Anisotropic Nonlinear Elastic Properties of an Icosahedral Quasicrystal

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We show that the nonlinear behavior of transverse acoustic waves can reveal the anisotropic structure of an icosahedral quasicrystal, at the macroscopic level. We report experiments performed in *i*-Al-Pd-Mn. We observe that a primary transverse acoustic wave can generate a second harmonic transverse acoustic wave. We also observe a specific relation between the polarization directions of those waves. These observations are manifestations on a macroscopic scale of the long-range order in quasicrystals.

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At the microscopic level, diffraction studies show that quasicrystals exhibit a structural orientational long-range order responsible for icosahedral symmetries. Thus, quasicrystals are fundamentally anisotropic. At the macroscopic level, physical properties are expected to be anisotropic and this point must be investigated. However, the symmetry of the icosahedral group is so high that macroscopic properties are isotropic unless they are described by a tensor with rank $N \geq 5$ [1]. Therefore, the commonly observed properties are isotropic and do not reveal the anisotropic structure of the quasicrystal. Here are two examples. The magnetization is governed by a second-rank tensor and is found to be isotropic in icosahedral Al-Cu-Fe [2]. The linear elastic properties are governed by a fourth-rank tensor (so called, second-order elastic constants) and are found to be isotropic in Al-Li-Cu and Al-Pd-Mn [3–5]. Small anisotropy of the nonlinear magnetic properties was reported in Al-Pd-Mn and attributed to the anisotropy of N-rank magnetic tensors ($N \geq 6$). However, the data could not be fitted within this assumption [6]. Anisotropy of the ultrasonic attenuation was also reported but was attributed to structural defects (phasons) [5]. Therefore, to our knowledge, no clear evidence for intrinsic anisotropic physical properties has been reported at the macroscopic level. The nonlinear propagation of elastic waves is a macroscopic phenomenon which can distinguish icosahedral from isotropic symmetry since the nonlinear elastic properties depend on a sixth-rank tensor (so called third-order elastic constants) [7]. We present in this paper a theoretical analysis of the nonlinear propagation of transverse waves in an icosahedral solid, and we show these waves can generate second harmonic transverse acoustic waves. We stress that this process is forbidden in an isotropic solid and can be used to reveal the anisotropic structure of quasicrystals. We also report here such experiments performed in an Al-Pd-Mn single quasicrystal. The results are in agreement with our theoretical analysis and, in particular, second harmonic generation is observed when propagation is along a threefold axis. Therefore, our results clearly reveal, at the macroscopic level, the anisotropic structure of the icosahedral Al-Pd-Mn.

Let us call XYZ the standard orthogonal coordinate system, aligned with three twofold axes. In XYZ, the Brugger third-order elastic constants are C_{ijk}. There are four independent terms C_{111}, C_{112}, C_{113}, and C_{456}, instead of three for isotropic symmetry [8] [in our opinion, the erratum in [8] still contains a mistake and the correct expression for C_{456} is $C_{456} = -\frac{1}{2}C_{144} - \frac{1}{2}(\tau - 1)C_{155} + \frac{1}{2}\tau C_{166}$]. The isotropic case is deduced from the icosahedral one with the additional relation $C_{112} = C_{113}$. Thus, it is useful to define the quantity

$$\Delta = C_{112} - C_{113}, \qquad (1)$$

which measures the departure from the isotropic case. Whether Δ is large enough to induce observable effects is an open question. Fundamentally, $\Delta \neq 0$ because the X and Y directions are not equivalent, although they are both twofold axes. They have the same environment but with different orientations: both axes are surrounded by two threefold and two fivefold axes. However, in the XY plane, one axis is surrounded by two threefold axes, whereas the other is surrounded by two fivefold axes. This difference is rather subtle and a small value of Δ is expected. A sensitive acoustic probe is therefore desirable. Transverse acoustic waves are such sensitive probes. Indeed, because of the quadratic character of the nonlinear terms, symmetry arguments show they do not produce second harmonic waves in isotropic solids (contrary to longitudinal waves). This is confirmed by calculus [9]. Let us show that this process is allowed in an icosahedral crystal for propagation along a threefold axis and forbidden for propagation along a twofold or a fivefold axis.

The nonlinear equations of motion are conveniently expressed in an orthogonal coordinates system xyz where x is aligned with the propagation direction and z with a symmetry axis (if such an axis exists). The derivation of the nonlinear equations of motion is lengthy but straightforward. Let us first consider the propagation along a threefold axis. xyz is deduced from XYZ by a rotation through the angle α about Z, where $\cos\alpha = \tau/\sqrt{3}$ and $\sin\alpha = 1/\tau\sqrt{3}$ [$\tau = (1 + \sqrt{5})/2$ is the golden number]. Accordingly, x is along a threefold axis and z is along a twofold axis. Approximate equations of motion can be obtained by a perturbation method [10,11]. For fundamental transverse waves propagating along a threefold axis, we get

$$u_i = u_i^{[I]} + u_i^{[II]} \qquad (i = 1, 2, 3), \tag{2}$$

$$\rho \frac{\partial^2 u_i^{[I]}}{\partial t^2} - C_{44} \frac{\partial^2 u_i^{[I]}}{\partial x^2} = 0 \qquad (i = 2, 3), \tag{3}$$

$$\rho \frac{\partial^2 u_2^{[II]}}{\partial t^2} - C_{44} \frac{\partial^2 u_2^{[II]}}{\partial x^2} = \frac{-2\Delta}{9} \frac{\partial}{\partial x}\left[\left(\frac{\partial u_2^{[I]}}{\partial x}\right)^2 - \left(\frac{\partial u_3^{[I]}}{\partial x}\right)^2\right], \tag{4}$$

$$\rho \frac{\partial^2 u_3^{[II]}}{\partial t^2} - C_{44} \frac{\partial^2 u_3^{[II]}}{\partial x^2} = \frac{4\Delta}{9} \frac{\partial}{\partial x}\left[\frac{\partial u_2^{[I]}}{\partial x} \frac{\partial u_3^{[I]}}{\partial x}\right], \tag{5}$$

where u is the acoustic displacement field, $u^{[I]}$ is the fundamental field (i.e., the field when the nonlinear terms are neglected), and $u^{[II]}$ is a small correction arising from the nonlinear terms. C_{44} is a second-order elastic constant. ρ is the mass density. Taking into account the initial conditions (i.e., assuming that a transverse acoustic wave with a single frequency component $\omega/2\pi$ is emitted at $x = 0$), we find

$$u^{[I]} = \begin{pmatrix} 0 \\ a\cos\phi \\ a\sin\phi \end{pmatrix} \cos(\omega t - kx), \tag{6}$$

$$u^{[II]} = -\frac{a^2k^2\Delta}{18C_{44}} \begin{pmatrix} 0 \\ \cos 2\phi \\ -\sin 2\phi \end{pmatrix} x\cos(2\omega t - 2kx), \tag{7}$$

where a, ϕ, and $k = \pm\sqrt{\rho\omega^2/C_{44}}$ are the amplitude, the polarization angle, and the wave vector of the fundamental wave, respectively. Therefore, a transverse wave propagating along a threefold axis produces a transverse second harmonic wave which grows linearly with x. The polarization angle ψ of this harmonic wave (with respect to y) is given by

$$\psi = -2\phi. \tag{8}$$

This relation is consistent with the threefold symmetry. Conversely, it is easily seen that such a relation is not consistent with an isotropic symmetry axis. Thus, from an experimental point of view, if such a relation is observed, we may safely conclude that the solid structure is anisotropic without any detailed theoretical analysis of the nonlinear propagation in either isotropic or anisotropic solids.

Transverse waves propagating along an arbitrary direction will, in general, produce second harmonic transverse waves (twofold and fivefold axis directions are exceptions; see below). However, the relation between the polarization direction of the fundamental and harmonic waves would be more complicated than given by (8). Propagation along a fivefold axis or along a twofold axis can be studied in the same way as propagation along a threefold axis. When studying propagation along a fivefold axis, xyz is deduced from XYZ by a rotation through the angle β about Z, where $\cos\beta = 1/\sqrt{1+\tau^2}$ and $\sin\beta = \tau/\sqrt{1+\tau^2}$. When studying propagation along a twofold axis, xyz is the standard coordinate system XYZ. The equations of motion of transverse waves are similar to Eqs. (2)–(5) except that the right-hand terms of (4) and (5) are zero. Thus, transverse waves propagating either along a fivefold axis or along a twofold axis do not produce a harmonic wave.

Equations (2)–(5) are also valid in an isotropic solid but, in that case, Δ vanishes and we see that transverse waves propagate undistorted: there is no harmonic generation by transverse acoustic waves in an isotropic solid.

We studied the icosahedral quasicrystalline phase $Al_{68.2}$-$Pd_{22.8}Mn_{9.0}$. The sample is a single quasicrystal grown using the Czochralski technique. The detailed production and characterization of the sample have been reported previously by other authors [12]. Figure 1 is a sketch of the sample orientation and mounting. It is oriented by x-ray diffraction. A twofold axis is found (here named A2) and defines the z direction. Then, a threefold and a fivefold axis, both perpendicular to A2 are determined (A3 and A5). In case of propagation along the threefold axis (the fivefold axis), A3 (A5) defines the x direction. The y direction is such that xyz is a direct Cartesian

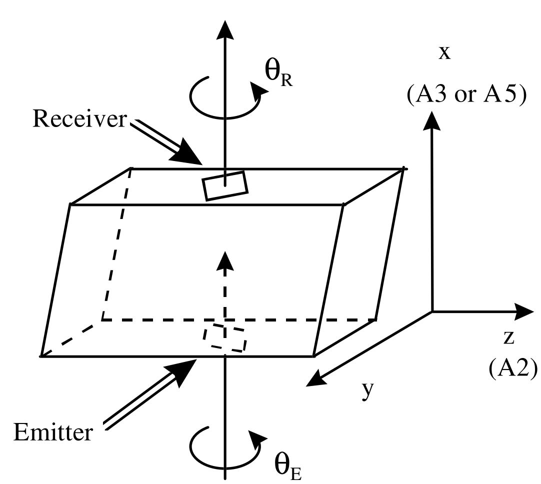

FIG. 1. Orientation of the sample and of the acoustic transducers. θ_E and θ_R are the polarization angles of the emitter and of the receiver, in the yz plane, with respect to y.

coordinate set. Two sets of faces, perpendicular to A3 and A5, are then cut and polished, in the same sample. The sample thickness is 7.7 and 5.4 mm along A3 and A5, respectively. Acoustic transducers are glued on the opposite parallel faces. A transducer emits a pulse of transverse acoustic wave at 22 MHz (the high frequency electrical excitation is filtered with a bandpass filter), and another one detects the acoustic pulse after propagation in the sample. The emitter is glued with orthoterphenyl (melting point ≈60 °C) and the receiver is glued with phenylsalicylate (salol, melting point ≈40 °C). Thus, it is possible to rotate the receiver in the yz plane, by successive melting and freezing of the salol bond, without modifying the characteristics of the emitter (polarization direction, electromechanical coupling factor, ...). The receiver can detect signals between 15 and 60 MHz (resonance frequency: 44 MHz). The transducers are $LiNbO_3$ plates (163° rotated Y cut) with a well controlled polarization. Their polarizations are in the yz plane and the polarization angles are measured with respect to the y axis: θ_E and θ_R for the emitter and the receiver, respectively. As far as linear elasticity is considered, the sample behaves as if it were isotropic. In our experiments, the emitter therefore launches a pulse of transverse wave, polarized in the yz plane, with polarization angle θ_E. The receiver is used to detect both the fundamental wave and the possible second harmonic wave. Bandpass filtering at 44 MHz is provided when the second harmonic wave is looked for. In an experimental run, the emitter is fixed and the receiver is rotated in the yz plane. Different runs correspond to different values of θ_E.

When transverse waves propagate along A3, the frequency spectrum of the first transmitted pulse displays two peaks, at the excitation frequency 22 MHz and at the double frequency 44 MHz. Figures 2(a) to 2(f) display the magnitude of the 22 and 44 MHz components versus the receiver polarization angle θ_R, for characteristic values of the emitter polarization angle θ_E. The relative uncertainty on the magnitudes is about 10%. It mainly results from the fluctuations of the receiver coupling factor arising from the successive melting and freezing of the salol bond. We observe that each component at 22 and 44 MHz goes through a maximum and a minimum value. Let us call θ_{R1} and θ_{R2} the location of the maximum of each components. We observe that $(\theta_{R1} - \theta_{R2})$ depends on θ_E. We have also measured the amplitude of the 44 MHz component versus that of the 22 MHz component, for given values of θ_E and θ_R. A quadratic relation is observed.

When transverse waves propagate along A5, the double frequency component is very small and does not depend on θ_R. Figures 2(g) and 2(h) display the measurements for $\theta_E = 0°$. Similar results were obtained for $\theta_E = 90°$.

Clearly, the double frequency component which is observed when transverse waves propagate along A3 results from some nonlinear process. This process originates

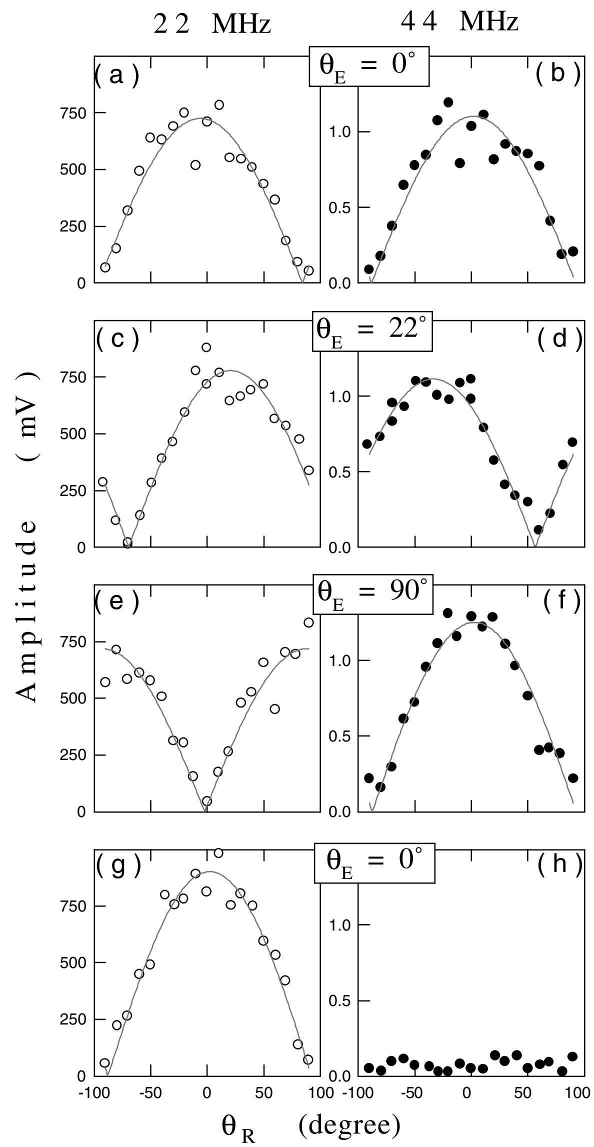

FIG. 2. Amplitude of the 22 and 44 MHz components of the first transmitted pulse versus the receiver polarization angle θ_R, for various values of the emitter polarization angle θ_E. Open circle: 22 MHz. Solid circle: 44 MHz. (a) to (f): propagation along A3. (g) and (h): propagation along A5. The full lines are fits based on $|A\cos(\theta_R - \theta)|$ with free parameters A and θ.

from the sample and cannot be located in the electronic setup, including the transducers. Otherwise, $(\theta_{R1} - \theta_{R2})$ would not depend on θ_E and a large harmonic signal would also be observed when transverse waves propagate along A5. Therefore, our results give evidence that a transverse acoustic wave propagating along A3 produces a double frequency harmonic transverse acoustic wave. We now discuss the only propagation along A3. The amplitudes measured at 22 and 44 MHz are maximum (minimum) when the polarizations of the relevant wave and of the receiver are parallel (perpendicular). We have investigated the relation between the polarization angles ψ and ϕ of the

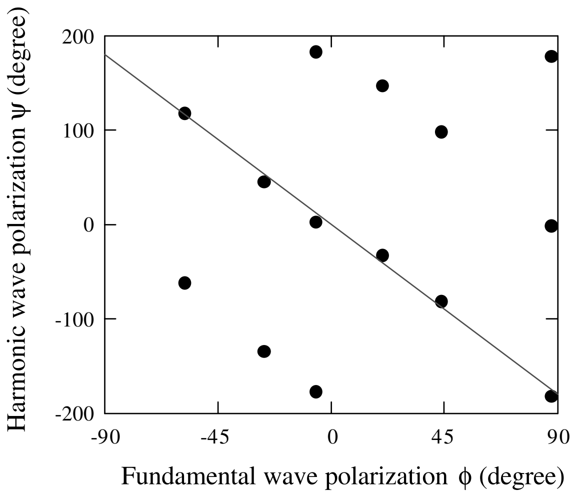

FIG. 3. Polarization direction ψ of the second harmonic wave versus polarization direction ϕ of the fundamental wave. The full line is a theoretical line deduced from Eq. (8).

second harmonic and fundamental waves. For that purpose, we have fitted the amplitudes measured at 22 and 44 MHz with $|A\cos(\theta_R - \theta)|$ where A and θ are free parameters and where θ is the wave polarization angle. Figure 2 displays some fits and Fig. 3 displays the experimental relation between ψ and ϕ. Actually ψ and ϕ are determined modulo π. Thus, in Fig. 3, ϕ is arbitrarily set in $[-\pi/2, \pi/2]$ and ψ is plotted as a multivalued function. The full line is deduced from Eq. (8). Very good agreement between the experimental points and the theoretical relation ($\psi = -2\phi$) is observed. It must be pointed out that the polarization directions rather than the polarization angles are determined. This is not a problem since opposite directions are related through a π phase shift and polarization directions rather than polarization angles have a physical meaning. Nevertheless, it would be significant to know the phase relation between the fundamental and harmonic vibrations. Unfortunately, in our experiments, the phase difference between two acoustic waves with different frequencies cannot be measured because the phase shift between the input acoustic signal and the output electric signal of the receiver depends on the frequency and is not known.

The production of a second harmonic wave by transverse acoustic waves shows that the solid is anisotropic since this process is forbidden in an isotropic solid. This point is confirmed by the experimental relation between the polarization directions of the fundamental and harmonic waves which is inconsistent with isotropic symmetry. Last, the different behavior of transverse acoustic waves propagating along A3 or A5 also demonstrates that the solid is anisotropic. Our theoretical analysis shows that the observed macroscopic properties are consistent with the icosahedral symmetry, revealed by diffraction experiments, at the microscopic level. In principle, the sign of Δ could be deduced from the phase relation between the fundamental and harmonic vibrations, but we already mentioned that this information is not available in our experiment. In principle again, the value of Δ could be deduced from a comparison of the respective amplitudes of the fundamental and harmonic waves [see Eqs. (6) and (7)]. Unfortunately, the electromechanical coupling factors at 22 and 44 MHz, and thus the waves displacement amplitudes, cannot be accurately measured. Moreover, the acoustic attenuation should be taken into account. Another kind of experiment should be devised to measure Δ.

In conclusion, the propagation of acoustic waves is a macroscopic phenomenon which can distinguish a quasicrystal from a crystal or from a glass: linear properties can distinguish a quasicrystal from a crystal (unlike crystals, the linear elastic tensor is isotropic) and nonlinear properties can distinguish a quasicrystal from a glass (unlike a glass, the nonlinear elastic tensor is anisotropic). We have studied the nonlinear propagation of transverse acoustic waves in an icosahedral Al-Pd-Mn single domain. Our results show clear manifestations on a macroscopic scale of the anisotropic structure of this solid and therefore confirm the existence of an internal long-range order.

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