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Negative thermal expansion and low-frequency modes in cyanide-bridged framework materials

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We analyze the intrinsic geometric flexibility of framework structures incorporating linear metal–cyanide–metal (M–CN–M′) linkages using a reciprocal-space dynamical matrix approach. We find that this structural motif is capable of imparting a significant negative thermal expansion (NTE) effect upon such materials. In particular, we show that the topologies of a number of simple cyanide-containing framework materials support a very large number of low-energy rigid-unit phonon modes, all of which give rise to NTE behavior. We support our analysis by presenting experimental verification of this behavior in the family of compounds $Zn_xCd_{1-x}(CN)_2$, which we show to exhibit a NTE effect over the temperature range 25−375 K more than double that of materials such as ZrW_2O_8.

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Negative thermal expansion (NTE), the decrease in volume or length of a material with increasing temperature, is an unusual property exhibited by relatively few materials.[1–5] The phenomenon is known to arise from a range of different physical mechanisms, including magnetostriction in ferromagnetic materials,[6] valence transitions in intermetallic[7] and fulleride[8] materials, and the population of low-energy phonon modes, as is well recognized in a number of oxide-based framework materials.[4,6,7,9–11] Such materials have generated significant scientific and commercial interest as they possess the potential to compensate for the more usual positive thermal expansion (PTE) behavior of other materials.

The oxide-based framework materials, favored for their strong NTE behavior, are perhaps the most widely studied of the NTE families. They share a very basic structural similarity, in that they can be considered as a network of coordination polyhedra, connected via single-atom metal–oxygen–metal (M–O–M′), such as the Zr–O–W linkage in ZrW_2O_8) or oxygen–metal–oxygen (O–M–O′, such as the O–Cu–O linkage in Cu_2O) linkages. It is widely accepted that the mechanism driving NTE in these materials involves transverse vibrational displacement of the central linking atom in these motifs away from the M⋯M′ or O⋯O′ axes [Fig. 1(a)]. This motion, which has the effect of drawing the two anchoring atoms closer together, increases in magnitude with increasing temperature.

We were intrigued by the anomalously large and negative coefficient of thermal expansion reported for $Zn(CN)_2$.[12] More recently, NTE has also been reported in the Prussian Blue analog $Fe[Co(CN)_6]$.[13] These materials are fundamentally different from the NTE materials described above in that their structures are based on a framework of metal–cyanide–metal (M–CN–M′)—rather than M–O–M′—linkages. Here we describe how the relatively simple concept of replacing the M–O–M′ moiety by its diatomic M–CN–M′ analog within general framework structures can have a profound effect on their intrinsic flexibility, favoring the existence of a large number of low-frequency NTE vibrational modes. We present crystallographic thermal expansion data for four members of the $Zn_xCd_{1-x}(CN)_2$ family, which we show to exhibit the strongest isotropic NTE behavior yet reported. Detailed analysis of these data reveals the dynamical origin of NTE in the family.

Viewed simplistically, one can easily visualize how linear M–CN–M′ linkages might give rise to a local NTE effect: The moiety possesses two transverse vibrational modes similar to the bending mode of M–O–M′ bridges [Fig. 1(b)]. The first of these involves displacement of the C and N atoms away from the M⋯M′ axis in the same direction; in the second, the displacement occurs in opposite directions. Both modes have the effect of drawing the anchoring metal atoms closer together with increasing temperature.

For polymeric crystalline materials such as $Zn(CN)_2$, the vibrational motion of individual structural elements cannot be considered in isolation; for example, the metal anchors of any one M–CN–M′ bridge are elements of a number of such bridges, and the vibrational motion of one will affect that of the others. This effect will be particularly strong for those metal centers whose coordination geometry is tightly constrained. The highly directional nature of M–CN bonding (which often possesses significant covalent character) and the fact that $[M(CN)_n]$ coordination polyhedral geometries are generally well preserved in crystalline materials[14] suggest that deformation of the metal coordination polyhedra within cyanide-containing materials such as $Zn(CN)_2$ would carry a high energy penalty. Consequently, one cannot rea-

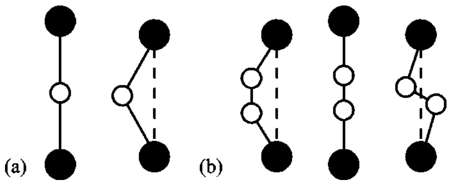

FIG. 1. A representation of local vibrational modes responsible for NTE behavior in structures containing (a) single-atom and (b) diatomic linkages. The filled circles represent heavy (usually metal) atoms, and the open circles represent light bridging atoms, such as oxygen (O) or cyanide (CN) species. In both cases, population of these vibrational modes leads to a decrease in the overall metal⋯metal distance.

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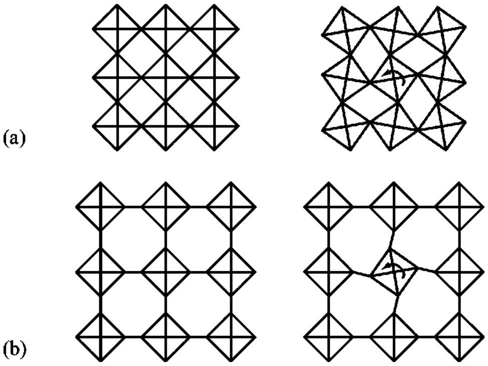

FIG. 2. Framework flexibility in the 2D perovskite topology containing (a) single-atom and (b) diatomic linkages. The framework in (a) is such that the rotation of any chosmen rigid unit induces a rotation of equal magnitude in all units, such that adjacent units rotate in opposite directions. This motion corresponds to the single RUM possessed by the framework topology (which occurs for the single wave vector $\mathbf{k}=\langle\frac{1}{2}\frac{1}{2}\rangle^*$). On the other hand, incorporation of diatomic linkages within the framework allows each rigid unit to rotate independently. This is a property of the large concomitant increase in the number of RUMs: The structure in (b) possesses a RUM at all wave vectors.

sonably expect to observe significant local transverse vibrations of the sort illustrated in Fig. 1(b) unless they can be coupled throughout the crystal lattice in the form of phonon modes that preserve the metal coordination geometries. Such modes are termed rigid unit modes (RUMs) and are experimentally found to occur at very low energy (typically 0–2 THz). As such, they generally dominate the dynamical behavior of the materials in which they occur; in particular, NTE behavior is often found in those materials whose structures support RUMs that involve the local vibrational motion described above.[15]

We begin by showing that not only are many cyanide-containing framework structures capable of supporting RUMs, but the number of RUMs in such materials is significantly larger than for their oxide-bridged analogs. Indeed, we find that the presence of diatomic linkages—such as the M–CN–M′ moiety—within a number of general framework structures imparts significant structural flexibility, while respecting the geometric integrity of the rigid coordination polyhedra. Moreover, the local vibrational motion of M–CN–M′ linkages within these phonon modes involves—in all cases—a linear combination of the two modes illustrated in Fig. 1(b), giving rise to NTE behavior.

Consider the two-dimensional (2D) perovskite structure [Fig. 2(a)]. Its topology consists of a network of corner-sharing square units (corresponding to, for example, square-planar $[\mathrm{MO_4}]$ coordination centers) and possesses a single RUM at the wave vector $\mathbf{k}=\langle\frac{1}{2}\frac{1}{2}\rangle^*$. Replacement of the single-atom bridges in this structure by a diatomic linkage has the effect of "spacing" the square units by a set of rods [Fig. 2(b)]. Remarkably, this subtle topological change yields a structure that possesses RUMs at all wave vectors across the Brillouin zone (BZ). Indeed, the RUMs are so many that the rotations of each square unit can be considered decoupled from those of the remaining units; i.e., any arbitrary combination of rotations of the squares can be accommodated by the structure (as an appropriate linear superposition of RUMs). Each mode in this set of RUMs serves to reduce the cell volume, and so possesses NTE character.

TABLE I. The number of RUMs possessed by the β-cristobalite (eight rigid units per unit cell) and perovskite (one rigid unit per unit cell) framework topologies incorporating single-atom (M–O–M′) and diatomic (M–CN–M′) linkages.

		Number of RUMs per unit cell	
Topology	**k**	M–O–M′	M–CN–M′
$\mathrm{ReO_3}$	$\langle\xi\ \zeta\ \eta\rangle^*$	0	3
	$\langle\xi\ \zeta\ 0\rangle^*$	0	4
	$\langle\xi\ 0\ 0\rangle^*$	0	5
	$\langle 0\ 0\ 0\rangle$	0(+3)	3(+3)
	$\langle\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\rangle^*$	3	3
β-cristobalite	$\langle\xi\ \zeta\ \eta\rangle^*$	0	32
	$\langle\xi\ \xi\ \zeta\rangle^*$	2	32
	$\langle\xi\ 0\ 0\rangle^*$	4	32
	$\langle\xi\ \xi\ \xi\rangle^*$	6	32
	$\langle 0\ 0\ 0\rangle$	9(+3)	30(+3)

We extend our analysis to two topological classes of greater physical relevance. The first corresponds to the framework structure of $\mathrm{ReO_3}$ (the perovskite structure), which consists of corner-linked octahedra. The structure obtained by replacement of its single-atom bridges by diatomic linkages corresponds to that of $\mathrm{Fe[Co(CN)_6]}$.[13] The second topology studied is that of β cristobalite ($\mathrm{SiO_2}$) and consists of a network of corner-linked tetrahedra. In this case, the appropriate cyanide-containing analog corresponds to one of the two (identical) interpenetrating frameworks found in $\mathrm{Zn(CN)_2}$.

We used the split-atom dynamical matrix method as implemented within the program CRUSH (Refs. 16 and 17) to calculate the number of RUMs in each structure across the BZ. The results (given in Table I) indicate that the incorporation of diatomic linkages within both structure types dramatically increases the number of RUMs present. Indeed, the number of RUMs at arbitrary **k** is sufficiently large that—for both topologies—each rigid unit retains many degrees of freedom. In addition to a degree of translational freedom, the rotations of each rigid unit are decoupled from the remainder of the framework. The framework volume is greatest when in a relaxed conformation, and so any RUM-type motion can serve only to reduce the overall volume; i.e., all RUMs in these materials possess a NTE characteristic.

There is reason to believe these results are examples of a more general phenomenon. Firstly, those RUMs that exist for any given framework topology constructed from single-atom bridges will be preserved by the incorporation of diatomic linkages. Secondly, the M–CN–M′ moiety appears to decouple the rotational—and to some extent, translational—motion of the rigid units. This has the effect of introducing a large number of RUMs at arbitrary wave vector, which fundamentally influences the RUM dominance of the weighted density of states.

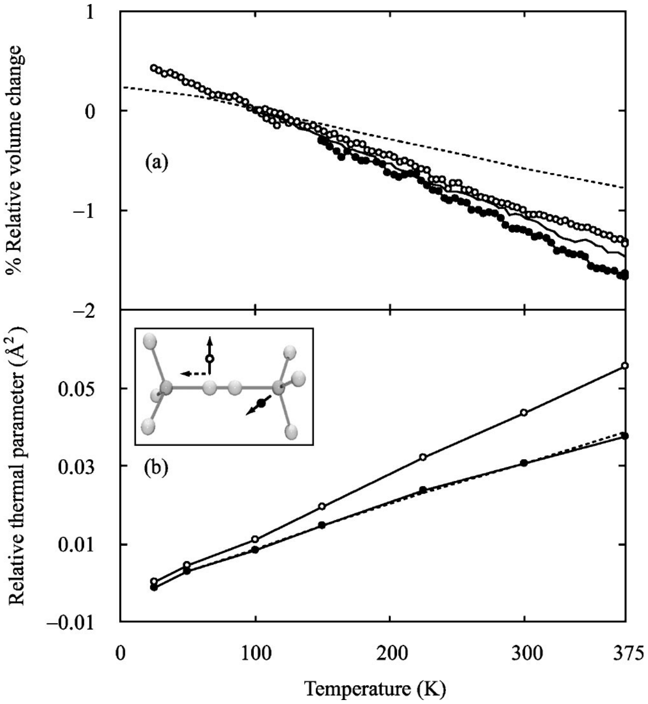

FIG. 3. Temperature-dependent structural behavior of the $Zn_xCd_{1-x}(CN)_2$ family as determined by single crystal x-ray diffraction. (a) The unit cell volume change (relative to 100 K) for $Zn(CN)_2$ (open circles), $Zn_{0.80}Cd_{0.20}(CN)_2$ (solid line), and $Cd(CN)_2$ (filled circles). The thermal expansion behavior of ZrW_2O_8 (broken line) is included for comparison (data taken from Ref. 9). (b) Atomic displacement (thermal) parameters for $Zn(CN)_2$ (relative to 100 K): the transverse (open circles) and longitudinal (filled circles) displacement of the C and N atoms (open circles); and the isotropic (by symmetry) displacement of the Zn atoms (broken line). The more rapid increase in the transverse displacement parameters of the C and N atoms indicates that transverse vibrational modes of the Zn–CN–Zn′ bridge are populated more rapidly with increasing temperature than longitudinal modes. The inset illustrates the Zn–CN–Zn′ moiety: the two Zn atoms have tetrahedral coordination. The arrows give the directionality of each of the three displacement parameters.

We return now to our consideration of NTE behavior in $Zn(CN)_2$. The crystal structures of $Zn(CN)_2$ and the isostructural $Cd(CN)_2$ have been studied extensively elsewhere;[12,18–20] they can be described as a pair of interpenetrating β-cristobalite-like frameworks in which each metal center binds four cyanide ligands in a tetrahedral arrangement and each ligand acts as a linear bridge between two metal centres. We found the intermediate $Zn_xCd_{1-x}(CN)_2$ compounds shared the same basic structure, with the two types of metal center distributed randomly throughout the framework. Our interest in studying a series of isostructural compounds arises from a desire to elucidate whether the origin of NTE behavior in $Zn(CN)_2$ is primarily chemical or topological in nature.

The paper of Williams *et al.*[12] in which this NTE behavior was reported cites measurements of the cubic unit cell parameter a (Ref. 21) at just two temperatures: 10 and 295 K. As thermal expansion behavior is well known to be nonlinear and indeed discontinuous for many materials, we noted the possibility that any extrapolation of thermal expansion behavior from two measurements alone would be inconclusive. Consequently, we sought first to establish the thermal expansion behavior of four members of the $Zn_xCd_{1-x}(CN)_2$ family ($x=0$, 0.64, 0.80, and 1) at intervals of approximately 4 K for temperatures up to 375 K. We used single crystal x-ray diffraction to follow the temperature dependence of the unit cell volume for each compound; our results [Fig. 3(a)] indicate continuous and linear NTE behavior in all four materials.

TABLE II. Thermal expansion behavior of members of the $Zn_xCd_{1-x}(CN)_2$ family as determined by single crystal x-ray diffraction. The behavior of ZrW_2O_8 (taken from Refs. 2 and 9) is included for comparison.

Compound	$\alpha/10^{-6}\ K^{-1}$	T/K
$Zn(CN)_2$	−16.9 (2)	25–375
$Zn_{0.80}Cd_{0.20}(CN)_2$	−17.8 (2)	100–375
$Zn_{0.64}Cd_{0.36}(CN)_2$	−19.5 (3)	100–375
$Cd(CN)_2$	−20.4 (4)	150–375
ZrW_2O_8	−9.1	0.4–430
	−4.9	430–950

It is possible to quantify the extent of NTE behavior by considering the linear coefficient of thermal expansion α, defined at constant pressure as the relative rate of change of the unit cell parameter a with respect to temperature. Our data give values of α for the $Zn_xCd_{1-x}(CN)_2$ materials approximately double that of ZrW_2O_8; furthermore, these remained constant over the temperature ranges studied (Table II).

Having established the NTE behavior of this family, we proceeded to assess whether our crystallographic data were consistent with the RUM analysis proposed above. To do so, we performed full single crystal data collections and refinements for the $x=0$, 0.80, and 1 members at various temperatures.[22] The anisotropic refinement of single crystal[11,23] and powder[4] diffraction data has helped provide detailed information on the structural mechanisms for NTE in other systems. In the present case, thermal population of RUMs would be expected to give rise to local displacements of the CN linkage of the type illustrated in Fig. 1(b). The magnitude of these displacements enters our crystallographic refinement as the transverse displacement parameters of the C and N atoms.

For each of the materials investigated, this displacement parameter was found to increase significantly more rapidly than any other in the structure, providing a strong indication that such local vibrational modes are the dominant dynamical phenomenon [Fig. 3(b)]. Moreover, if we assume that the transverse displacement parameter of the C and N atoms approximates the root mean square harmonic thermal displacement of these atoms, and that bond expansions are negligible, then this temperature-dependent amplitude may be used to estimate the coefficient of thermal expansion, based on geometric considerations alone[24]

$$\alpha \simeq -\frac{2}{\sqrt{3}ar}\frac{\mathrm{d}U}{\mathrm{d}T},$$

where U is the relevant displacement parameter and r the average crystallographic metal–cyanide bond length. This calculation is easily performed for $Zn(CN)_2$ and $Zn_{0.80}Cd_{0.20}(CN)_2$ to give estimates for α (-16×10^{-6} and -15×10^{-6} K^{-1}, respectively) that agree excellently with those measured directly. The same calculation for $Cd(CN)_2$ is complicated by the effects of a low-temperature phase transition at approximately 150 K, a feature we have not explored further.

In conclusion, our results have established that the replacement of single-atom bridges in framework materials for diatomic analogs impacts profoundly on framework flexibility. In particular, those materials for which the rigid-unit approximations are appropriate might be expected to possess a very significant number of RUMs with NTE character. In the absence of other effects on thermal expansion behavior (such as the inclusion of counterions or solvent within the extra-framework cavities), one might reasonably expect such materials to exhibit overall NTE behavior, perhaps to significantly greater extents than is possible for “traditional” NTE materials. Additionally, we have shown that the crystallographic behavior of the $Zn_xCd_{1-x}(CN)_2$ family is entirely consistent with our analysis and have characterized their extraordinarily large NTE effect. Given the apparent generality of our geometric results, we expect that similar—if not more extreme—NTE behavior may be discovered in many other members of the broad family of cyanide-containing framework materials.

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[22] Crystallographic data have been deposited in the Inorganic Crystal Structure Database [$Zn(CN)_2$: ICSD-413098 to ICSD-413104; $Cd(CN)_2$: ICSD-413105 to ICSD-413108; $Zn_{0.80}Cd_{0.20}(CN)_2$: ICSD-413109 to ICSD-413112].

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