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An alternative explanation for the negative Poisson's ratios in α-cristobalite

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Abstract

Materials with a negative Poisson's ratio (auxetic) exhibit the unusual property of becoming wider when stretched and thinner when compressed. A naturally occurring auxetic material which has attracted a lot of research in recent years is α-cristobalite, a silicate for which negative Poisson's ratios have been experimentally measured. We present the results of force-field based molecular modelling studies which will provide an insight into nano-level deformations that occur when this silicate is subjected to externally applied uniaxial mechanical stresses. These results will suggest that the auxetic behaviour can be explained in terms of a 'rotation of rigid units' model and, more specifically we will show that the auxetic behaviour in the (0 1 0) and (1 0 0) planes may be explained in terms of 'rotating rectangles' which are the projections of the three-dimensional silicate framework in the (0 1 0) and (1 0 0) planes.

Keywords: Auxetic; Cristobalite; Negative Poisson's ratios; Mechanical properties

1. Introduction

Materials with a negative Poisson's ratio (auxetic) exhibit the counterintuitive behaviour of becoming wider when stretched and thinner when compressed [1]. This behaviour imparts many beneficial effects on the materials' macroscopic properties (e.g. increased indentation resistance [2,3], a natural ability to form dome-shaped surfaces [1], etc.) that make auxetics superior to their conventional counterparts in many practical applications [3].

Although it has long been known that negative Poisson's ratios are theoretically feasible (for example, the theory of classical elasticity suggests that isotropic materials may exhibit Poisson's ratios within the range $-1 \leq \nu \leq +0.5$ [4]), real interest in materials exhibiting this unusual yet very useful property started in 1987 when samples of auxetic foams were produced from conventional ones through a simple compression/heating process [5]. Since then, several auxetics have been predicted, discovered and/or manufactured including various naturally occurring auxetics such as cubic metals [6], zeolites [7] and silicates [8,9] and man-made auxetics such as nanostructured [1,10–12], liquid crystalline [13,14] and microporous [15–17] polymers and foams [5,18–20]. In all of these cases, the negative Poison's ratios can be explained in terms of models based on the geometry of the materials' nano/microstructure and the way this geometry changes as a result of uniaxially applied loads (the deformation mechanism).

2. Negative Poisson's ratio in α-cristobalite

An auxetic material which has attracted considerable attention is the naturally occurring silicate α-cristobalite for which auxetic behaviour for loading in certain directions was independently discovered and reported by Keskar and Chelikowsky [8] who studied this mineral using ab initio modelling techniques and by Yeganeh-Haeri et al. [9] who measured the single crystalline mechanical properties of α-cristobalite experimentally using brillouin spectroscopy. The experimental work of Yeganeh-Haeri et al. [9] suggests that negative Poisson's ratios can be measured in the (1 0 0) and (0 1 0) planes of α-cristobalite for loading in any direction in these planes. It also suggests that the Poisson's ratios are most negative for loading at ca.

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45° to the main crystallographic axis, i.e. in the case of the (1 0 0) plane, the maximum auxeticity is observed for loading in the [011] and [01$\bar{1}$] directions whilst the case of the (0 1 0) plane, the maximum auxeticity is observed for loading in the [101] and [10$\bar{1}$] directions.

This silicate is particularly interesting as the extent of the single crystalline auxetic behaviour is so pronounced that the isotropic polycrystalline aggregate Poisson's ratios are also predicted to be negative within the range $-0.21 < \nu < -0.12$. These isotropic polycrystalline values of the Poisson's ratios relate to the idealised scenario where the crystal domains in a sample of α-cristobalite are arranged in such a way that the resulting material is isotropic, in which case the maximum and minimum values of the polycrystalline Poisson's ratios can be calculated using:

$$\nu^{\max} = \frac{3K^{\text{Voigt}} - 2G^{\text{Reuss}}}{6K^{\text{Voigt}} + 2G^{\text{Reuss}}} \quad \text{and} \quad \nu^{\min} = \frac{3K^{\text{Reuss}} - 2G^{\text{Voigt}}}{6K^{\text{Reuss}} + 2G^{\text{Voigt}}} \tag{1}$$

where K^{Voigt} and G^{Voigt} are the polycrystalline bulk and shear moduli as estimated using the Voigt method [21] whilst K^{Reuss} and G^{Reuss} the polycrystalline bulk and shear moduli as estimated using the Reuss method [22] since that Voigt moduli refer to the greatest possible moduli whilst those calculated through the Reiss method are the lowest possible moduli [23].

There have been various attempts to explain this unusual behaviour of α-cristobalite. For example, Keskar and Chelikowsky [8] proposed a model which suggests that the negative Poisson's ratio in α-cristobalite can be explained in terms of rotations of rigid SiO_4 tetrahedra. This model was later extended by Alderson et al. [24–26] who suggest that the experimentally measured auxetic behaviour in α-cristobalite can be explained in terms of a concurrent tetrahedral model (CTM) where a dilation tetrahedral model (DTM) occurs concurrently to rotating tetrahedral models (RTMs) [26].

3. An alternative explanation: rotating rectangles

We propose an alternative explanation for the experimentally observed auxetic behaviour in α-cristobalite based on the fact that that when one looks at the (0 1 0) and (1 0 0) planes of the crystal structure of α-cristobalite (i.e. the planes where auxetic behaviour was identified [9]), one may notice that the atomic positions form a geometric pattern which may be trivially described as rectangles connected together at their vertices (see Fig. 1a). This arrangement of rectangles may exhibit auxetic properties if the rectangles rotate relative to each other, and in the idealised scenario where perfectly rigid rectangles are connected together through simple hinges with the geometry illustrated in Fig. 1b, this system would exhibit in-plane Poisson's ratios of −1 [27].

This can be shown mathematically since for a periodic system, the on-axis Poisson's ratios in the Ox_1–Ox_2 plane may be defined by

$$\nu_{21} = (\nu_{12})^{-1} = -\frac{d\varepsilon_1}{d\varepsilon_2} \tag{2}$$

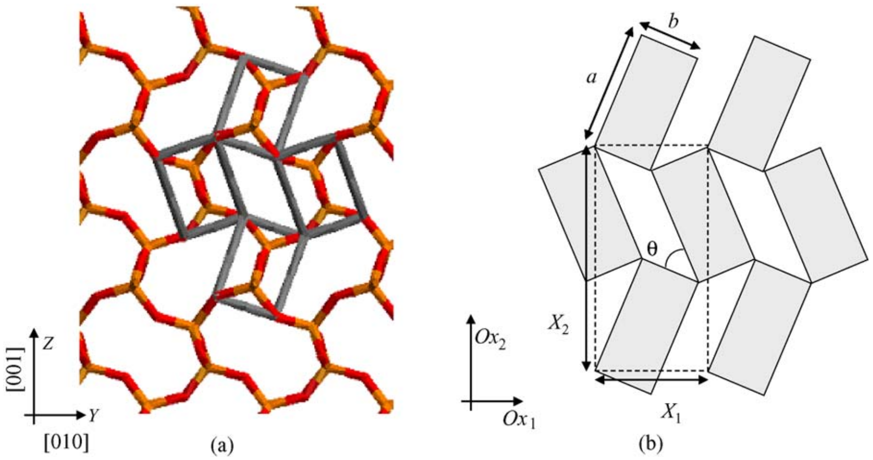
where $d\varepsilon_i$ represent infinitesimally small strains in the Ox_i directions which may be defined in terms of infinitesimally small changes 'dX_i' in the magnitudes of the unit cell projections 'X_i' by $d\varepsilon_i = dX_i/X_i$.

In this case, for an idealised system made from hinged perfectly rigid rectangles of size '$a \times b$' deforming solely though relative rotation of the rectangles, i.e. from changes in the value of θ, the unit cell projections X_i may be assumed to be functions of the single variable θ and the Poisson's ratios may be written as

$$\nu_{21} = (\nu_{12})^{-1} = -\frac{d\varepsilon_1}{d\varepsilon_2} = -\frac{dX_1/X_1}{dX_2/X_2} = -\frac{dX_1/d\theta}{dX_2/d\theta}\frac{X_2}{X_1} \tag{3}$$

Thus, referring to Fig. 1b, since:

$$X_1 = 2b\sin\left(\frac{\pi}{4} + \frac{\theta}{2}\right) \quad \text{and} \quad X_2 = 2a\sin\left(\frac{\pi}{4} + \frac{\theta}{2}\right) \tag{4}$$



(a) (b)

Fig. 1. (a) The projection in the (1 0 0) plane of α-cristobalite with the 'rotating rectangles' model highlighted; (b) an illustration of how the '$a \times b$ rectangles' are connected in the 'rotating rectangles' model being proposed here.

i.e.:

$$\frac{dX_1}{d\theta} = b\cos\left(\frac{\pi}{4}+\frac{\theta}{2}\right) \quad \text{and} \quad \frac{dX_2}{d\theta} = a\cos\left(\frac{\pi}{4}+\frac{\theta}{2}\right) \tag{5}$$

the Poisson's ratios simplify to:

$$\nu_{21} = (\nu_{12})^{-1} = -1 \tag{6}$$

However, in real materials such as α-cristobalite, the assumption that the rectangles are perfectly rigid is unrealistic and in such cases, one would expect that the Poisson's ratios would be less negative and the actual magnitudes would depend, amongst other things, on the rigidity of the rectangles.

4. Evidence for the new 'rotating rectangles' model

In an attempt to obtain evidence that the 'rotating rectangles' model operates in α-cristobalite and can be used to explain the observed auxetic effect, we performed force-field based molecular modelling simulations to simulate the effect of uniaxial loading on the molecular structure of α-cristobalite.

All simulations were carried out using the commercially available molecular modelling package Cerius^2 (Release 3.0) developed by Accelrys Inc. Within this package, one can find several force-fields which are parameterised for simulating SiO_2 systems, namely the Universal [28], Burchart [29], BKS [30] and CVFF [31] force-fields. In view of the lack of published data comparing these force-fields, we performed a preliminary study aimed at assessing the suitability of these various force-fields for reproducing known properties of α-cristobalite including the equilibrium lattice parameters and the Poisson's ratios. In all simulations, the unit cell of α-cristobalite was aligned relative to the global *XYZ*-coordinate system in such a way that the [0 0 1] direction is parallel to the *Z*-axis and the (1 0 0) plane is parallel to the *YZ*-plane. The energy expressions were set up using the default force-field parameters and settings. (In the case of the Universal force-field, the partial charges were calculated using the Charge Equilibration procedure developed by Rappé and Goddard [32] since this force-field does not contain any information on the atomic charges.) Non-bond interactions were summed up using the Ewald method [33]. The energy of these systems were minimised to the default Cerius^2 high convergence criteria which include a condition that the RMS gradient must be less than 0.001 kcal mol^{-1} Å^{-1}. No constraints on the shape and size of the unit cell were applied during the minimisations. For each force-field, the single crystalline mechanical properties were obtained by simulating the 6 × 6 stiffness matrix **C** of the minimised systems which can be calculated from the second derivative of the energy expression, *E*, since:

$$c_{ij} = \frac{1}{V}\frac{\partial^2 E}{\partial\varepsilon_i \partial\varepsilon_j}, \quad i, j = 1, 2, \ldots, 6$$

where *V* is the volume of the unit cell, ε_1, ε_2 and ε_3 are the strains in the *X*, *Y* and *Z* directions, respectively, whilst ε_4, ε_5 and ε_6 are the shear strains in the *YZ*-, *XZ*- and *XY*-planes, respectively. The on-axes Poisson's ratios may then be calculated the terms in the compliance matrix $\mathbf{S} = \mathbf{C}^{-1}$ since, for example,

$$\nu_{yz} = -\frac{\varepsilon_z}{\varepsilon_y} = -\frac{s_{32}}{s_{22}}, \qquad \nu_{zy} = -\frac{\varepsilon_y}{\varepsilon_z} = -\frac{s_{23}}{s_{33}}$$

whilst the off-axes mechanical properties may be obtained from the off-axes simulated stiffness matrix and its inverse, the off-axes compliance matrix, which may be obtained using standard transformation of axes techniques [34].

An analysis of the simulated properties suggests that all four force-fields can correctly reproduce the fact that α-cristobalite exhibits maximum negative Poisson's ratios in the (0 1 0) and (1 0 0) planes for loading at ca. 45° to the major axes. However, as illustrated in Table 1 which compares values of the simulated lattice parameters and Poisson's ratios with the experimentally determined values, the Burchart force-field simulates the lattice parameters closest to the experimentally determined values, followed closely by the CVFF force-field whilst the CVFF force-field can reproduce the magnitudes of the experimentally measured negative Poisson's ratios much better than the other three force-fields, including the Burchart force-field. In particular, the CVFF force-field was the only force-field which correctly predicts negative on-axis Poisson's ratios in the *YZ*- and *XZ*-planes. This force-field also predicted a range for the Poisson's ratios for the isotropic polycrystalline aggregate closest to the one obtained from the experimental data [9]. In view of this, it was concluded that CVFF is the most suitable force-field for simulating the mechanical properties of α-cristobalite.

In order to verify the hypothesis that the auxetic behaviour in α-cristobalite is due to a 'rotating rectangles' mechanism, a series of minimisations at different uniaxial stress were performed using the CVFF force-field. In these simulations, all stresses were applied in the [0 1 1] direction (i.e. at 45° to the [0 0 1] axis, in the (1 0 0) plane) as this direction corresponds

Table 1
A comparison of the simulated lattice parameters and Poisson's ratios with the experimentally determined values

	Lattice parameters			Single crystalline Poisson's ratios in the (1 0 0) plane (*YZ*-plane)				Polycrystalline Poisson's ratios	
	a, *b* (Å)	*c* (Å)	α, β, γ (°)	On-axis		45° off-axis		ν_{min}	ν_{max}
				ν_{yz}	ν_{zy}	ν_{yz}	ν_{zy}		
Experimental	4.978	6.948	90.000	−0.098	−0.070	−0.497	−0.497	−0.211	−0.115
CVFF	4.965	6.619	90.000	−0.160	−0.074	−0.317	−0.317	−0.127	−0.026
Burchart	4.978	6.684	90.000	0.022	0.100	−0.305	−0.305	−0.039	0.072
BKS	4.889	6.528	90.000	0.073	0.050	−0.417	−0.417	−0.074	0.026
UFF	4.940	6.606	90.000	0.138	0.079	−0.007	−0.007	0.092	0.125

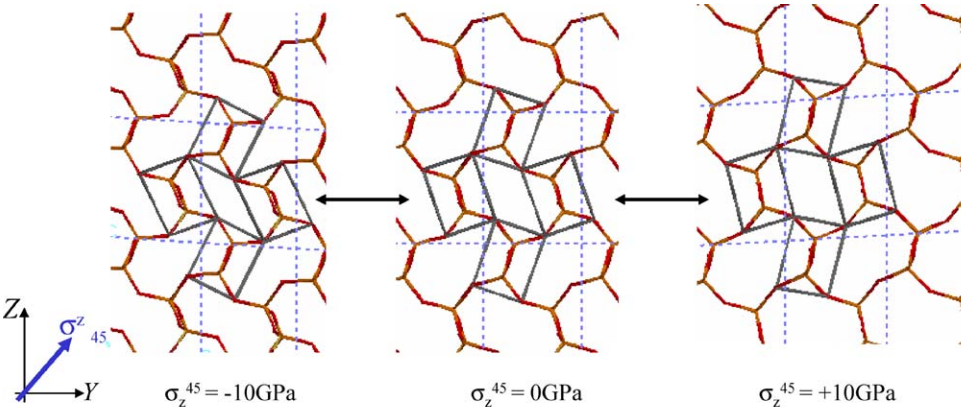


Fig. 2. An illustration of how the molecular structure of α-cristobalite changes as a result of uniaxially applied loads in the [0 1 1] direction.

to the direction where α-cristobalite shows maximum auxetic behaviour in the (1 0 0) plane, and hence one would expect that loading in this direction will make the auxetic effect more pronounced.

A pictorial representation of the minimum energy conformations of α-cristobalite at the various applied loads as viewed down the [1 0 0] direction are shown in Fig. 2. A visual comparison of these conformations clearly suggests that the ‘rectangles’ identified in Fig. 1a have rotated with respect to each other when subjected to the uniaxial loads with the result that the structure ‘opens up’ hence producing the observed negative Poisson’s ratio. The simulations also suggest that the ‘rectangles’ do not remain perfectly rigid but deform, although these deformations appear to be less pronounced than the relative rotation of the rectangles. To quantify these observations, we have identified a typical ‘rotating rectangles’ unit and measured the variations of the projections in the (1 0 0) plane of various distances between two atoms (e.g. l_1–l_4 which corresponds to the side lengths of the rectangles and d_1, d_2 which correspond to opposite corners of adjacent rectangles) and various angles between three atoms (e.g. ω_1–ω_4 which correspond to the internal angles of the rectangles, θ_1, θ_2 which correspond to the angles between the rectangles). As illustrated in Fig. 3, these measurements confirmed that the angles between the different rectangles (θ_1, θ_2) and the distances between adjacent rectangles (d_1, d_2) change must faster than any of the other geometric parameters relating

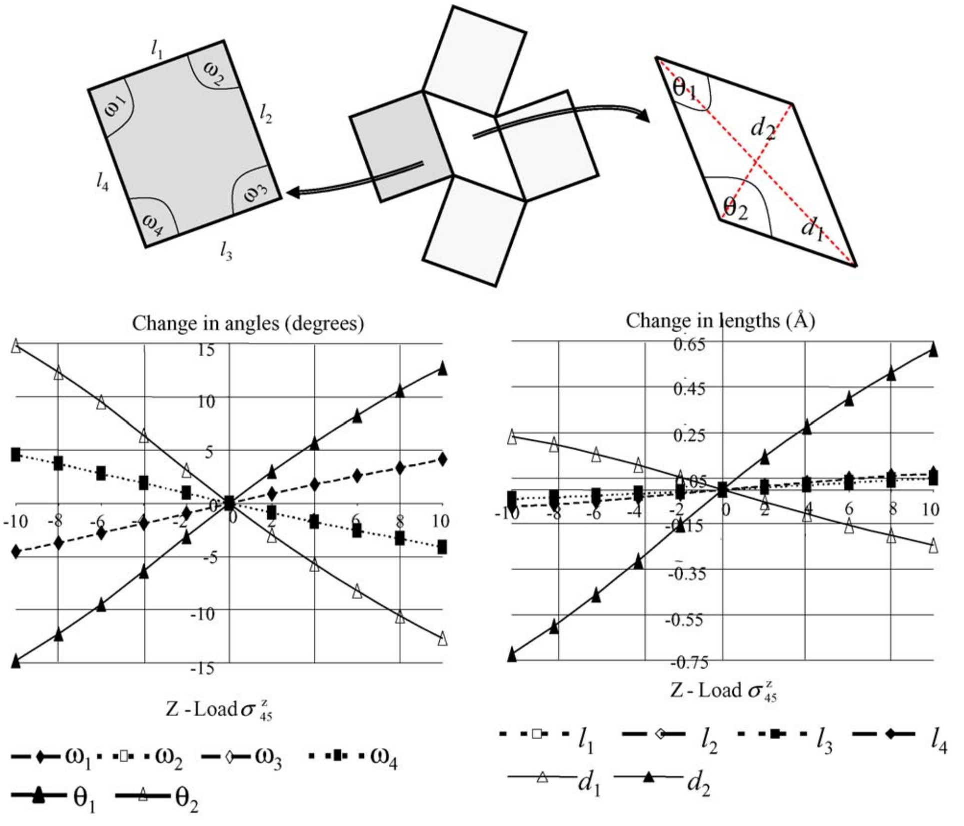


Fig. 3. An illustration of how various geometric parameters change as a result of applied stresses in the [0 1 1] direction.

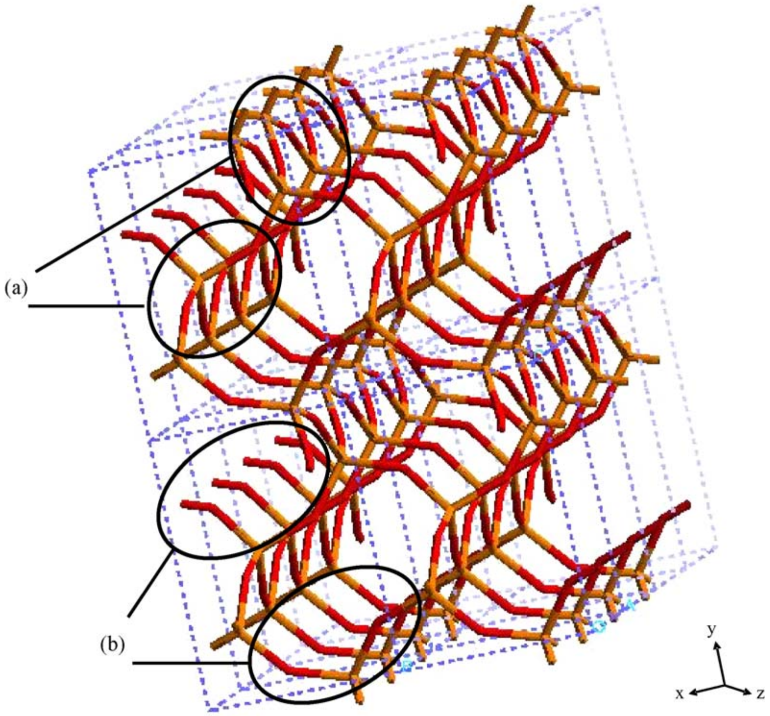


Fig. 4. The 3D structure of α-cristobalite and its relationship to the 2D 'rotating rectangles' model proposed here: (a) the rigid 'columnar structures' with a 'rectangular' projection in *YZ*-plane; (b) the soft Si–O–Si bonds representing the hinges.

to a single rectangle (l_1–l_4 and ω_1–ω_4) thus confirming that the shape and size of the rectangles changes to a lesser extent than the angles between the rectangles. Similar results were obtained in the (0 1 0) plane for loading in the [1 0 1] direction.

These observations are very significant as they clearly illustrate the validity of the hypothesis that auxetic behaviour in α-cristobalite can be explained in terms of a simple two-dimensional 'rotating rectangles' model. Furthermore, they also provide us with an explanation for the deviations between the idealised 'rotating rectangles' model which suggests that the Poisson's ratios should be −1 [27] and the actual values of the Poisson's ratios which are less negative, a phenomenon which is due to the fact that in the real material, the 'rectangles' are not perfectly rigid.

It is also very significant that as illustrated in Fig. 4, the directions of maximum auxeticity in the (0 1 0) and (1 0 0) planes correspond to directions of the lines joining two opposite corners of the 'parallelograms' which form between four rectangles (and which may, therefore, be treated as the major axes of the 'rotating rectangles' model). As a result of this, the anisotropy in the Poisson's ratio can be directly mapped to the 'rotating rectangles' model that is being proposed here, hence adding more confidence to the hypothesis that this new model plays a very significant role in generating the observed auxetic behaviour.

5. Discussion and conclusion

In this paper we have proposed an alternative explanation for the observed auxetic behaviour in the naturally occurring silicate α-cristobalite, were the auxetic effect is explained in terms of a two-dimensional model which describes cross-sections of the crystal in terms of 'connected rectangles'. This new explanation is supported by force-field based molecular modelling simulations which confirm that uniaxial loads result in deformations in the crystal structure which may be described in terms of rotations of these rectangles.

Two-dimensional geometry-based models describing particular cross-sections of materials (such as the one described here) are particularly suitable for studying the Poisson's ratios since the Poisson's ratio is in itself a property which describes the behaviour of a 2D cross-section of a material and the way this deforms when the material is subjected to uniaxial loads. In fact, the technique of using 2D models has been successfully used to explain the values of the Poisson's ratios in various classes of materials [1,5,7,11,15–17,20]. However, in reality, the crystal structure of α-cristobalite is a three-dimensional structure composed of connected SiO_4 tetrahedra, and hence any deformations in α-cristobalite will necessarily involve deformations and/or re-orientations of these SiO_4 tetrahedra. In other words, the 'rotating rectangles' model proposed here is simply a representation of the net effect of the projection of these tetrahedral deformations and/or re-orientations in specific planes. In this respect, it is important to relate the 2D 'rotating rectangles' model to the 3D crystal structure of α-cristobalite. For example, as illustrated in Fig. 5, the 'rigid rectangles' in the (1 0 0) plane correspond to the 2D projections of SiO_4 tetrahedral units connected in such a way that they form a columnar-like structure aligned parallel to the third direction (the [1 0 0] direction). Adjacent columnar-like structures are connected through 'soft' Si–O–Si bonds located at regular intervals down the third

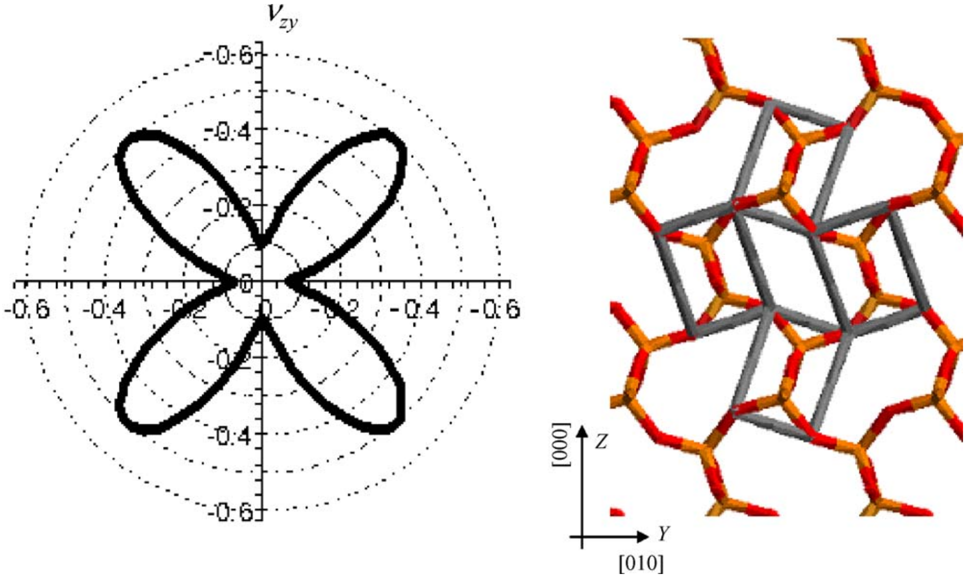


Fig. 5. The off-axes Poisson's ratio in the (1 0 0) plane: note that the directions of maximum auxeticity approximately correspond to the 'major axes' of the rotating rectangles' model.

direction which may bend more easily than the more 'rigid' columnar-like structures. As a result, the columnar-like structures are more rigid than the units connecting them and hence when the system is loaded, the deformations will be concentrated around the Si–O–Si 'hinges' with the net effect that the columns (the cross-sections of which are the rectangles) rotate relative to each other to generate the experimentally observed negative Poisson's ratios. Similar geometric features may also be observed in the (0 1 0) plane.

The identification of the role of the 'rotating rectangles' mechanism in α-cristobalite is particularly significant as it confirms that 'rotation of rigid units' play a very important role in generating auxetic behaviour at the molecular level. Furthermore, the correct identification of the mechanism which nature uses to achieve the unusual effect of auxetic behaviour can provide researchers working in the field with a 'working model' which they can use to produce new man-made auxetics at the nano-, micro- and/or macro-level which exhibit negative Poisson's ratios by mimicking the behaviour of this naturally occurring nanostructured material.

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