On the origin of auxetic behaviour in the silicate α-cristobalite†

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The experimentally observed negative Poisson's ratios in the silicate α-cristobalite are explained through a two-dimensional 'rotation of rigid units' model involving 'rotating rectangles' hence providing a new insight into the way nature can achieve this unusual property.

The Poisson's ratio is one of the fundamental mechanical properties of materials which defines how a material changes shape when uniaxially loaded. More specifically, the Poisson's ratio v_{ij} in the Ox_i–Ox_j plane for loading in the Ox_i direction is defined by:

$$v_{ij} = -\frac{\text{strain in the transverse } Ox_j\text{−direction}}{\text{strain in the loading } Ox_i\text{−direction}} = -\frac{\varepsilon_j}{\varepsilon_i}$$

Most everyday materials have a positive Poisson's ratio, meaning they get thinner when stretched and fatter when compressed. However, auxetic materials are materials with negative Poisson's ratios (*i.e.* they get fatter when stretched and thinner when compressed).[1] The classical theory of elasticity suggests that isotropic materials can exhibit Poisson's ratios within the range $-1 \leqslant v \leqslant 0.5$, and the allowed range is wider for anisotropic solids.[2] It has been shown that negative Poisson's ratios result in many beneficial enhancements in other properties of materials such as an enhanced resistance to indentation[3,4] and enhanced sound absorption properties[5] which means that the use of auxetic materials could result in the production of superior quality products.

In recent years, auxetic behaviour has been predicted and/or experimentally measured in a number of materials including synthetic foams,[4,6–10] nano- and microstructured polymers,[1,11–15] metals,[16] silicates[17–19] and zeolites.[20] In these materials, the negative Poisson's ratios are the result of the particular geometry of the material's micro- or nanostructure and the way the micro/nanostructure deforms when the material is subjected to a uniaxial stress (the deformation mechanism).

A naturally-occurring auxetic material which has attracted a lot of attention in recent years is the silicate α-cristobalite for which single crystalline auxetic behaviour for loading in certain directions was independently discovered and reported by Keskar and Chelikowsky (through *ab initio* modelling)[17] and by Yeganeh-Haeri *et al.* (experimentally using laser Brillouin spectroscopy).[18] It has also been reported that the extent of auxeticity in the single crystal is such that isotropic polycrystalline aggregates of α-cristobalite are also predicted to exhibit a negative Poisson's ratio.

A number of attempts have been made to explain this unusual behaviour by looking at how the SiO_4 tetrahedra change shape or re-orient themselves when the system is loaded. For example, Keskar and Chelikowsky showed that cooperative rotation of rigid tetrahedra leads to auxetic behaviour,[17] and Alderson and co-workers have shown that concurrent rotations and dilation of the SiO_4 tetrahedra can give very accurate predictions of the Poisson's ratio values.[19] Here we propose a much simpler representation for this unusual behaviour, namely that if one looks at the (010) and (100) planes of this mineral (*i.e.* the planes where negative Poisson's ratios were experimentally measured), one may notice that the atomic positions form a geometric pattern which may be trivially described as the rectangles equivalent of the 'rotating squares' structure (see Fig. 1a). The rotating squares structure has previously been reported to exhibit auxetic properties[21] Like their 'squares' equivalent, 'rotating rectangles' are capable of exhibiting auxetic behaviour and it has been shown that an idealised structure where perfectly rigid rectangles are connected together through simple hinges with the geometry illustrated in Fig. 1b will have in-plane Poisson's ratios of -1.[22]

In view of this, we have used force-field based simulations to simulate the mechanical properties of α-cristobalite. Simulations were performed using the molecular modelling package Cerius[2] V3.0 (Molecular Simulations Inc., San Diego, USA). In the simulation, the crystal was aligned relative to the global XYZ coordinate system in such a way that the [001] direction is parallel to the Z-axis and the (100) plane is parallel to the YZ-plane. An energy expression was set up using the CVFF force-field[23] with non-bond interactions summed using the Ewald summation

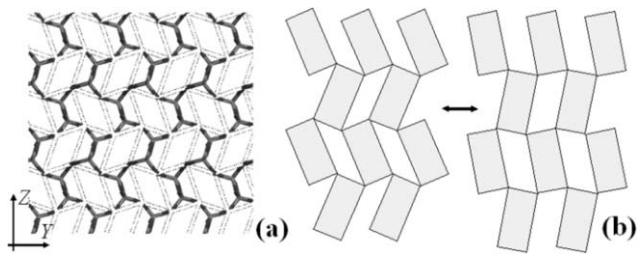

Fig. 1 (a) The (100) plane of α-cristobalite with the 'rectangles' highlighted, (b) an illustration of the idealised 'rotating rectangles' model (see also the ESI† for an animated version of this image). Note the (100) plane corresponds to the YZ plane in the global XYZ orthogonal coordinate system.

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† Electronic supplementary information (ESI) available: animations of the deformation mechanism described in Fig. 1b and Fig. 3a. See http://dx.doi.org/10.1039/b508098c

Table 1 A comparison of the CVFF simulated lattice parameters with the experimentally obtained values

	Experimental	CVFF
a, b	4.978 Å	4.965 Å (−0.26%)
c	6.948 Å	6.619 Å (−4.74%)
α, β, γ	90.000°	90.000° (0%)

procedure.[24] The stiffness matrix was simulated from the second derivative of the energy expression since:

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

from which the off-axes Poisson's ratios were calculated using standard axes transformation techniques.[25] These simulations and calculations confirmed that the CVFF force-field reproduces fairly accurately the equilibrium structure of the material and the experimentally measured single crystalline mechanical properties including the auxetic behaviour. In particular, the simulated lattice parameters compared very well with the experimentally obtained values (less than 5% difference, see Table 1). Furthermore, as illustrated in Fig. 2, the CVFF simulations reproduced the experimental observation that in the (010) and (001) planes the negative Poisson's ratios have their largest magnitude when the uniaxial stresses are applied at $\sim 45°$ to the major axis of the crystal.

We have also simulated the atomic-level deformations that take place when α-cristobalite is uniaxially loaded by performing a series of energy minimisations at different values of uniaxial stresses applied in a direction 45° to the Z axis in the YZ plane (*i.e.* in the [011] direction of the undeformed crystal). This direction was chosen as it corresponds to one of the directions of maximum auxeticity in the (100) plane. From these simulations, one could clearly observe in the (100) plane that the 'rectangles' rotate with respect to each other when subjected to these loads with the result that the structure 'opens up' when the uniaxial load is increased, thereby producing the observed negative Poisson's ratio (see Fig. 3a).

To quantify this observation, we identified a typical 'rotating rectangles' unit and measured the projections in the (100) plane of the distances between the atoms at the corners of the rectangles (for example, l_1–l_4) and the angles between three adjacent 'corner' atoms (for example, ω_1–ω_4 and θ_1 & θ_2) at the different stresses. These measurements correspond to the lengths of the sides of the rectangles (l_1–l_4), the internal angles of the rectangles (ω_1–ω_4) and the angles between the rectangles (θ_1 and θ_2). As illustrated in Fig. 3b, these measurements confirmed that the angles between the different rectangles (θ_1 and θ_2) change much faster than any of the other geometric parameters relating to a single rectangle (l_1–l_4 and ω_1–ω_4) thus confirming that the shape and size of the rectangles change to a lesser extent than the angles between the rectangles. Similar results were obtained in the (010) plane for loading in the [101] direction.

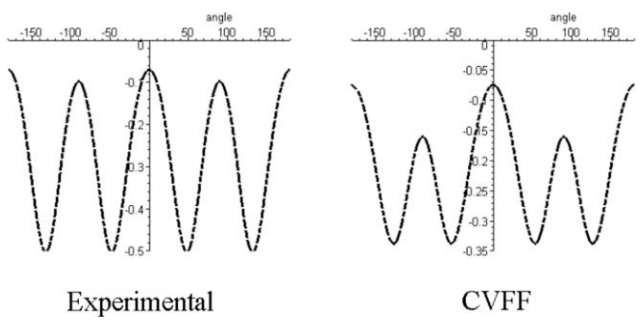

Fig. 2 The off-axis Poisson's ratios in the (100) plane.

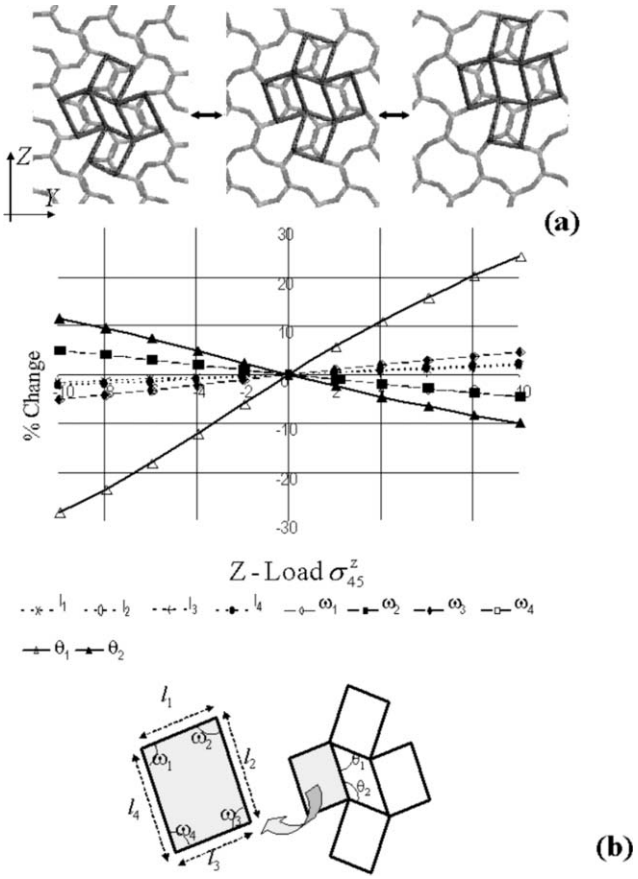

Fig. 3 (a) Molecular level deformation in α-cristobalite described in terms of 'rotating rectangles' (see also ESI† for an animated version of this image). (b) Plots of the percentage changes of various geometric parameters as a function of the load in the [011] direction.

These results may be explained in terms of the crystal structure of α-cristobalite where, as illustrated in Fig. 4, the 'rigid rectangles' 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. Adjacent columnar-like structures (the cross-sections of which are the rectangles) are connected through 'soft' Si–O–Si bonds located at regular intervals down the third direction which may bend more easily than the more columnar-like structures. The result is that when the system is loaded, the deformation will be concentrated around the Si–O–Si 'hinges'. Similar geometric features may also be observed in the (010) plane.

It should be noted that whilst the idealised 'rotating rectangles' model illustrated in Fig. 1b exhibits constant in-plane Poisson's ratios of −1 the experimental results and the CVFF simulations predict less negative values of the Poisson's ratios which are also dependent on the direction of loading. Such deviations from the idealised scenario are to be expected and can be explained by the

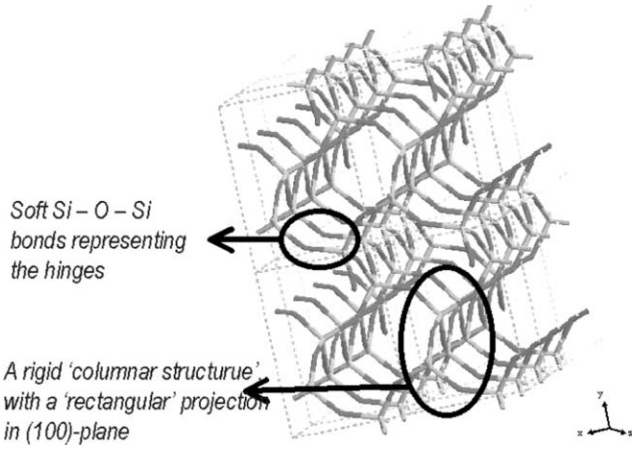

Fig. 4 The geometric features in α-cristobalite which make up the 'rectangles' and the 'hinges'.

fact that in real materials such as α-cristobalite, the situation where units (in this case the rectangles) are perfectly rigid is unrealistic. Instead, one would expect that these units are non-rigid to some degree, as in fact illustrated in Fig. 3b which clearly shown that the parameters l_1–l_4 and ω_1–ω_4 are changing (although to a lesser extent than θ_1 and θ_2) as the silicate is loaded. It is also very significant that the directions of maximum auxeticity in the (010) and (100) 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). Hence, the anisotropy in the Poisson's ratio can be directly mapped to the 'rotating rectangles' model that is being proposed here.

It is also worthwhile to note that in reality, the deformation of α-cristobalite will still involve deformations and/or re-orientations of the SiO_4 tetrahedra. The application of the rotating rectangles model here is simply a representation of the net effect of the projection of these tetrahedral deformations and/or re-orientations in specific planes. In fact, two-dimensional geometry-based models are particularly deployable for studying the Poisson's ratios and have been extensively used to explain the values of the Poisson's ratios in various classes of materials.[1,6,9–14,20,26] This is because the Poisson's ratio is a property which describes how a two-dimensional cross-section of a material is deforming when subjected to a load. Hence 2D models are particularly useful to consider how particular cross-sections of a material are being affected when the material is subjected to uniaxial stresses.

The identification of the role of the 'rotating rectangles' mechanism in α-cristobalite is thus very significant as we are now able to understand more clearly how nature may achieve negative Poisson's ratios at the molecular level. We envisage that this will be of great help to synthetic chemists who are working on the synthesis of man-made materials which exhibit this unusual yet very useful effect. In essence α-cristobalite can be used as a 'template' for the design of synthetic auxetic materials which mimic naturally-occurring ones with the added benefit that they can be tailor-made for specific practical applications.

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