrystals. The present review is focused on the problems associated with experimentally determining the symmetry of the elastic constant tensor of icosahedral and decagonal quasicrystals. The notions of elastic isotropy and anisotropy are discussed in terms of their relation to the components of the elastic constant tensor, along with experimental approaches to the verification of whether the medium under consideration is elastically isotropic. The Debay contribution to the specific heat of quasicrystals, computed from the measured elastic moduli, is compared with the results of calorimetric experiments. The review does not cover a number of problems related to the effects of double-well tunneling systems on the velocity and absorption of sound in quasicrystals at temperatures below 1 K. These problems were detailed in Ref. [17].

2. The icosahedral system

The dependence of the stress tensor σ_{ij} on the strain tensor u_{ij} is invariant under inversion transformation. For this reason, the classification of crystals in terms of their elastic properties corresponds to the classification by diffraction symmetry classes or Laue classes. Thus, 32 crystallographic point groups of periodically ordered crystals are grouped into 11 Laue classes, with one class for each of the triclinic, monoclinic, and rhombic systems, and two classes for each of the hexagonal, tetragonal, rhombohedral, and cubic systems [18]. Both three-dimensional crystallographic point groups of the icosahedral system 235 and $m\bar{3}5$ belong to the Laue class $m\bar{3}5$ [19, 20]. The free elastic energy of a quasicrystal of the Laue class $m\bar{3}5$, corresponding to phonon

deformations alone, has the form [2–5]

$$F_{\text{el}} = \frac{1}{2} c_{xxxx}(u_{xx}^2 + u_{yy}^2 + u_{zz}^2) + c_{xyxy}(u_{xx}u_{yy} + u_{xx}u_{zz} + u_{yy}u_{zz}) + (c_{xxxx} - c_{xyxy})(u_{xy}^2 + u_{xz}^2 + u_{yz}^2). \quad (1)$$

In what follows, we shall apply the Voigt's notations widely used in the scientific literature on crystal elastic properties. In these notations, components of the tensor c_{ijkl} of rank four are written as $C_{\alpha\beta}$ with two indices running through 1, 2, 3, 4, 5, and 6, to which pairs of indices xx , yy , zz , yz , zx , and xy correspond, respectively [21]. Expression (1) for the free energy of a quasicrystal of the Laue class $m\bar{3}5$ relates to the elastic constant matrix

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C' & 0 & 0 \\ 0 & 0 & 0 & 0 & C' & 0 \\ 0 & 0 & 0 & 0 & 0 & C' \end{pmatrix}, \quad (2)$$

where

$$C' = \frac{1}{2} (C_{11} - C_{12}), \quad (3)$$

which is identical with the elastic modulus matrix of an isotropic medium [18]. The deformation of quasicrystals of the icosahedral system is determined by two independent elastic moduli C_{11} and C_{12} , and their elastic properties are isotropic. The difference between the elastic properties of icosahedral quasicrystals and elastically isotropic media arises when the third-order elastic constants are taken into consideration [22]. It should be recalled that none of the periodically ordered crystals possesses the property of elastic isotropy, because their deformation is determined by at least three independent elastic moduli.

In what follows, we consider elastic isotropy and anisotropy and their relation to the components of the elastic constant tensor. Also, we describe an experimental approach to the clarification of whether the medium under study possesses elastic isotropy. By way of example, let us consider the periodically ordered crystals of a cubic system that incorporates Laue classes $m3m$ (crystallographic point groups 432, $43m$, $m3m$) and $m3$ (crystallographic point groups 23 and $m3$). The elastic constant matrix of cubic crystals assumes the form [18]

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}. \quad (4)$$

Three elastic moduli C_{11} , C_{44} , and C_{12} are independent. The elastic constant matrix of cubic crystals is different from that of an isotropic medium only in that

$$C_{44} \neq \frac{1}{2} (C_{11} - C_{12}). \quad (5)$$

It therefore appears useful to compare isotropic media with cubic crystals. A convenient measure of deviation from the elastic isotropy is the anisotropy shear parameter that can be

defined as

$$\varepsilon_s = 1 - \frac{2C_{44}}{C_{11} - C_{12}}. \quad (6)$$

The second term on the right-hand side of expression (6) is known as the Zener ratio and constitutes the ratio of the squares of the velocities of the purely transverse acoustic waves polarized in the (001) crystallographic plane and propagating along the [100] and [110] directions. For isotropic media, the parameter ε_s equals zero.

The first experimental observations of isotropic elasticity in icosahedral quasicrystals were reported for icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$. It was shown by ultrasound [23, 24] and inelastic neutron scattering [25] techniques that the sound velocity in $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ single crystals varied by no more than 1–2%, depending on the direction. In the icosahedral Al–Mn–Pd quasicrystals, accurate measurements of the speed of sound were made by Amazit et al. [22]. These authors found that the velocities v_t and v_l of the transverse and longitudinal acoustic waves, respectively, propagating along the fivefold and twofold axes differ from one another by no more than 0.2%, while the velocity of transverse acoustic waves propagating along the twofold axis is independent of polarization within the limits of experimental error of order 0.01%. However, the analysis of the experimental technique employed in Ref. [22] indicates that, the sound velocities v_t and v_l having been measured only for two crystallographic directions, the data obtained cannot, strictly speaking, be regarded as proof of elastic isotropy defined as the equality of the parameter ε_s to zero, because it is impossible to derive modulus C_{12} from them [26].

Elastic isotropy of a quasicrystal having icosahedral symmetry was experimentally established with a high degree of accuracy and reliability by Spoor and co-workers [26] using resonant ultrasound spectroscopy of icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$. The resonant ultrasound spectroscopy technique [27, 28] permits one to determine all components of the elastic modulus tensor from the mechanical resonance frequencies of a free sample measuring about 1 mm. Among all other techniques for the measurement of elastic moduli, this method ensures the highest absolute accuracy because it requires only very weak dry contacts between the corners of the sample and the ultrasound transducers; hence, no correction for the binding material is needed.

Spoor et al. [26] measured resonant frequency spectra of icosahedral and cubic single crystals of the ternary Al–Li–Cu system cut in rectangular parallelepipeds with a volume of 0.1 and 0.3 mm³, respectively. The frequencies of some 30 resonances were measured for each sample with the quality factor in the range from 10³ to 10⁵. The approximation of these resonances by the Lorentz function allowed their frequencies to be determined with a relative accuracy in the range of 10^{−4} to 10^{−6}.

The resonant frequencies of a sample can be evaluated from the known elastic moduli [29–31], whereas the inverse problem needs to be solved when determining elastic moduli from the known resonant frequencies. In resonant ultrasound spectroscopy, the analysis of resonant frequencies is based on the minimization of the function

$$F = \sum_{i=1}^n \left(\frac{f_i}{g_i} - 1 \right)^2, \quad (7)$$

where f_i and g_i are the calculated and observed frequencies of resonance i , respectively, and n is the number of measured resonances. The minimum of function F in the multidimensional space of elastic moduli is usually found with the help of the Levenberg–Marquart algorithm for the nonlinear optimization [27, 28].

Table 1 represents elastic moduli obtained in Ref. [26] from the analysis of resonant frequencies of icosahedral and cubic Al–Li–Cu single crystals on the assumption that the study samples have at least cubic symmetry, so that no more than three components of the elastic modulus tensor are independent. The root-mean-square deviation of the frequency spectrum for either phase does not exceed 0.1%, suggesting excellent agreement between the computed and the observed frequencies. Table 1 also includes parameters ε_s of anisotropy.

Table 1. Results of analysis of the resonant frequency spectra of icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ and cubic $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ single crystals [26]. The elastic moduli $C_{\alpha\beta}$ are determined on the assumption that the study samples possess at least cubic symmetry, i.e., have three independent moduli each; units of measurement — 10¹² dyn cm^{−2}.

| Phase | Standard deviation, % | C_{11} | C_{12} | C_{44} | ε_s |
|---------------------------------------|-----------------------|----------|----------|----------|-----------------|
| $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ | 0.07 | 1.122 | 0.304 | 0.409 | 0.0002 ± 0.0007 |
| $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ | 0.09 | 1.112 | 0.311 | 0.396 | 0.0105 ± 0.0014 |

Parameter $\varepsilon_s = 0.0105 \pm 0.0014$ for cubic $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ is comparable with the parameter of anisotropy for tungsten. At the same time, its value is several times higher than the measurement error, i.e., the cubic $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ is elastically anisotropic with a high level of confidence. Conversely, the parameter of anisotropy of icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ is only 0.0002 ± 0.0007 . Thus, the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ quasicrystal is much more isotropic than any of the periodically ordered crystals, and its elastic isotropy is confirmed by the fact that the measurement error of ε_s is much higher than the value of the parameter of anisotropy ε_s itself. Experimental errors related to the measurement of the parameter of elastic anisotropy in the icosahedral and cubic Al–Li–Cu quasicrystals by resonant ultrasound spectroscopy are presented in Fig. 1 where parameter ε_s for either phase is plotted as a

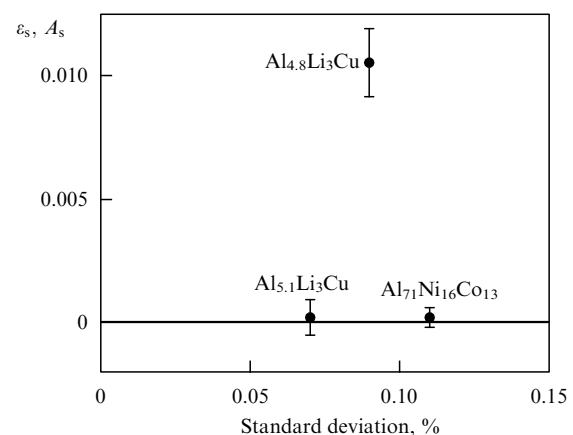


Figure 1. Parameter ε_s of shear anisotropy of the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ quasicrystal and its periodic approximant, the cubic $\text{Al}_{4.8}\text{Li}_3\text{Cu}$, and parameter A_s of azimuthal shear anisotropy of the decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ quasicrystal as a function of the root-mean-square deviation in the resonant frequency spectrum.

function of the root-mean-square deviation in the resonant frequency spectrum.

Knowing the elastic moduli C_{11} and C_{12} , it is possible to calculate the contribution of lattice excitations to the low-temperature specific heat and Debye temperature θ_D of icosahedral Al–Li–Cu. At low temperatures, only long-wave acoustic modes contribute to the specific heat of quasicrystals given by the expression

$$C_D(T) = \frac{2\pi^2 k_B^4}{5\hbar^3} \frac{1}{v_s^3} T^3, \quad (8)$$

where $1/v_s^3$ is the averaged inverse third power of long-wave phase velocities v_i of three acoustic modes [32]. For an elastically isotropic medium, $1/v_s^3$ is written as

$$\frac{1}{v_s^3} = \frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right), \quad (9)$$

and the velocities of longitudinal and transverse acoustic waves are $v_l = \sqrt{C_{11}/\rho}$ and $v_t = \sqrt{C'/\rho}$, respectively (ρ is the density). Substitution of the elastic modulus values obtained in Ref. [26] and the density estimated in Ref. [23] into expressions (8) and (9) yields $C_D/T^3 = 13.2 \mu\text{J} (\text{g-atom K}^4)^{-1}$. It is worth noting that coefficient β of the cubic-in- T contribution to the low-temperature specific heat of icosahedral Al–Li–Cu, determined in Ref. [33] from calorimetric measurements in a temperature range of 1–6 K, is equal to $19 \mu\text{J} (\text{g-atom K}^4)^{-1}$, i.e., larger than the C_D/T^3 ratio of the Debye model, calculated from the results of acoustic measurements [26]. An excess contribution to the low-temperature specific heat $C_p(T)$, proportional to T^3 , is characteristic of many icosahedral quasicrystals, including fci Al–Cu–Fe, Al–Mn–Pd, and Al–Re–Pd [33, 34].

The acoustic contribution to the specific heat is often characterized by the Debye temperature θ_D . For quasicrystals, the usual definition of θ_D based on the number of atoms per unit cell of a periodically ordered crystal is unambiguous. The Debye temperature of a quasicrystal is naturally defined as

$$\theta_D = \frac{\hbar}{k_B} \left(\frac{6\pi^2 N_A}{V_0} \right)^{1/3} v_s, \quad (10)$$

where V_0 is the volume of one gram-atom. The use of this definition for icosahedral Al–Li–Cu yields $\theta_D = 528$ K.

3. The decagonal system

Let us now consider elastic properties of decagonal quasicrystals. The decagonal system is divided into two Laue classes $10/m$ and $10/mmm$ that incorporate three-dimensional crystallographic point groups: 10 , $10/m$, and 1022 , $10mm$, $\overline{10}m2$, $10/mmm$, respectively [11, 35]. In the frame of reference with the z -axis chosen along the tenfold axis, the free elastic energy of the quasicrystal of a Laue class $10/m$ or $10/mmm$, corresponding to phonon deformations alone, has the form [11]

$$\begin{aligned} F_{\text{el}} = & \frac{1}{2} c_{xxxx} (u_{xx}^2 + u_{yy}^2) + \frac{1}{2} c_{zzzz} u_{zz}^2 \\ & + c_{xxzz} (u_{xx} u_{zz} + u_{yy} u_{zz}) + c_{xyyy} u_{xx} u_{yy} \\ & + (c_{xxxx} - c_{xyyy}) u_{xy}^2 + 2c_{xzzz} (u_{xz}^2 + u_{yz}^2). \end{aligned} \quad (11)$$

The number of independent components of the elastic modulus tensor is five. The difference between the elastic properties of quasicrystals belonging to Laue classes $10/m$ and $10/mmm$ appears only when the third-order elastic constants or when the phason degrees of freedom are taken into consideration [11]. The elastic modulus matrix of decagonal quasicrystals assumes the form

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C' \end{pmatrix}, \quad (12)$$

where C' is given by expression (3). C_{11} , C_{33} , C_{44} , C_{12} , and C_{13} are usually chosen as independent moduli. Equality (3) reduces to two the number of independent elastic moduli determining a deformation with nonzero components u_{xx} , u_{xy} , and u_{yy} of the strain tensor, i.e., deformation in the quasiperiodic xy -plane, as for an isotropic medium. Thus, the elastic properties of a decagonal quasicrystal are isotropic in the plane perpendicular to the axis of tenfold symmetry; in other words, a decagonal quasicrystal possesses the property of *transverse elastic isotropy*. Of all periodically ordered solids, only hexagonal crystals offer this property [21].

The connection of transverse elastic isotropy and anisotropy with the components of the elastic modulus tensor can be discussed by analogy with icosahedral quasicrystals (see Section 2). We shall refer to periodically ordered crystals of the tetragonal Laue class $4/mmm$ that includes crystallographic point groups 422 , $4mm$, $\overline{4}2m$, and $4/mmm$. The elastic modulus matrix of the crystals of Laue class $4/mmm$ is written as [18]

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix}. \quad (13)$$

The six moduli C_{11} , C_{33} , C_{44} , C_{66} , C_{12} , and C_{13} are usually chosen as independent ones. The elastic modulus matrices of a tetragonal crystal of Laue class $4/mmm$ and a transversely isotropic medium are different only in that

$$C_{66} \neq \frac{1}{2} (C_{11} - C_{12}). \quad (14)$$

It is therefore possible to compare transversely isotropic media with tetragonal crystals of a Laue class $4/mmm$ as the most similar in terms of elastic properties. The following parameter of azimuthal shear anisotropy is chosen as the measure of deviation from the transverse isotropy state:

$$A_s = 1 - \frac{2C_{66}}{C_{11} - C_{12}}. \quad (15)$$

The second term on the right-hand side of expression (15) is the ratio of the squares of the velocities of the pure transverse acoustic waves polarized in the (001) plane and propagating

along the [100] and $\bar{1}00$ directions. For transversely isotropic media, $A_s = 0$.

Elastic isotropy of a quasicrystal with decagonal symmetry exemplified by Al–Ni–Co was experimentally established in Ref. [36] using resonant ultrasound spectroscopy, as in the case of icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ [26] considered in Section 2. Components of the elastic modulus tensor were measured in a single crystal of the decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ compound cut in a $2.0 \times 1.2 \times 1.2$ mm rectangular parallelepiped with the edges parallel to the twofold and tenfold axes. The resonant frequency spectrum was measured in the frequency range of 1–3 MHz, where a total of 30 resonances were observed. The quality factor Q of the sample varied from 1.5×10^3 to 2.5×10^3 , depending on the excited mode.

The accuracy with which the elastic moduli were determined was assessed on the assumption that the function F close to the minimum was a quadratic function of the elastic moduli [see expression (7)]. In this case, the surfaces of the constant value of function F had an ellipsoid shape. The measurement error for the elastic modulus was estimated from the lengths of the ellipsoid semiaxes, corresponding to the value of F that was 2% larger than the minimal one. As a rule, when the root-mean-square deviation of the measured spectrum from the calculated one did not exceed 0.1%, the measurement errors determined using this criterion were larger than all errors, including those related to the reproducibility. They were 1, 0.02, and 3% for the compressional, shear, and nondiagonal moduli, respectively [27].

The elastic moduli of the off-decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ quasicrystal, presented in Table 2, were determined on the assumption that this quasicrystal had a symmetry corresponding at least to the Laue class $4/mmm$. This means that not more than six components of the elastic modulus tensor were independent. In such an analysis of resonant frequencies, the root-mean-square deviation was only 0.11%, while the measurement errors of pure shear moduli C_{66} and C' were 0.03%. The parameter of azimuthal shear anisotropy A_s calculated from C_{66} and C' was 0.0002 ± 0.0004 . The very small value of the parameter A_s (below the experimental error) suggests practically perfect transverse elastic isotropy, as expected for the decagonal quasicrystal. For comparison with the measurement errors of the parameter of anisotropy ε_s of the icosahedral and cubic Al–Li–Cu phases discussed in Section 2, the parameter of azimuthal shear anisotropy A_s of the decagonal Al–Ni–Co quasicrystal in Fig. 1 is plotted as a function of the root-mean-square deviation in the resonant frequency spectrum.

Table 2. Elastic moduli of the decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ quasicrystal, determined from the mechanical resonance frequency spectrum on the assumption that the number of independent moduli is n [36]; units of measurement — 10^{12} dyn cm^{-2} .

| n | T, K | C_{11} | C_{33} | C_{44} | C_{66} | C_{12} | C_{13} |
|-----|---------------|----------|----------|----------|----------|----------|----------|
| 6 | 290 | 2.3430 | 2.3221 | 0.7019 | 0.8845 | 0.5736 | 0.6662 |
| 5 | 5 | 2.4199 | 2.4019 | 0.7282 | 0.9175 | 0.5849 | 0.6669 |

Up to the present, we have discussed the deformation of a decagonal Al–Ni–Co quasicrystal in the quasiperiodic plane. Let us now move to the comparison of the elastic properties in the quasiperiodic plane in which the translational symmetry is absent and in the direction of the

decagonal axis along which the long-range order of the periodic type is present. Let us introduce the definition of polar elastic anisotropy, i.e., the deviation from the state of complete elastic isotropy. For the quantitative assessment of the polar anisotropy of a transversely isotropic medium, it is possible to apply two parameters; one is polar shear anisotropy

$$P_s = 1 - \frac{2C_{44}}{C_{11} - C_{12}}, \quad (16)$$

where $2C_{44}/(C_{11} - C_{12})$ is the ratio of the velocities squared of the purely shear waves propagating in the (001) plane and polarized along the [001] direction and in the (001) plane, respectively; the other is polar compression anisotropy

$$P_c = 1 - \frac{C_{11}}{C_{33}}. \quad (17)$$

The second term on the right-hand side of expression (17) is the ratio of the squares of the velocities of the pure longitudinal acoustic waves propagating in the (001) plane and along the [001] direction. For both parameters of polar anisotropy, the zero value corresponds to the state of complete elastic isotropy.

Parameters P_s and P_c for decagonal Al–Ni–Co quasicrystal are 0.207 and -0.009 , respectively, suggesting an unexpectedly weak polar elastic anisotropy. Because the elastic moduli C_{11} and C_{33} are closely related to the interatomic potentials, the proximity to zero of the polar compression anisotropy P_c defined by expression (17) can imply that the coupling forces along the periodic direction and the directions in the quasiperiodic plane are practically identical, in agreement with the concept of universal local order in decagonal and icosahedral phases [37].

The polar elastic anisotropy of a decagonal Al–Ni–Co quasicrystal can be illustrated by constructing a slowness surface that characterizes the dependence of the inverse phase velocity $s = v^{-1}$ of a monochromatic elastic wave on the direction of the wave normal and serves as the geometric site of the points given by the radius vectors of the inverse phase velocity $\mathbf{s} = \mathbf{n}/v$ in the wave normal space, i.e., in the coordinates n_x , n_y , and n_z . The normal to the surface of the inverse phase velocity coincides with the direction of the group velocity vector $\mathbf{V} = \partial\omega/\partial\mathbf{k}$. There are three sheets of the slowness surface commonly labelled according to the polarization of the corresponding acoustic waves: quasilongitudinal (L) for the inner sheet, and quasishear (T_1 , T_2) for the two outer sheets, each of them having a center of symmetry. The slowness surface and the constant frequency surface defined by the relation $\omega(\mathbf{k}) = \text{const}$ have identical shapes and differ only in scale.

The propagation of a monochromatic elastic wave through an anisotropic medium is described by the Christoffel equations

$$(\Gamma_{ik} - \rho v^2 \delta_{ik}) u_k = 0, \quad (18)$$

where $\Gamma_{ik} = c_{ijkl} n_j n_l$ is the Christoffel tensor, and u_k is the polarization vector [38]. The dependence of the phase velocity on the direction of the wave normal is represented by the equation

$$|\Gamma_{ik} - \rho v^2 \delta_{ik}| = 0. \quad (19)$$

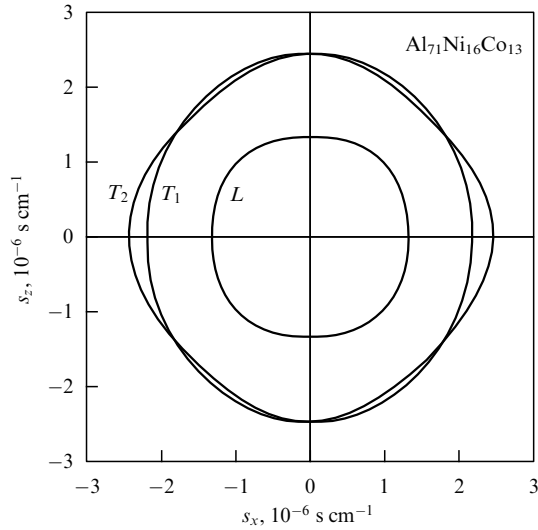


Figure 2. Zonal section of the slowness surface of the decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ quasicrystal by a plane containing the decagonal z -axis.

For transversely isotropic media, the solutions of equation (19) are given by the expressions

$$\begin{aligned} \rho v_{T_1}^2 &= C_{44} + \frac{1}{2} c \sin^2 \theta, \\ \rho v_{L,T_2}^2 &= C_{44} + \frac{1}{2} (a \sin^2 \theta + h \cos^2 \theta) \\ &\pm \frac{1}{2} [(a \sin^2 \theta + h \cos^2 \theta)^2 - 4(ah - d^2) \sin^2 \theta \cos^2 \theta]^{1/2}, \end{aligned} \quad (20)$$

where θ is the angle between the wave normal vector \mathbf{n} and the polar axis z ; parameters a , c , d , and h are defined as follows: $a = C_{11} - C_{44}$, $c = C_{11} - C_{12} - 2C_{44}$, $d = C_{13} + C_{44}$, $h = C_{33} - C_{44}$ [21].

The transverse isotropy of media makes the slowness surface circularly symmetric about the polar z -axis. Figure 2 depicts the zonal section of the slowness surface of a decagonal Al–Ni–Co quasicrystal by a plane containing the polar z -axis. The section was obtained from expressions (20) and (21) using the values of the elastic moduli $C_{\alpha\beta}$ (see Table 2). All the sheets of the slowness surface are convex throughout, hence the one-to-one correspondence between the group velocity vector \mathbf{V} and the wave normal vector \mathbf{n} within each sheet. In other words, each vector \mathbf{n} corresponds to one direction of \mathbf{V} , and vice versa. On the whole, the shape of the sheets of the slowness surface suggests weak polar anisotropy.

The weak polar elastic anisotropy is also evidenced by the dispersion curves $\omega(q)$ measured for certain symmetric directions of the decagonal Al–Ni–Co quasicrystal by the inelastic neutron scattering technique [39, 40]. It is worthwhile to note that the sound velocities obtained from the dispersion curves in the limit of small wave vectors are in good agreement with the elastic moduli determined by resonant ultrasound spectroscopy.

The knowledge of all elastic moduli $C_{\alpha\beta}$ makes it possible to calculate the contribution of lattice excitations to the low-temperature specific heat of the decagonal Al–Ni–Co quasicrystal from expression (8). For a transversely isotropic medium, the average of the inverse third power of the long-wave phase velocities v_i for three acoustic modes can be

written as [32]

$$\frac{1}{v_s^3} = \frac{1}{3} \sum_{i=T_1, T_2, L} \int_0^\pi \frac{1}{v_i^3(\theta)} \frac{\sin \theta d\theta}{2}. \quad (22)$$

Numerical integration of equation (22) using expressions (20) and (21) for the angular dependence of sound velocities $v_i(\theta)$ and elastic moduli $C_{\alpha\beta}$ measured at 5 K (see Table 2) gives $v_s = 4.9 \times 10^3 \text{ m s}^{-1}$. The substitution of the obtained mean sound velocity v_s into expression (8) leads to the coefficient of the acoustic contribution to the low-temperature specific heat $C_D/T^3 = 8.9 \mu\text{J (g-atom K}^4)^{-1}$, in good agreement with the coefficient $\beta = (9.5 \pm 0.6) \mu\text{J (g-atom K}^4)^{-1}$ of the cubic-in-temperature contribution to the low-temperature specific heat measured in the same sample [41]. The Debye temperature $\theta_D = 602 \text{ K}$ corresponds to the ratio C_D/T^3 obtained.

4. Conclusions

Precise measurements of the elastic moduli of the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ quasicrystal by resonant ultrasound spectroscopy have provided evidence that this quasicrystal constitutes an elastically isotropic medium, in agreement with theoretical predictions. The parameter of elastic anisotropy is only 0.0002 ± 0.0007 . This means that the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ quasicrystal is more isotropic than any periodically ordered crystal. In contrast, the cubic $\text{Al}_{4.8}\text{Li}_3\text{Cu}$ crystal, i.e., the periodic approximant of the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ quasicrystal, possesses reliably measurable elastic anisotropy, even if a very weak one.

Detailed experimental analysis of the resonant frequency spectrum of a single crystal of decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ has demonstrated that the number of independent elastic moduli responsible for the deformation in the quasiperiodic plane equals two, as for an isotropic medium. This quasicrystalline phase possesses transverse elastic isotropy to an accuracy of 0.0002 ± 0.0004 . Weak polar elastic anisotropy of the decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ quasicrystal suggests its closeness to the state of complete elastic isotropy and is consistent with the hypothesis of universal local order in decagonal and icosahedral quasicrystals.

To conclude, the application of resonant ultrasound spectroscopy has made it possible to experimentally determine the symmetry of the elastic modulus tensor of quasicrystals with icosahedral and decagonal structures, using the icosahedral $\text{Al}_{5.1}\text{Li}_3\text{Cu}$ and decagonal $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ quasicrystals as examples. In terms of elastic properties, icosahedral and decagonal quasicrystals may be regarded as isotropic and transversely isotropic media, respectively.

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