

Odd solid predictions

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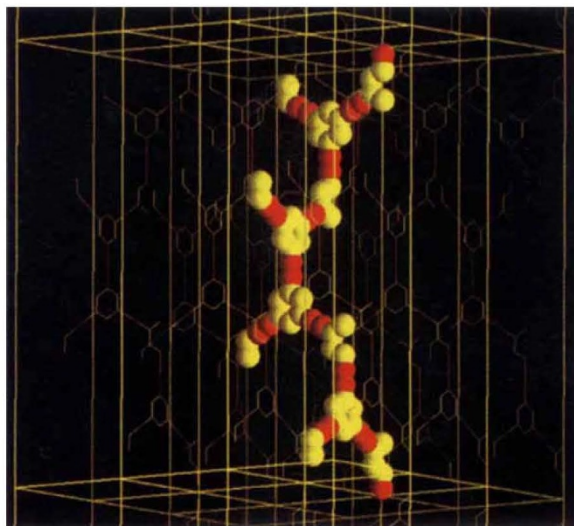
WHEN stretched, most materials become thinner in cross-section and less dense; when heated, most expand. These intuitive relationships are a consequence of the anisotropic nature of the chemical bond and the asymmetry of the potential energy surface that describes this pairwise interaction. Although there are examples of materials with anomalous thermal and mechanical behaviour, such behaviour can usually be traced to microstructural details at a length scale well above the molecular level. On page 735 of this issue¹, Baughman and Galvão describe something else again — they predict that a class of materials they call 'hinged network crystals' will have decidedly counterintuitive properties, which stem from a unique bonding connectivity.

As the name implies, hinged network crystal phases have the peculiar feature that the entire lattice can undergo reorganization by a nearly barrierless twisting type motion around a set of parallel torsions extending across the infinite lattice. What is unique about this motion is that it can occur without involving a change in the network bond lengths, so it takes place smoothly, like a hinge. It is fascinating to explore the massive scale of concerted atom displacements that pervades the entire phase with molecular models. Because the process involves purely torsional rotation, the deformation requires very little energy (it is extremely compliant). If the internal dimensions of the unit cell are large relative to the diameter of individual network strands, then the torsion requires minimal energy. That is what Baughman and Galvão call the 'uncrowded' type of hinged network phase. On the other hand, if the strands of the network fill the space of the unit cell, the torsional motion is restricted and the unusual properties may no longer be observed. In this case, the compliant deformation is constrained by repulsive van der Waals interactions and other deformation mechanisms predominate.

The structure of the proposed phases can be envisaged as arising from two sets of non-parallel chains. The two sets stack on top of one another in alternating fashion. Covalent bonding between chains in adjacent layers forms a periodic, three-connected network that extends indefinitely. The prototype network has the same structure as the known inorganic materials ThSi_2 or LaPtSi . However, these examples fall into the 'crowded'

category. An example of an 'uncrowded' hinged network crystal is shown in the figure, where the tri-connected vertices are 1,3,5-substituted arenes joined by acetylene bonds. These more open forms exhibit a soft shear deformation around the set of parallel $-\text{C}\equiv\text{C}-$ bonds that extend throughout the solid.

The mechanical and thermal properties



Connectivity diagram and space-filling model of an uncrowded hinged network crystal¹. The tri-connected vertices are aromatic rings and the edges are acetylene bonds. A molecular fragment of this network has recently been synthesized (Z. Wu and J.S.M., unpublished data; ref. 5).

predicted for these networks are unusual. Baughman and Galvão performed their calculations on a network of polydiacetylene chains which have sp^2 carbon atom vertices and $-\text{C}\equiv\text{C}-$ edges. Tensile stress along the direction of the helical axis causes the chains to untwist. As a consequence, the material exhibits a negative Poisson's ratio (in other words, it becomes thicker in cross-section when stretched)². Furthermore, this structure is predicted to become denser when stress is applied along any of the three unit cell directions and it is calculated to have a large negative thermal expansion coefficient.

The mechanisms behind these unusual characteristics are fundamentally different from those that have been invoked to account for a negative Poisson's ratio in other materials. Such behaviour has been attributed to unusual microstructure such as inverted honeycombs. And although other molecular-based networks have been proposed as giving a negative Poisson's ratio, they were essentially an extrapolation of the inverted honeycomb down to the molecular level³. The mechanism put forth by Baughman and Galvão is a completely new concept, in that it is based

on a shear deformation that results from untwisting of helical chains. Moreover, a mechanistic relationship between negative thermal expansion and a negative Poisson's ratio has previously never been postulated.

The difficulty in verifying the unique properties of these phases is that, at present, there is no way to make such phases in extended form. The rational synthesis of extended solid-state structures remains a considerable challenge. Approaches based on topochemical reactions — that is, the transformation

of a molecular crystal to extended solids — might be feasible. But special difficulties of the present phases, such as the intricate bonding connectivity and the openness (that is, non-close-packed atoms) required of the 'uncrowded' phases, make such routes unlikely. Happily, though, there is a growing determination to tackle these issues⁴, and in the short term the preparation of finite approximations to infinite networks are well within the capabilities of today's chemists. For example, a molecular fragment of the network shown in the figure has already been synthesized (Z. Wu and J.S.M., unpublished results; ref. 5).

Once these phases are synthesized, the question of applications will arise. Such materials would have special mechanical properties, including excellent toughness and resistance to damage, as well as high Young's modulus for stress along an axis that gives a negative Poisson's ratio. If the chains have extended π -conjugation, and therefore are semiconducting, it may well be that they will have interesting mechano-coupled optical and electrical properties as well.

Baughman and Galvão present an intriguing mechanism that leads to very odd mechanical properties in solids. Their approach is an example of computer-aided molecular design of materials. But to be more than just a curiosity, synthetic chemists must now extract the essential features of hinged molecular crystals and map them into real materials — which should be even more fascinating than the model. □

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