NEGATIVE LINEAR COMPRESSIBILITY

Giant response

Materials displaying negative linear compressibility are, at present, the exception rather than the rule. An unusually large and persistent example of this phenomenon in the molecular framework material zinc dicyanoaurate dramatically expands the range of mechanical responses conceivable in other materials.

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Our everyday experience with most materials, be they naturally occurring or synthetically prepared, is that they shrink when squeezed. Indeed, the opposite scenario of a material that simultaneously expands in all three spatial directions under an applied hydrostatic pressure is thermodynamically forbidden[1]. However, it has recently become appreciated that some materials reduce their volume by becoming longer in one direction while becoming shorter in the others, a phenomenon known as negative linear compressibility (NLC). Writing in *Nature Materials*, Andrew Cairns and colleagues[2] now report the discovery of an exceptionally large NLC in the α-polymorph of zinc dicyanoaurate ($Zn(Au(CN)_2)_2$), therefore demonstrating the effect can be much larger than previously thought possible.

Negative linear compressibility has so far only been reported in a handful of systems, such as the naturally occurring materials selenium, lanthanum niobate and methanol monohydrate[3,4]. This in itself makes the phenomenon interesting, but it has also been suggested as the basis for potential niche applications such as sensitive pressure sensors and compensators in systems affected by humidity or high pressure. What makes zinc dicyanoaurate stand out is the extent of the NLC it exhibits — up to an order of magnitude stronger than its long-established canonical counterparts — making the term 'giant' NLC quite appropriate. Furthermore, the study also demonstrates that the large response is maintained over a wide range of pressures, another uncommon yet potentially useful characteristic.

Various mechanisms have been proposed to explain the unusual phenomenon of NLC, ranging from models based on systems having rhombic or honeycomb geometries that deform like wine racks[3,5], to systems made up of bimaterial strips[6] or ones constructed from tetragonal beams[7]. Another interesting category of systems is represented by mechanical metamaterials, whose properties depend on their structure rather than their precise chemical composition[8]. These undergo a negative-compressibility transition, which is achieved by having particles interacting through carefully chosen potentials, such that any externally applied forces do not need to be exerted in all directions for the negative-compressibility transition to occur.

In the case of zinc dicyanoaurate, the giant NLC behaviour arises from its honeycomb-like structure, which couples a large volume reduction to an abnormally large uniaxial expansion (Fig. 1a), enhanced by helical supramolecular springs dominated by Au...Au aurophilic interactions (Fig. 1b) that can accommodate very large linear strains. With increasing hydrostatic pressure, this structure effectively ensures that a compression in two directions is accompanied by an expansion in the other direction, thus resulting in an overall reduction of the volume. The key to generating the giant NLC in zinc dicyanoaurate are the 'spring'-like deformations occurring between the helical interactions of the gold atoms (Fig. 1b). These aurophilic interactions are highly compressible in comparison with the other interactions and chemical bonds in the crystal.

By highlighting the strong dependence of the macroscopic properties of zinc dicyanoaurate to the manner in which its molecular-scale constituent parts vary with pressure, Cairns and co-workers have demonstrated the concept that supramolecular motifs can be used to design systems with qualitatively different mechanical responses. Although similar geometric relationships have already been established for materials exhibiting other related negative properties, such as negative Poisson's ratio (a property resulting in so-called auxetic behaviour)[9] and negative thermal expansion[10], it is now becoming increasingly clear that the phenomenon of NLC may also be explained and harnessed using this approach.

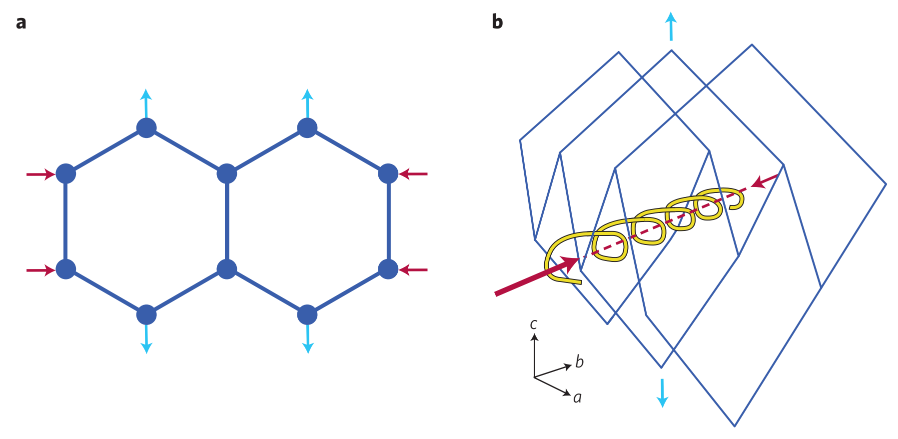

Figure 1 | Negative linear compressibility mechanisms[2]. **a**, A schematic representation of the compression mechanism for a hexagonal honeycomb. Contraction in one direction (red arrows) is coupled to an expansion in a perpendicular direction (blue arrows). **b**, The mechanism of NLC in zinc dicyanoaurate involves rapid compression of the aurophilic helices (red arrows), which leads to an expansion of the framework in the *c* direction via flexing of the honeycomb-like channels (blue arrows).

The work by Cairns *et al.* underlines the fact that the search for materials displaying NLC is far from over, and that many more interesting mechanisms giving rise to this property are conceivable. For instance, the concept of supramolecular springs could, in principle, be used in conjunction with other known mechanisms for NLC to enhance the effect even further. These developments and discoveries relating to systems exhibiting such highly anomalous yet potentially useful macroscopic properties are greatly encouraging and may pave the way to a new generation of advanced functional materials with exceptional properties. ❐

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