Rational Design of Materials with Extreme Negative Compressibility: Selective Soft-Mode Frustration in KMn[Ag(CN)$_2$]$_3$

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S *Supporting Information*

ABSTRACT: We show that KMn[Ag(CN)$_2$]$_3$ exhibits the strongest negative linear compressibility (NLC) effect over the largest pressure range yet observed. Variable pressure neutron powder diffraction measurements reveal that its crystal lattice expands along the c axis of its trigonal cell under increasing hydrostatic pressure, while contracting along the a axis. This corresponds to a "wine-rack"-like mechanism for NLC that we find also results in anisotropic negative thermal expansion (NTE) in the same material. Inclusion of extra-framework K$^+$ counterions has minimal effect on framework flexibility (and hence the magnitude of NTE/NLC) but selectively frustrates the soft phonon modes responsible for destroying NLC in the related material Ag$_3$[Co(CN)$_6$].

The vast majority of materials shrink under increasing pressure. However it has been known for some time that in certain structure types volume reduction can be achieved by actually *expanding* the crystal lattice along specific directions.[1–3] This effect, termed negative linear compressibility (NLC), is a remarkably rare phenomenon. Only a dozen or so examples are known, and in most of these the effect is relatively weak.[1,4,5] On the macroscopic scale the phenomenon of NLC is not necessarily counterintuitive: both trellis fencing and wine racks are "packed away" by pulling in one direction. The challenge for the materials chemist is to engineer this same functionality on the atomic scale such that it becomes an intrinsic material property to be exploited appropriately. NLC is of strong practical interest in, for example, the development of highly sensitive pressure detectors for seismic, sonar and aircraft applications, as components of essentially incompressible composites, and in "smart" materials for next-generation body armor.[1,2,6] For all such applications, the primary objective is to develop materials that exhibit the strongest possible NLC effect over the largest possible pressure range.

Quantitative comparison of NLC among different materials is made possible via the isothermal compressibility, defined as the relative rate of change of dimension with pressure, $K_l = (\partial(\ln l)/\partial p)_T$, measured at constant temperature. For crystalline materials the value of K normally lies between 5 TPa^{-1} (stiffer, less compressible) and 50 TPa^{-1} (softer, more compressible).[7] In contrast, NLC materials have $K < 0$ TPa^{-1}; but until very recently the most negative values observed were just -2 and -1.2 TPa^{-1} for α-cristobalite structured BAsO$_4$ and trigonal Se, respectively.[8,9]

We[4] and others[5] have since shown that stronger NLC can be found in framework structures that show very anisotropic negative thermal expansion (NTE) behavior—i.e. on heating their structures contract in one or more directions. There is actually no thermodynamic requirement that NTE and NLC coexist,[10] but what is emerging is an empirical interdependence of the two phenomena. So, for example, the framework material Ag$_3$[Co(CN)$_6$] shows "colossal" NTE along the c-axis of its trigonal crystal lattice;[11] NLC is found in the same direction with $K_c = -75$ TPa^{-1} until a phase transition at 0.19 GPa, and $K_c = -5$ TPa^{-1} thereafter.[4] Methanol monohydrate also exhibits strong NTE and NLC along a shared axis, in this case with $K_a = -3.1$ TPa^{-1}.[5] There are, however, fundamental reasons why these two "new-generation" NLC materials are unlikely to be suitable for practical application. Methanol monohydrate is stable only at temperatures below 160 K.[5] In Ag$_3$[Co(CN)$_6$], the 0.19 GPa phase transition actually involves a significant volume collapse, and hence, while the linear compressibilities measured on either side of the transition are certainly negative, the average compressibility taken over a pressure range 0–2 GPa (typical for many practical applications[12]) is actually quite strongly positive: $K = +41$ TPa^{-1}.[4]

Here we study KMn[Ag(CN)$_2$]$_3$ [Figure 1a],[13] which we show to exhibit the strongest persistent NLC effect yet reported: $K = -12.0(8)$ TPa^{-1} over the entire pressure range $0 < p < 2.2$ GPa. Our motivation for choosing this particular material comes from trying to retain the key structural motifs responsible for extreme NTE/NLC behavior in Ag$_3$[Co(CN)$_6$], while eliminating those aspects associated with its volume collapse at 0.19 GPa. So it is intentional that the structure of KMn[Ag(CN)$_2$]$_3$, which has been reported previously,[14] is closely related to that of Ag$_3$[Co(CN)$_6$].[15] In particular, both share the motifs responsible for extreme NTE/NLC: an ultraflexible cyanide lattice whose dimensions are determined by low-energy Ag$^+$···Ag$^+$ "argentophilic" interactions [Figure 1b].[11,16] The key modification is the inclusion of K$^+$ ions within cavities of the dicyanometallate framework, lowering the crystal symmetry from $P\bar{3}1m$ to $P312$.[17] Because K$^+$ is not covalently bound to the framework, we anticipated structural flexibility—and hence NTE/NLC behavior—would largely be retained. Indeed in a systematic study of a number of isostructural KM^{II}[A^I(CN)$_2$]$_3$ materials, Korčok et al.
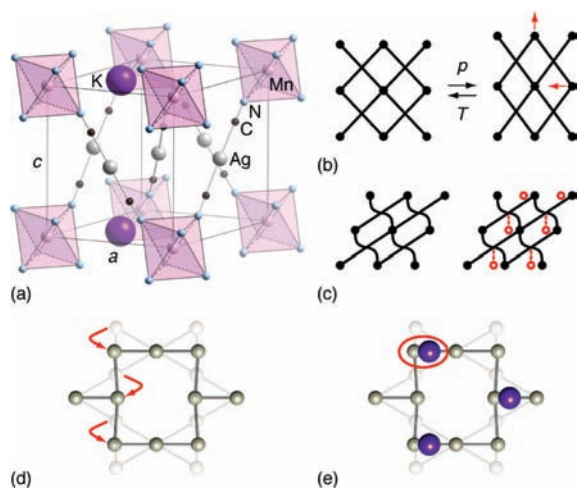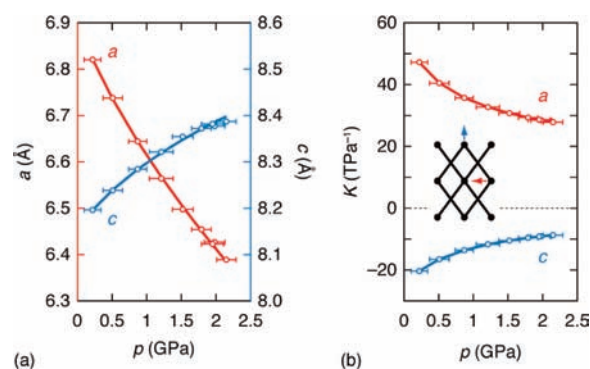
Figure 1. (a) Crystal structure of $KMn[Ag(CN)_2]_3$: $[MnN_6]$ octahedra are connected via almost linear $NC-Ag-CN$ units, with K^+ ions positioned above and below alternating Ag_3 Kagome triangles. (b) Schematic representations of the "wine-rack" NTE/NLC mechanism. (c) In $Ag_3[Co(CN)_6]$ NLC is destroyed by shear-induced framework collapse at 0.19 GPa (left); this mechanism is frustrated in $KMn[Ag(CN)_2]_3$ via incorporation of extra framework ions (open red circles; right). (d) Rearrangement of the Ag Kagome sublattice, viewed here down the c-axis, couples to framework shear in $Ag_3[Co(CN)_6]$. (e) These displacements would give unphysical $Ag^+ \cdots K^+$ distances in $KMn[Ag(CN)_2]_3$; the soft mode responsible is stiffened and the phase transition responsible for destroying NLC is avoided.

Figure 2. (a) Pressure-dependence of the lattice parameters of KMn-$[Ag(CN)_2]_3$ determined using time-of-flight neutron powder diffraction and (b) compressibilities extracted via an empirical fit (bold lines in (a)) as described in the text. Negative compressibility along the c-axis is evident in the increase in the value of c with increasing pressure.

observed retention of strong anisotropic NTE throughout the family.[16] However, by virtue of its interaction with the Kagome sublattice of Ag^+ ions, K^+ might be expected to influence strongly the existence of a high-pressure phase transition. Central to this idea is the observation that the shear instability responsible for volume collapse in $Ag_3[Co(CN)_6]$ is coupled to a translation of two-thirds of the Ag^+ ions to a site that in $KMn[Ag(CN)_2]_3$ would result in a very short $K^+ \cdots Ag^+$ contact ($\sim$3.6 Å, cf. 4.8 Å in the native compound) [Figure 1c–e].[4] Our hope therefore was that the presence of K^+ ions would selectively stiffen the soft-mode responsible for a pressure-induced phase transition, while leaving the low-energy modes that drive NTE and NLC essentially undamped.

Measurements of the temperature-dependent (100–300 K) structure and unit cell parameters for $KMn[Ag(CN)_2]_3$ were performed using single-crystal X-ray diffraction.[16] The coefficients of thermal expansion $\alpha_l = (\partial(\ln l)/\partial T)_p$ extracted from these measurements were $\alpha_a = +61(2)$ MK^{-1} and $\alpha_c = -60(3)$ MK^{-1}, reflecting strong positive thermal expansion perpendicular to the trigonal cell axis and strong NTE parallel to this axis; these values are similar in magnitude to those reported for $KCd[Ag(CN)_2]_3$ (+75 and −65 MK^{-1}, respectively)[18] and about half as large as the "colossal" values of $Ag_3[Co(CN)_6]$ itself (+144(9) and −126(4) MK^{-1}).[11,18] Consequently, the presence of K^+ ions does not fundamentally affect framework flexibility in $KMn[Ag(CN)_2]_3$.

In contrast, we do find evidence that the Ag^+ positions and displacements are influenced by the presence of extra-framework K^+. First, the Kagome lattice of Ag^+ ions is distorted such that Ag_3 triangles above or below K^+ ions are about 12% larger than those above or below vacant sites. Second, the thermal derivative dU_{eq}/dT of the Ag displacement parameter is about 15% lower

in $KMn[Ag(CN)_2]_3$ than in $Ag_3[Co(CN)_6]$ and $Ag_3[Fe(CN)_6]$.[11,19] This value is a crude measure of the energy of Ag displacement modes (large dU_{eq}/dT indicating low energy).[20]

In order to investigate the pressure-dependent behavior of $KMn[Ag(CN)_2]_3$, we performed time-of-flight neutron powder diffraction measurements across the pressure range $0.2 < p < 2.2$ GPa using the WISH diffractometer at ISIS.[21,22] All data could be accounted for using a structural model based on the $P\bar{3}12$ cell of the ambient phase. We found no evidence for any structural phase transitions throughout the pressure range studied. Lattice parameters were extracted from the powder neutron diffraction data using the GSAS Rietveld refinement package;[23] a plot of these values is given in Figure 2a. The absence of discontinuities also reflects the persistence of the ambient phase throughout the pressure range studied. Linear compressibilities were determined via error-weighted fits to the lattice parameters using an empirical expression of the form $l = l_0 + \lambda(p - p_c)^\nu$ [Figure 2b].[4] The mean values we obtain are $K_a = +33.2(13)$ TPa^{-1} and $K_c = -12.0(8)$ TPa^{-1}. To the best of our knowledge, this is the strongest NLC effect ever reported over such a large pressure range. Importantly NLC in KMn-$[Ag(CN)_2]_3$ is now similar in magnitude to the *positive* compressibilities of "normal" materials, suggesting that effectively incompressible composites might genuinely be attainable.

Despite the absence of any necessary link between NLC and NTE, our results for $KMn[Ag(CN)_2]_3$ reinforce the emerging strategy of looking for extreme NLC in compounds that exhibit anisotropic NTE. Consequently, NLC might be expected to recur for much of the $MM'[A(CN)_2]_3$ family (M = alkali metal, M' = divalent transition-metal cation, and A = group 11 monocation).[14,18,24,25] For all such materials there will be a risk that the very flexibility responsible for NTE will also favor low-pressure soft-mode instabilities associated with volume collapse. Our key result here has been to show how relatively simple chemical modifications can frustrate such a collapse mechanism while preserving the geometric flexibility that results in extreme NLC.

■ ASSOCIATED CONTENT

ⓈSupporting Information. Synthesis, crystallographic methods, single-crystal X-ray structural information, CIF files, variable pressure neutron powder diffraction data and GSAS fits,

temperature- and pressure-dependent lattice parameter values. This material is available free of charge via the Internet at http://pubs.acs.org.

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