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Designing next-generation negative compressibility materials.

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Negative compressibility is a rare but desirable property whereby a material's crystal structure actually expands in one (negative linear compressibility, NLC) or two (negative area compressibility, NAC) principal directions against application of increasing hydrostatic pressure. The performance of such materials—for use in, for e.g., sensitive interferometric or ferroelectric pressure sensing devices, advanced actuators, or prototype artificial muscle—critically depends on the magnitude of intrinsic negative response. NLC and NAC have been previously reported in a diverse range of materials: from the elemental forms of selenium and tellurium, to transition metal oxides, halides and chalcogenides [1], to more recent reports of NLC in molecular materials, and metal–organic and metal–cyanide frameworks. We explore, using examples from our work [2,3] as well as that of others, how understanding known NLC and NAC materials can inform material design, and how the versatile chemistry of molecular frameworks—the connecting of cationic metal nodes with anionic molecular linkers in one or more dimensions—allows for the targeting, enhancing and coupling of functionalities. By analysis of the negative response across all known NLC and NAC materials we develop new understanding into the underlying mechanisms of these unusual responses. Structural motifs identified point towards strategies for designing the next-generation of these materials, including the simple "wine-rack," "honeycomb" and "spring" mechanisms, where hinging about nodes requires volume reduction by simultaneous expansion and contraction in perpendicular directions (Figure 1). We discuss the first report of "giant" NLC in zinc(II) dicyanoaurate(I), $Zn[Au(CN)_2]_2$, where the crystal structure expands >10% over 1.8 GPa [2], the unprecedented prolonged NAC in silver (I) tricyanomethanide, $Ag(C_4N_3)$ [3], and conclude with our perspective on the challenges and opportunities that remain in the quest for even more extreme responses.

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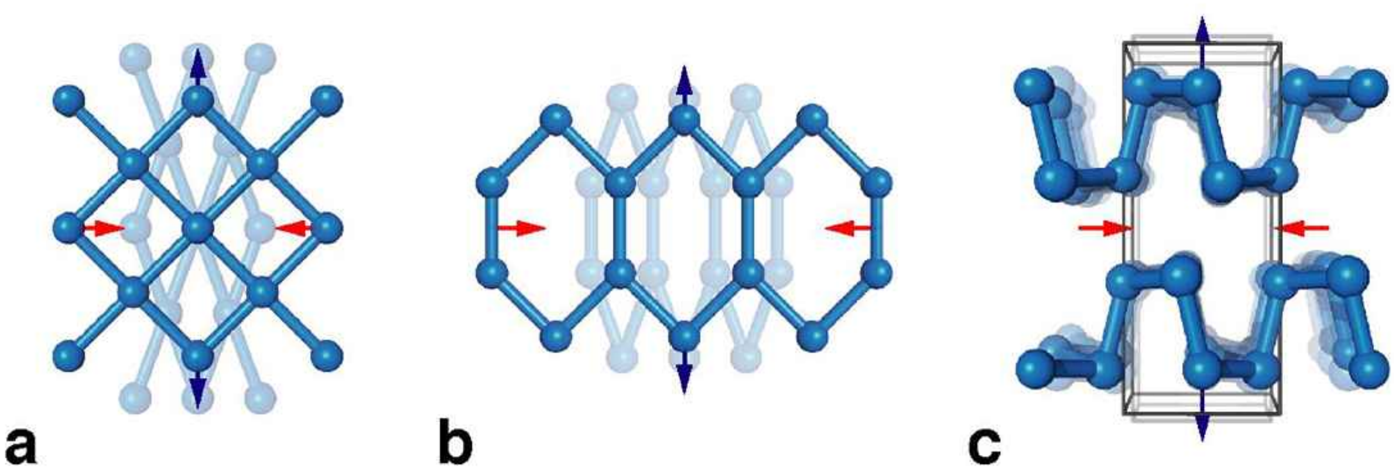

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