MATERIALS SCIENCE

Unusual Thermoelastic Properties of Methanol Monohydrate

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A simple material can shrink in one direction when heated, and expand in that direction when squeezed by hydrostatic pressure.

When a material is heated, we expect it to expand, and when squeezed on all sides by hydrostatic pressure, we expect it to shrink, but materials or structures can respond in unexpected ways. Some may exhibit negative thermal expansion (NTE)—shrinking when heated (*1*–*8*)—or negative compressibility (NC) (*8*–*13*)—expanding when subjected to a positive hydrostatic pressure—and some may exhibit both properties. For crystalline materials, the response can be anisotropic—observed along only some directions in a crystal (see the figure), and may only be observed in particular ranges of temperatures or pressures. On page 742 in this issue, Fortes *et al*. (*8*) report such anomalous properties from an experimental investigation on methanol monohydrate, a simple molecular crystal of a deuterated 1:1 compound of methanol and water. Such materials, used singly or in combination with conventional materials, can have useful mechanical and optical properties.

In simple terms, conventional positive thermal expansion is the result of populating higher vibrational states at higher temperatures. These higher vibrational states explore the higher asymmetric portions of interatomic potentials, which increases the mean interatomic distances and leads to an increase in the dimensions of the material (*1*). Positive

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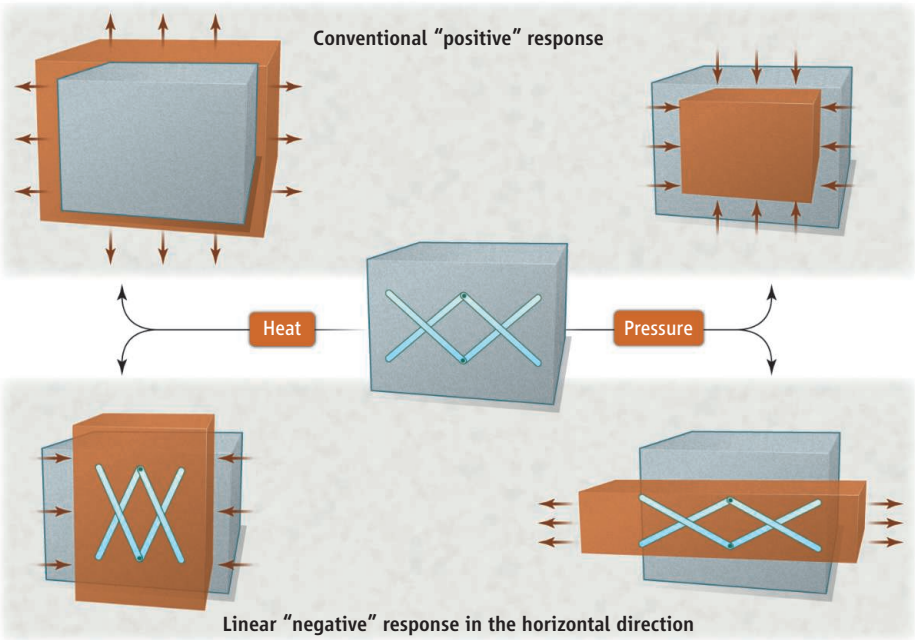

Responding to heat and pressure. Conventional materials expand when heated and shrink under pressure. Fortes *et al*. show that methanol monohydrate has an unconventional response. At low temperatures, it shrinks in one direction as temperature increases, and expands in the same direction under pressure. A model suggests that these changes are caused by hinging motions in crystal lattices similar to those of a folding wine rack.

compressibility arises because the atoms are pushed closer to each other when the material is subjected to a positive hydrostatic pressure.

The unconventional "negative" responses may usually be explained by examining the changes in the nano- or microstructure of the material driven by changes in temperature and pressure. Fortes *et al*. (*14*) previously showed that one of the planes that run through a methanol monohydrate crystal—called the **ac** plane—can be described as an ordered array of water molecules connected in chains; adjacent chains are interconnected by hydrogen bonding with methanol to form a sheet-like structure. These sheets are stacked on top of each other along the third or b direction in the crystal.

The experiments carried out by Fortes *et al*. show that methanol monohydrate exhibits linear NTE in the **a** direction at temperatures between 4.2 and 160 K and an unusually high but positive linear thermal expansion in the **b** direction. In addition, methanol monohydrate also exhibits the not-so-frequently reported property of linear NC in the **a** direction—the same as that of the NTE—at hydrostatic pressures ranging from room pressure to 500 MPa at 160 K. This property is accompanied by a very high positive linear compressibility in the b direction, so the overall volume decreases under hydrostatic compression.

The anomalous thermomechanical behavior of methanol monohydrate is explained in terms of a simple geometry-based model. The deformation mechanism of the lattice of molecules in the **ab** plane mimics that of a folding wine rack. Positive hydrostatic pressure would close up the lattice in one direction but increases its dimension in the other direction. Mechanisms of this type have also been used by others to describe NTE, NC, or both (*4*–*7*, *10*, *12*, *13*). For example, modeling work by Baughman *et al*. (*4*, *10*) suggested that this type of deformation mechanism can lead to NTE and NC in a hypothetical three-dimensional carbon allotrope made from sp^2 and sp hybridized carbon atoms. Such a material could also have a negative Poisson's ratio or auxetic behavior—unlike a piece of soft candy getting thinner when stretched, an auxetic material gets thicker (*15*).

The "negative" thermomechanical properties measured by Fortes *et al*. in methanol monohydrate may affect the field of planetary science because both methanol and water may be important constituents of cryovolcanic eruptions on icy moons. Closer to home, materials exhibiting NTE and NC properties have many practical applications. In particular, NTE materials are often used in the manufacture of composite materials to tailor the overall thermal expansion coefficient to some particular value. In the electronics industry, NTE materials are used to make substrates and heat sinks that match the thermal expansion of silicon. Composites made from NTE and conventional materials can be designed to exhibit a zero thermal expansion coefficient for use as mirror substrates in various telescope and satellite applications to prevent them changing their shape with variations in temperature (*16*). NTE materials are also used in laminates to control or eliminate curvatures arising from thermal stresses (*17*). Similarly, NC materials can be used in applications requiring extremely sensitive pressure detectors. Also, it has been postulated that NC materials may have a very high refractive index, which would provide substantial advantages in designing optics (*10*).

The report by Fortes *et al*. of a material exhibiting negative linear compressibility still does not provide the required experimental evidence to fully challenge the common belief that overall negative volumetric compressibility cannot occur, but will certainly encourage scientists to study in more detail this phenomenon. Their work highlights the importance of studying the thermomechanical properties of materials through an approach that examines materials with the help of geometry-based models describing their nano- or microstructure. Such models may provide a blueprint for the design of improved materials that mimic the anomalous behavior of methanol monohydrate.

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