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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

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

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

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

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

Thus, referring to Fig. 1b, since:

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

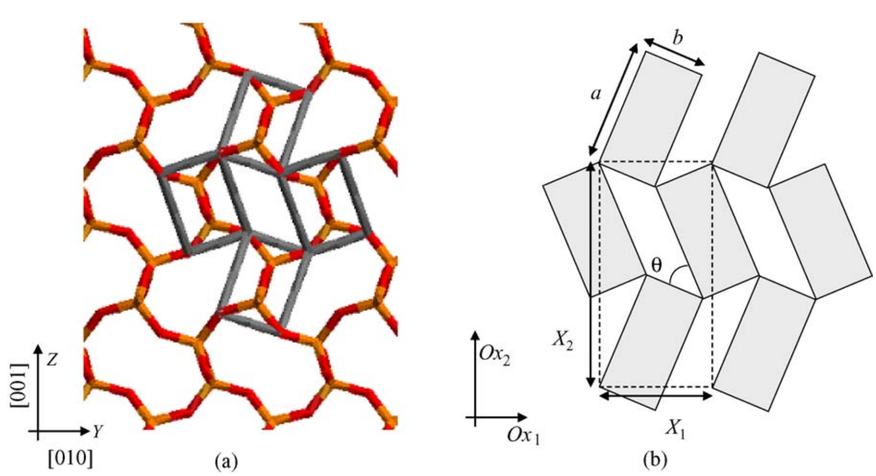

Fig. 1. (a) The projection in the (1 0 0) plane of α-cristobalite with the 'rotating rectangles' model highlighted; (b) an illustration of how the '$a \times b$ rectangles' are connected in the 'rotating rectangles' model being proposed here.