Natrolite: A zeolite with negative Poisson's ratios

Joseph N. Grima,[a)] Ruben Gatt, and Victor Zammit
Department of Chemistry, University of Malta, Msida MSD 06, Malta

Jennifer J. Williams and Kenneth E. Evans[b)]
School of Engineering, Computer Science and Mathematics, University of Exeter, Exeter, EX4 4QF, United Kingdom

Andrew Alderson[c)]
Centre for Materials Research and Innovation, University of Bolton, Bolton, BL3 5AB, United Kingdom

Richard I. Walton[d)]
Department of Chemistry, The University of Warwick, Coventry, CV4 7AL, United Kingdom

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The recently published experimental elastic constants [C. Sanchez-Valle, S. V. Sinogeikin, Z. A. Lethbridge, R. I. Walton, C. W. Smith, K. E. Evans, and J. D. Bass, J. Appl. Phys. **98**, 053508 (2005)] for single crystals of the orthorhombic aluminosilicate zeolite NAT (natrolite, $Na_2(Al_2Si_3O_{10})2H_2O$, *Fdd*2) throw valuable light on the potential of NAT as a material which exhibits single crystalline negative Poisson's ratios (auxetic). On performing an off-axis analysis of these elastic constants we confirm that the zeolite natrolite exhibits auxetic behavior in the (001) plane. This supports our preliminary report that NAT-type zeolites exhibit auxetic behavior through a mechanism involving microscopic rotation of semi-rigid structural units. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2718879]

Materials with negative Poisson's ratios (auxetic) exhibit the unexpected property of becoming fatter when stretched and thinner when compressed.[1] This property was first reported more than half a century ago when iron pyrites single crystals were described as having a negative Poisson's ratio.[2] At that time, this phenomenon was generally regarded as an anomaly since commonly used materials did not exhibit this property and there was little understanding of how real materials could behave in this manner. However, over the last two decades, auxetic behavior has been predicted, discovered, or deliberately introduced in various materials[1,3–16] including nanostructured and liquid crystalline polymers,[1,3–6] metals,[7] silicates[8–11] and microstructured materials[12–14] (e.g., foams[12,13] and microporous polymers[14]). Several auxetic macrostructures have also been proposed.[17–19] In all of these systems, the negative Poisson's ratios are a consequence of the way that the geometry of the macro/micro/nanostructure of the material changes when uniaxial mechanical loads are applied. Auxetics are not solely of interest because they exhibit the unusual property of expanding when stretched but also because they exhibit various enhanced physical characteristics over their conventional counterparts ranging from increased indentation resistance[20] to improved acoustic damping properties.[21] As a result of these enhanced characteristics, auxetic materials have potential in many practical applications.[20,21]

Zeolites, materials characterized by highly geometric nanostructures, find practical applications where the separation of material at the molecular level is important (e.g., as molecular sieves and ion exchange membranes). Although various properties of single crystalline zeolites have been extensively studied,[22] little information is known on their single crystalline mechanical properties, and in particular their Poisson's ratios.[23–26] Recently, modeling studies have indicated the potential for zeolitic-like structures to exhibit negative Poisson's ratios.[23–25] Specifically, we have reported that molecular mechanics simulations suggest that the SiO_2 equivalents of various zeolite frameworks exhibit negative Poisson's ratios, a property which can generally be explained in terms of the geometry of their nanoporous frameworks.[23] Zeolites with negative Poisson's ratios are highly desirable since it has been shown that a porous auxetic material offers potential benefits in mass transport applications due to the increased change in the size/shape of the pore structure associated with the high volume change characteristic of a negative Poisson's ratio material undergoing an external applied load.[23–25] Thus, auxetic zeolites have a potential of acting as smart molecular sieves where the sorption properties, in particular molecular selectivity, could be controlled through the application of mechanical loads.[23–25]

One of the zeolite frameworks which was suggested to be auxetic in the preliminary force-field based study[23] was the SiO_2 equivalent of natrolite (NAT). Recently, experimental elastic constants for orthorhombic aluminosilicate NAT single crystals ($Na_2(Al_2Si_3O_{10})2H_2O$, *Fdd*2) have been determined from the acoustic velocities measured in different crystalline orientations by Brillouin scattering spectroscopy at ambient conditions.[27] It is the purpose of this article to show that the experimental data in Ref. 27 confirm our preliminary hypothesis in Ref. 23 that NAT exhibits auxetic behavior as illustrated in Figs. 1 and 2.

a)Electronic address: joseph.grima@um.edu.mt
b)Electronic address: k.e.evans@ex.ac.uk
c)Electronic address: a.alderson@bolton.ac.uk
d)Electronic address: r.i.walton@warwick.ac.uk

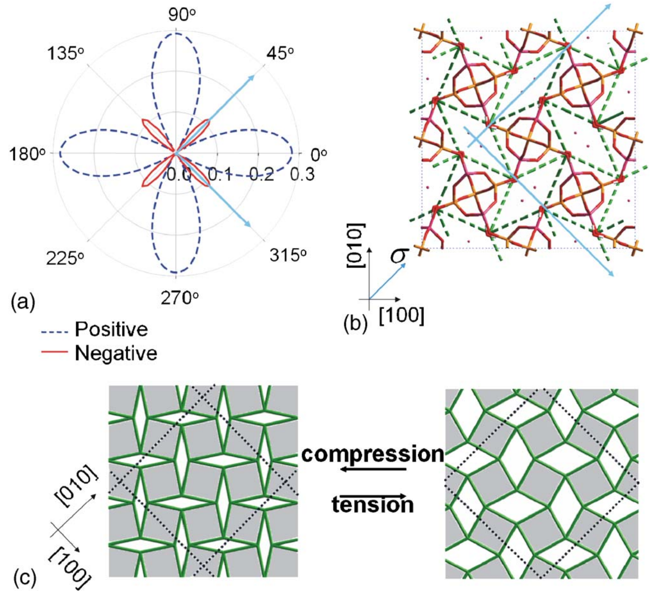

FIG. 1. (Color online) (a) An off-axis analysis of the experimentally determined Poisson's ratios in the (001) plane of NAT[27] which confirms that NAT is auxetic in the (001) plane with maximum auxeticity ($v=-0.12$) being exhibited at ±45° to the [100] and [010] crystallographic axes; (b) the crystal structure of NAT with the "connected squares" model highlighted; and (c) the "idealized rotating rigid squares" model which exhibits negative Poisson's ratios of −1 irrespective of the size of the squares and the direction of loading.[16] Note that the directions of maximum auxeticity may be directly mapped to the nanostructure of NAT.

In fact, an analysis of the full set of experimental stiffness coefficients (c_{ij}) using standard axis transformation techniques,[28] clearly indicates that NAT exhibits conventional behavior in the (100) and (010) planes [see Fig. 3(a)] but exhibits negative Poisson's ratios for loading in certain directions with maximum auxeticity ($v=-0.12$) being exhibited for loading at 45° to the main crystallographic axis in the (001) plane, as illustrated in Figs. 1(a) and 2. Auxetic behavior is not limited to the (001) plane as illustrated in Fig. 2 which also gives details of the angular spread of auxeticity. This is a very important finding, confirming the presence of negative Poisson's ratio behavior in a naturally occurring single-crystalline zeolite. The magnitude of the negative Poisson's ratio, −0.12, measured in natrolite compares well

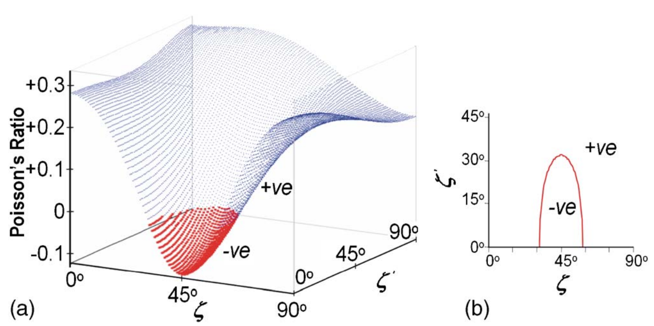

FIG. 2. (Color online) (a) A 3D plot of the Poisson's ratio in one quadrant which confirms that maximum auxeticity occurs in the (001) plane (i.e., $\zeta'=0°$) for loading at $\zeta=45°$ to the [001] direction. This plot was obtained by transforming $\nu_{[001][100]}$ by axis rotation by angle ζ around the [001] direction and by an axis rotation by angle ζ' around the [010] direction. (b) The range of angles ζ and ζ' where the Poisson's ratio in (a) is negative.

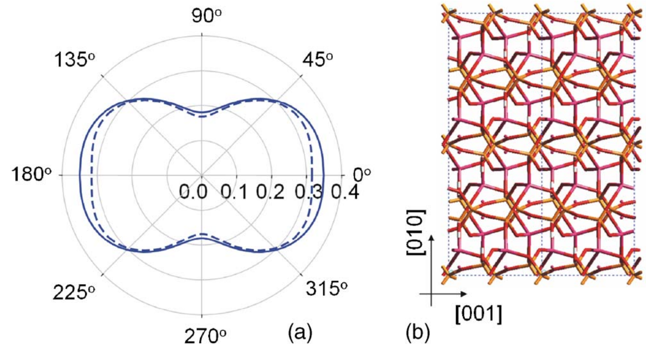

FIG. 3. (Color online) (a) The Poisson's ratios in the (010) plane (solid line, 0° corresponds to $\nu_{[001][100]}$) and the (100) plane (broken line, 0° corresponds to $\nu_{[001][010]}$) and (b) the structure of NAT in the (100) plane which is similar to that in the (010) plane.

with that of other auxetics: For example, single crystals of α-cristobalite[9] and paratellurite[29] ($\alpha-TeO_2$) exhibit minimum Poisson's ratios of −0.5 and −0.15, respectively, single crystalline cubic metal alloys[7,30] such as Ni_3Al, $Cu_{6.86}Al_{27.6}Ni_{3.8}$, and $CuAuZn_2$ exhibit minimum Poisson's ratios of −0.18, −0.67, and −0.81, respectively, while foams manufactured through a heating/compression process have been reported to exhibit isotropic Poisson's ratios of ∼−0.7.[12] [Various conventional materials also exhibit Poisson's ratio of comparable and even smaller magnitudes to that of NAT: For example, the Poisson's ratio of concrete measured in compression is typically in the range of 0.1–0.2 (Ref. 31) while cork has a Poisson's ratio of 0, i.e., it does not change in thickness when stretched or compressed.[32]]

The anisotropy in the experimentally determined Poisson's ratios in the (001) plane where maximum auxeticity is exhibited for loading in the [110] and $[1\bar{1}0]$ directions (i.e., $\nu_{[1\bar{1}0][110]}$ and $\nu_{[110][1\bar{1}0]}$) is very significant since it adds confidence to the preliminary work in Ref. 23 where negative Poisson's had also been predicted in the (001) plane with maximum auxeticity being exhibited in the same directions, an effect which may be described in terms of a "rotating squares" model.[23,33,34] In fact, as illustrated in Fig. 1 the framework of NAT is such that the projections of the atoms in the (001) plane form a geometric pattern which may be trivially described in terms of "connected squares", the corners of which correspond to the oxygen atoms of the Si-O-Al linking bonds [Fig. 1(b)]. Systems with such geometric features and connectivity are known to be able to exhibit auxetic behavior[23,33,34] and in-plane Poisson's ratios of −1 are realized if the idealized structure illustrated in Fig. 1(c) deforms solely through cooperative rotation of rigid squares (the idealized "rotating squares" model[33,34]). In real materials such as NAT, such idealized behavior leading to Poisson's ratios of −1 is difficult to achieve since the squares are merely the two-dimensional (2D) projection of a much more complex three-dimensional nanostructure which in reality will not behave as perfectly rigid units. Nevertheless, as discussed in the preliminary study in Ref. 23, molecular modeling simulations suggest that when the NAT framework is stretched in a direction of maximum auxeticity, the atomic-level deformations are such that one may clearly observe that

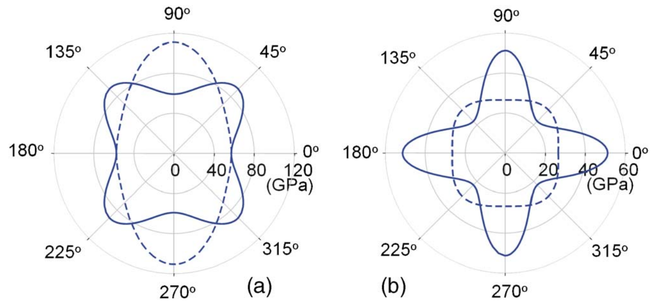

FIG. 4. (Color online) The (a) Young's moduli and (b) shear moduli of NAT. The solid lines correspond to the moduli in the (001) plane while the broken lines correspond to the moduli in the (100) plane where in the case of the Young's moduli, 0° corresponds to $E_{[100]}$ while in the case of the shear moduli, 0° corresponds to the $G_{[100][010]}$ (solid line) and $G_{[100][001]}$ (broken line).

the "squares" projected in the (001) plane rotate with respect to each other resulting in the observed negative Poisson's ratios. Thus, the experimental confirmation that the directions of maximum auxeticity in NAT correspond to major axes of the "rotating squares" model of NAT [i.e., the lines joining two opposite corners of the "rhombi" which form between four connected "squares" in NAT, see Fig. 1(b)] gives more weight to the hypothesis that auxetic behavior in NAT is indeed the result of these microscopic rotations. We note that the lack of auxeticity in the (100) and (010) planes is due to the fact that the geometry of the NAT framework in these planes does not contain the essential features for a mechanism resulting in auxetic behavior (e.g., the "rotating squares" mechanism) to operate [see Fig. 3(b)].

The anisotropy in the moduli is also worth noting. For example, as illustrated in Fig. 4(a), we observe that the significantly higher Young's moduli are exhibited for loading in the [001] direction when compared to the moduli in the (001) plane, as expected for zeolites such as natrolite which are much more "flexible" in the (001) plane where they may deform through the "rotating squares" mechanism [see Fig. 4(b)]. It is also interesting to note that the anisotropy in the moduli in the (001) plane may also be directly mapped to the anisotropy of the Poisson's ratio in this plane and to the nanostructure of NAT since we observe that the directions of maximum auxeticity coincide with maximum Young's moduli [Fig. 4(a)] and minimum shear moduli [see Fig. 4(b)].

We envisage that our article reporting negative Poisson's ratios in natrolite may have various important implications for future work on zeolites and auxetic materials. Experimental verification that other zeolites (e.g., JBW, THO) identified in the earlier modeling study[23] as auxetic would lead to improved confidence in the use of force-field based simulations for the design and modeling of inorganic auxetic materials. This work is also likely to encourage researchers in the field to investigate more thoroughly where auxetic zeolites could be exploited in practical applications (e.g., as tuneable molecular sieves in ion exchange and catalysis where porosity could be adjusted by application of stress[13]). The identification of the mechanism by which NAT exhibits negative Poisson's ratios is likely to provide impetus for further work on the design and production of new man-made auxetics tailored to particular practical applications.

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