

Negative area compressibility in silver(I) tricyanomethanide†

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The molecular framework Ag(tcm) (tcm⁻ = tricyanomethanide) expands continuously in two orthogonal directions under hydrostatic compression. The first of its kind, this negative area compressibility behaviour arises from the flattening of honeycomb-like layers during rapid pressure-driven collapse of the interlayer separation.

In the absence of a structural phase transition, it is a thermodynamic requirement that a system reduce its volume under hydrostatic pressure.¹ The phenomenon of negative compressibility is the counterintuitive effect whereby this volume reduction couples to an expansion of the material in at least one linear dimension.² Examples of such behaviour are rare even amongst anisotropic materials because buckling and bond compression mechanisms are almost always more effective at reducing crystal volume than is uniaxial or biaxial lattice expansion. Not only does the existence of negative compressibility challenge our understanding of the ways in which materials can respond to external stimuli, but the phenomenon is also of practical importance. It promises a means of developing artificial muscles, nanoscale actuators and high-performance pressure sensors for sonar and altitude measurements.^{2,3} In principle, the most extreme such response allowed thermodynamically is that of negative area compressibility (NAC), whereby a material expands along two orthogonal directions on increasing hydrostatic pressure. The possibility that tetragonal PbTiO₃ might show an extremely weak NAC effect has been raised⁴ and disputed;⁵ similarly weak effects are thought to occur at high pressure in NaV₂O₅ (ref. 6) and are predicted for TlGaSe₂.⁷

Instead the remarkably few negative compressibility materials that have been characterised unambiguously expand only along one principal axis when compressed hydrostatically (*i.e.*, negative linear compressibility, NLC).^{8–12} The distinction between NLC and NAC is more fundamental than magnitude alone: NAC materials increase their surface area under hydrostatic pressure, and so they can be used as substrates to provide order-of-magnitude amplification of piezoelectric response in *e.g.* ferroelectric sensors.²

One strategy for identifying negative compressibility candidates is to target framework materials that exhibit anisotropic negative thermal expansion (NTE): a material that shrinks in one direction on heating is likely to expand in that same direction on compression.¹³ While there is no requirement that deformation mechanisms under temperature and pressure be identical,¹⁴ there is empirical evidence of such a correspondence amongst molecular framework materials.^{8,9,12,15} The natural strategy then for identifying NAC candidates is to investigate framework materials that exhibit area-NTE. It is for this reason that we chose to investigate silver(I) tricyanomethanide, Ag(tcm): its layer-like network topology [Fig. 1(a)] is of a form often associated with area-NTE.^{16,17} In this compound, each Ag⁺ cation is coordinated by three tcm⁻ anions in an approximately trigonal arrangement; likewise each tcm⁻ anion is coordinated by three Ag⁺ centres.^{18,19} The resulting hexagonal (6,3) topology is sufficiently open that two honeycomb networks interpenetrate within each layer of the crystal structure [Fig. 1(b)]. Adjacent layers interact *via* long Ag⋯N contacts [$d(\text{Ag}\cdots\text{N}) > 3 \text{ \AA}$] that are sufficiently weak that the material behaves essentially as a two-dimensional framework, capable even of intercalation chemistry.¹⁹

Using single-crystal X-ray diffraction, we first established the thermal expansion behaviour of Ag(tcm) to verify whether or not the material exhibits area-NTE. Because the material crystallises in the orthorhombic (polar) space group *Ima2*,¹⁸ its thermal expansivity is uniquely determined by the relative rate of change of the unit cell lengths with temperature.¹⁷ We observe essentially linear thermal variation in these parameters over the

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of NAC quantified by the corresponding area compressibility $K_{(010)} = K_a + K_c = -7.5(8) \text{ TPa}^{-1}$.

Conventional engineering materials (e.g. iron) have linear compressibilities $K \sim 5 \text{ TPa}^{-1}$ that correspond to a decrease of ca. 0.5% in length for each 1 GPa pressure increase;²⁵ consequently, the NAC behaviour of Ag(tcm) is essentially as strong as the positive area compressibility of these 'normal' phases. Moreover, despite the fact that the orthorhombic symmetry of Ag(tcm) allows for different behaviour in the a and c directions, we find that both its compressibility and its thermal expansivity are essentially isotropic within the entire (a,c) plane. Isotropy is important for NAC applications because it avoids composite warping and performance breakdown.²

That NAC is driven by the same layer-rippling mechanism as area-NTE is evident in the variation of the parameter θ with increasing pressure [Fig. 2(d)]. The volume reduction accommodated by rapid collapse of the interlayer spacing (note $K_b \gg 5 \text{ TPa}^{-1}$) evidently couples with a reduction in the degree of layer rippling: $d\theta/dp < 0$. To substantiate further our interpretation of the NAC mechanism, we recast eqn (1) in terms of compressibilities; our refined values of θ give $K_A^{\text{calc}} = -\theta \tan(\theta/2)K_\theta = -26 \text{ TPa}^{-1}$. That the measured area compressibility $K_{(010)} = -7.5(8) \text{ TPa}^{-1}$ is somewhat smaller in magnitude reflects the expected $\sim 10 \text{ TPa}^{-1}$ contribution from (positive) bond compressibilities omitted from the geometric formalism of eqn (1), as discussed elsewhere for NLC materials.¹³ Indeed, that the p/T correspondence inferred in Fig. 1(c) holds qualitatively for Ag(tcm) is immediately evident in the close relationship between the temperature- and pressure-induced lattice parameter and layer rippling parameter variations documented in Fig. 2.

In conclusion, we find that silver(i) tricyanomethanide exhibits NAC over the pressure range $0 < p < 0.615 \text{ GPa}$ with an essentially isotropic area compressibility of similar magnitude (but opposite sign) to that of established engineering materials. From a structural viewpoint, the phenomenon can be understood in terms of pressure-driven damping of layer 'rippling', acting to increase the layer cross-sectional area at larger hydrostatic pressures. Variable-pressure spectroscopic measurements may provide valuable additional insight into the subtle variations in bonding interactions that occur throughout this process.²⁶ In favour of immediate application of Ag(tcm) in ultra-high-precision sensing devices are (i) the ease with which large single-crystal samples can be prepared under ambient conditions and using readily-available solvents, and (ii) its optical transparency. Moreover, the polarity of its crystal structure offers the possibility of designing multifunctional devices

based on Ag(tcm) in which the interplay between responses to electric field, temperature, and pressure are exploited to produce piezoelectric and thermoelectric devices.

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