

## Elastic Moduli of a Single Quasicrystal of Decagonal Al-Ni-Co: Evidence for Transverse Elastic Isotropy

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The single quasicrystal elastic moduli  $c_{ij}$  of decagonal Al-Ni-Co were determined using resonant ultrasound spectroscopy at selected fixed temperatures in the range between 5 and 290 K. Decagonal Al-Ni-Co is found to be transversely elastically isotropic to  $(0.02 \pm 0.04)\%$ . The elastic moduli  $c_{ij}(T)$  exhibit weak temperature dependences. The elastic Debye temperature  $\Theta_D^{\text{el}}$  calculated from  $c_{ij}$  measured at 5 K agrees well with the thermodynamic Debye temperature  $\Theta_D^{\text{th}}$  obtained from a low-temperature specific-heat experiment. [S0031-9007(97)04988-0]

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Decagonal quasicrystals share structural properties with solids exhibiting both periodic and quasiperiodic types of long-range translational order. They are periodic along the decagonal axis and quasiperiodic in the plane perpendicular to it, thus exhibiting an unconventional structural anisotropy. For decagonal quasicrystals in the Al-Cu-Co and Al-Ni-Co alloy systems (five-dimensional space group  $P10_5/mmc$  [1]) strong anisotropies of electrical, thermal, and optical conductivities have experimentally been established [2,3].

We are not aware of any published data of the elastic moduli of a decagonal quasicrystal, and in this Letter we report the results of high precision measurements of the complete set of the elastic moduli  $c_{ij}$  of a single quasicrystal of decagonal Al-Ni-Co using resonant ultrasound spectroscopy (RUS) [4,5], and find, with a remarkable level of confidence, this quasicrystal to be transversely elastically isotropic within  $(0.02 \pm 0.04)\%$ .

For both decagonal Laue-symmetry classes  $10/m$  and  $10/mmm$ , the elastic modulus matrix contains the following nonzero components:  $c_{11} = c_{22}$ ,  $c_{33}$ ,  $c_{44} = c_{55}$ ,  $c_{66} = \frac{1}{2}(c_{11} - c_{12})$ ,  $c_{12}$ , and  $c_{13} = c_{23}$  [6]. The number of independent elastic moduli  $c_{ij}$  is five, and these are usually chosen to be  $c_{11}$ ,  $c_{33}$ ,  $c_{44}$ ,  $c_{12}$ , and  $c_{13}$ . The equality  $c_{66} = \frac{1}{2}(c_{11} - c_{12})$  reduces the number of independent elastic moduli  $c_{ij}$  that determine a deformation in the quasiperiodic plane to two, as for an isotropic medium. Thus, decagonal quasicrystals are expected to be *transversely elastically isotropic*. Among periodically ordered solids only hexagonal crystals are intrinsically transversely elastically isotropic. For comparison, icosahedral quasicrystals possess overall elastic isotropy; i.e., a deformation is determined by two independent elastic moduli [7–10] and for icosahedral Al-Cu-Li, elastic isotropy has recently been verified to within 0.07% using the RUS technique by Spoor and co-workers [11].

We first briefly discuss the notion of transverse elastic isotropy and anisotropy in terms of the components of the elastic modulus matrix, and review the experimental

approach of verifying whether or not a medium is transversely elastically isotropic. As an example, consider periodic crystals belonging to the tetragonal Laue-symmetry class  $4/mmm$ , which have six independent elastic moduli. These are  $c_{11} = c_{22}$ ,  $c_{33}$ ,  $c_{44} = c_{55}$ ,  $c_{66}$ ,  $c_{12}$ , and  $c_{13} = c_{23}$ . The elastic modulus matrix of the Laue class  $4/mmm$  differs from that of a transversely isotropic solid only in one respect, namely, that the elastic modulus combination  $c_{11} - c_{12} - 2c_{66}$  is nonzero. Therefore it is useful to compare transversely isotropic solids to the elastically most similar *tetragonal* crystals. A convenient measure of the deviation from transverse isotropy is the ratio

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

of the squares of the velocities of the pure shear waves polarized in the (001) plane and propagating along the [110] and [100] directions, respectively. We call  $A_s$  the azimuthal anisotropy of shear. We also define the ratio of the squares of the velocities of the longitudinal waves propagating along the [110] and [100] directions, respectively, as the compressional anisotropy  $A_c$ , i.e.,

$$A_c = \frac{c_{11} + 2c_{66} + c_{12}}{2c_{11}} \quad (2)$$

For transversely isotropic solids  $A_s = A_c = 1$ .

The  $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$  single quasicrystals were grown in an alumina crucible using the self-flux method [3]. Scanning electron microscopy investigation of the as-grown single quasicrystals did not reveal any grain boundaries or precipitates. An electron-diffraction experiment has indicated the  $S1$  superstructure type of decagonal order and a negligible phason strain. One of the single quasicrystals was oriented using the back-reflection Laue technique and then polished into a rectangular parallelepiped with dimensions  $x = 1.963$  mm,  $y = 1.215$  mm, and  $z = 1.192$  mm, with  $x$  and  $y$  parallel to the twofold axes and  $z$  parallel to the decagonal axis. The Laue patterns obtained from the lapped faces of the specimen have indicated that the orientation of the faces with respect to the

quasicrystal's symmetry axes was within  $\pm 0.1$  deg. From the mass and the dimensions, the mass density of the specimen was determined to be  $\rho = 4.186 \pm 0.033$  g/cm<sup>3</sup>.

The resonant frequencies of the sample were measured using the RUS technique [4,5] that uses free-body mechanical resonances of small ( $\approx 1$  mm) samples and allows one to determine the complete elastic modulus matrix. Because only very weak dry contacts between the corners of the sample and the transducers are required, there are no bond corrections, so that RUS typically provides the highest absolute accuracy of any routine modulus measurement technique.

The room-temperature resonant frequency spectrum was measured using a commercial precision RUS phase-sensitive spectrometer [12]. The low-temperature data were taken with an amplitude-only RUS spectrometer [13]. The resonant frequency spectra were measured in the frequency range between 1 and 3 MHz, in which a total of 30 resonances was observed. The quality factor  $Q$  of our quasicrystal was in the range between 1500 and 2500 depending on the particular mode, indicating its high acoustic quality. The RUS frequency data were analyzed using a well-tested Lagrangian minimization/Levenberg-Marquardt code developed by one of us at LANL [14] that also provides error estimates based on the curvature in  $n$ -dimensional space (where  $n$  is the number of elastic moduli) of the least-squares-fit elastic moduli. In all our fits we used the measured value of the mass density  $\rho$ . The fitting procedure was done by assuming that the sample was a perfect parallelepiped with the faces aligned parallel to the quasicrystal's symmetry axes. The three sample dimensions were allowed to vary within 25  $\mu$ m from the measured values; however, the same set of the best-fit dimensions was used for different fits.

Assuming that our quasicrystal has at least the Laue-symmetry  $4/mmm$ , so that there are at most *six* independent components  $c_{ij}$  of the elastic modulus tensor, we determined the elastic moduli  $c_{ij}$  shown in Table I. The rms error for the data fitting was 0.11%, which indicates excellent agreement between the measured and the calculated frequencies. We estimate our error in the pure shear moduli  $c' = \frac{1}{2}(c_{11} - c_{12})$  and  $c_{66}$  to be 0.03%. We note that the tetragonal fit produces  $c_{66} = 0.8845$  dyn/cm<sup>2</sup>. This implies an azimuthal anisotropy of shear  $A_s$  of  $1.0002 \pm 0.0004$ , indicating almost perfect isotropy, as is expected for a decagonal quasicrystal. The deviation

of  $A_s$  from unity is less than our estimated errors. Thus our quasicrystal is transversely elastically isotropic to  $(0.02 \pm 0.04)\%$ . The compressional anisotropy  $A_c$  is  $0.9999 \pm 0.0002$ , again indicating remarkable isotropy.

It is instructive to compare the experimentally determined azimuthal anisotropy ratios  $A_s$  and  $A_c$  of Al-Ni-Co with those of a transversely isotropic periodic crystal. We reanalyzed previously published RUS results for a hexagonal C40 NbSi<sub>2</sub> single crystal [15] in the way described above, i.e., assuming that at most *six* elastic moduli are independent. For NbSi<sub>2</sub>, the tetragonal fit produces  $c_{ij}$  as shown in Table I that are consistent with a shear anisotropy  $A_s = 0.9858 \pm 0.0023$  and a compressional anisotropy  $A_c = 1.0057 \pm 0.0009$ . For both ratios, the deviations from unity are much larger than the experimental errors, which can be attributed to small amounts of internal strain or other slight sample defects. Sample flaws and preparation errors hamper the identification of transverse elastic isotropy for hexagonal NbSi<sub>2</sub>, but not for decagonal Al-Ni-Co. Therefore, the shear anisotropy ratio provides an upper bound for our experimental sensitivity to anisotropy and we can estimate transverse elastic anisotropy in decagonal Al-Ni-Co to be less than  $(0.02 \pm 0.04)\%$ . In order to highlight the experimental uncertainties of our analysis using the tetragonal  $4/mmm$  fit, in Fig. 1 we plot  $A_c - 1$  versus  $A_s - 1$  for both materials.

We also measured the resonant frequency spectra of our specimen of decagonal Al-Ni-Co at selected fixed temperatures in the range between 5 and 290 K. Since we have experimentally established transverse elastic isotropy of decagonal Al-Ni-Co, the spectra were fitted assuming five independent elastic moduli. The elastic moduli  $c_{ij}$  obtained from this fitting are shown in Fig. 2 as functions of temperature  $T$ , revealing that  $c_{ij}(T)$  are only weakly temperature dependent. The elastic moduli  $c_{ij}$  deduced from the resonant frequency spectra measured at 5 and at 290 K are also given in Table I.

We now determine the degree of polar elastic anisotropy, i.e., the deviation from complete elastic isotropy. For transversely isotropic solids, two parameters may be used to quantify polar anisotropy, i.e., the compressional anisotropy  $P_c = c_{33}/c_{11}$  and the anisotropy of shear  $P_s = c_{44}/c_{66}$ . For decagonal Al-Ni-Co  $P_c = 0.991$  and  $P_s = 0.794$ , revealing rather unexpectedly, a very weak polar elastic anisotropy. For

TABLE I. Room temperature elastic moduli of decagonal Al-Ni-Co and of hexagonal NbSi<sub>2</sub>. Units are in  $10^{12}$  dyn/cm<sup>2</sup>;  $n$  is the number of independent elastic moduli.

	$n$	$c_{11}$	$c_{33}$	$c_{44}$	$c_{66}$	$c_{12}$	$c_{13}$
Al-Ni-Co	6	2.3430	2.3221	0.7019	0.8845	0.5736	0.6662
Al-Ni-Co	5	2.3433	2.3222	0.7019	0.8846	0.5741	0.6663
Al-Ni-Co <sup>a</sup>	5	2.4199	2.4019	0.7282	0.9175	0.5849	0.6669
NbSi <sub>2</sub>	6	3.8223	4.6802	1.4474	1.5267	0.8124	0.8804

<sup>a</sup> $T = 5$  K.

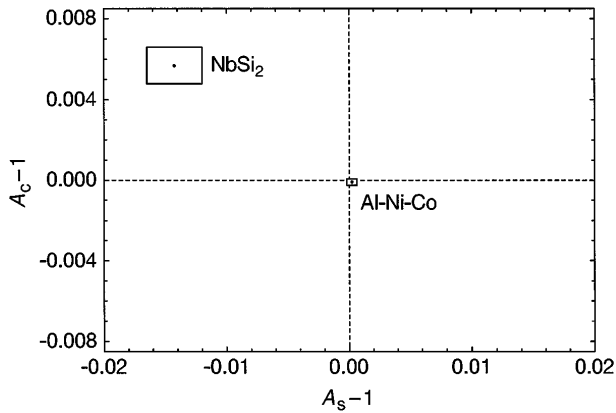


FIG. 1.  $A_c - 1$  vs  $A_s - 1$  for decagonal Al-Ni-Co and for hexagonal NbSi<sub>2</sub>. Error bars are shown as boxes.

these two parameters a value of 1 indicates elastic isotropy. We note that the compressional anisotropy  $P_c = 0.991$  is very close to unity. Since the elastic moduli  $c_{11}$  and  $c_{33}$  are closely related to potentials between atoms, this may imply almost equally strong atomic bonds along the periodic direction and in the quasiperiodic plane, supporting theoretical expectations considering a universal local order in decagonal and icosahedral quasicrystals [16].

A useful construction emphasizing elastic anisotropy is the constant frequency or slowness surface, which

$$\rho \left( \frac{q_{L,T_2}}{\omega} \right)^{-2} = c_{44} + \frac{1}{2} \{ a \sin^2 \theta + h \cos^2 \theta \pm [(a \sin^2 \theta + h \cos^2 \theta)^2 - 4(ah - d^2) \sin^2 \theta \cos^2 \theta]^{\frac{1}{2}} \}, \quad (4)$$

where  $\theta$  is the angle between the polar axis  $z$  and the wave vector  $\mathbf{q}$ , and the parameters  $a$ ,  $c$ ,  $d$ , and  $h$  are defined as follows:  $a = c_{11} - c_{44}$ ,  $c = c_{11} - c_{12} - 2c_{44}$ ,  $d = c_{13} + c_{44}$ , and  $h = c_{33} - c_{44}$ . Transverse isotropy makes the slowness surface circularly symmetric about the zonal axis  $z$  and in Fig. 3 we show the zonal section of the slowness surface obtained from Eqs. (3) and (4) using the room-temperature values of elastic moduli  $c_{ij}$ . As Fig. 3 reveals, the form of the sheets of the slowness surface again implies a rather weak polar anisotropy, in agreement with our estimates of the polar anisotropy parameters  $P_c$  and  $P_s$ .

We may also estimate the elastic moduli of a random, macroscopically isotropic aggregate of quasicrystals from the single quasicrystal elastic moduli. The isotropic bulk modulus  $K$  and shear modulus  $G$  can be obtained by averaging either the elastic moduli  $c_{ij}$  (Voigt [19]) or the elastic compliances  $s_{ij}$  (Reuss [20]). The isotropic moduli obtained from the room-temperature elastic moduli  $c_{ij}$  are shown in Table II. The Voigt and the Reuss averages represent the lowest upper and the highest lower bound, respectively, for the aggregate, and the close agreement between the two sets of values reflects the relatively low polar anisotropy of the single quasicrystal. We note the small Poisson's ratio  $\nu = 0.229$ , indicating that inter-

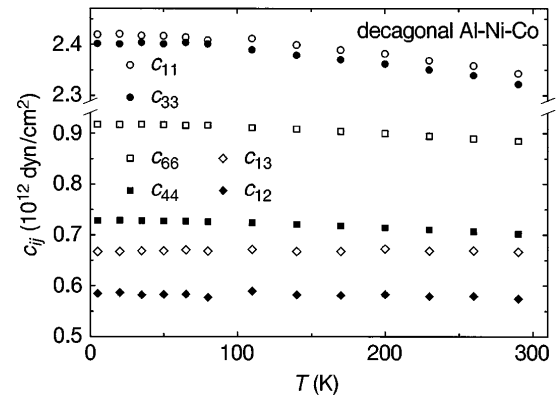


FIG. 2. Elastic moduli  $c_{ij}$  as functions of temperature.

may be obtained by solving the Christoffel equation [17] inserting the experimentally determined elastic moduli  $c_{ij}$  and the mass density  $\rho$ . There are three sheets of the slowness surface, commonly labeled according to the polarization of the corresponding acoustic waves: quasilongitudinal ( $L$ ) for the inner sheet, and pure shear ( $T_1$ ) and quasishear ( $T_2$ ) for the two outer sheets. For transversely isotropic solids, the slownesses  $q_i/\omega$  are given by [18]

$$\rho \left( \frac{q_{T_1}}{\omega} \right)^{-2} = c_{44} + \frac{1}{2} c \sin^2 \theta, \quad (3)$$

atomic forces in decagonal Al-Ni-Co are noncentral ( $\nu = 0.25$  is the lower limit for a central-force solid [21]).

Finally, we calculate the low-temperature specific heat  $C_{ph}(T)$  due to lattice excitations. At low temperatures

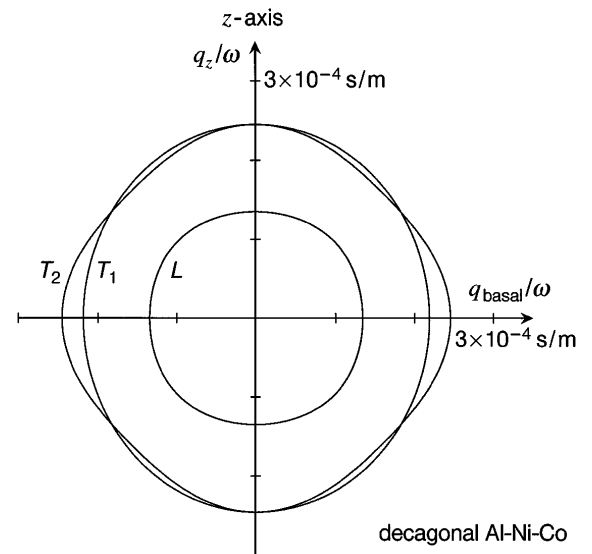


FIG. 3. Zonal section of slowness surface.

TABLE II. Room-temperature isotropic elastic moduli. Units are in  $10^{12}$  dyn/cm<sup>2</sup>.

Averaging scheme	$K$	$G$
Voigt	1.2025	0.7978
Reuss	1.2022	0.7891

only the long-wavelength acoustic modes contribute to  $C_{\text{ph}}(T)$ , which takes the form

$$C_{\text{ph}}(T) = \frac{2\pi^2 k_B^4}{5\hbar^3 v_s^3} T^3, \quad (5)$$

where  $1/v_s^3$  is the average of the inverse third power of the phase velocities  $v_i(\mathbf{q})$  of the three acoustic modes:

$$\frac{1}{v_s^3} = \frac{1}{3} \sum_{i=1}^3 \int \frac{1}{v_i^3(\theta)} \frac{\sin \theta d\theta}{2}. \quad (6)$$

Using the elastic moduli  $c_{ij}$  obtained at 5 K we deduce the average sound velocity  $v_s$  to be  $(4.91 \pm 0.02) \times 10^3$  m/s [22]. Inserting this value into Eq. (5) leads to an acoustic contribution to the low-temperature specific heat  $C_{\text{ph}} = (8.93 \pm 0.11)T^3 \times 10^{-6}$  J/molK, in fair agreement with the term  $\beta T^3 = (9.5 \pm 0.6)T^3 \times 10^{-6}$  J/molK of the low-temperature specific heat measured on this same specimen [3]. This is quite in contrast to the icosahedral Al-Mn-Pd and Al-Re-Pd quasicrystals, for which the existence of a large excess cubic-in- $T$  contribution to the low-temperature specific heat  $C_p(T)$  has recently been established [23].

It is common to characterize the acoustic specific heat of crystals using the Debye temperature  $\Theta_D$ . We note, however, that for a quasicrystal a common definition of  $\Theta_D$  involving the number of atoms per unit cell is not unambiguous. We define  $\Theta_D$  of a quasicrystal as

$$\Theta_D = \frac{\hbar}{k_B} \left( \frac{6\pi^2 N_0}{V} \right)^{1/3} v_s, \quad (7)$$

where  $N_0$  is the number of atoms in a volume  $V$ . Employing this definition we deduce the elastic  $\Theta_D^{\text{el}}$  and the thermodynamic  $\Theta_D^{\text{th}}$  Debye temperatures of decagonal Al-Ni-Co to be  $601.5 \pm 3.2$  and  $589 \pm 13$  K [3], respectively, in good agreement with each other.

To summarize, we reiterate that for a single quasicrystal of decagonal Al-Ni-Co we measured resonant ultrasound frequency spectra at selected fixed temperatures in the temperature range between 5 and 290 K. From the analysis of these spectra we have shown decagonal Al-Ni-Co to be transversely elastically isotropic within  $(0.02 \pm 0.04)\%$ . The weak polar anisotropy indicates that also this decagonal quasicrystal is close to being elastically isotropic, a rather unexpected result of this study. The elastic moduli  $c_{ij}$  depend only weakly on temperature. The elastic Debye temperature  $\Theta_D^{\text{el}}$  calculated using  $c_{ij}$  as determined from the frequency scans taken at 5 K agrees, within the experimental accuracy, with the thermodynamic Debye temperature  $\Theta_D^{\text{th}}$ .

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