Negative Thermal Expansion

DOI: 10.1002/anie.200704421

Nanoporosity and Exceptional Negative Thermal Expansion in Single-Network Cadmium Cyanide

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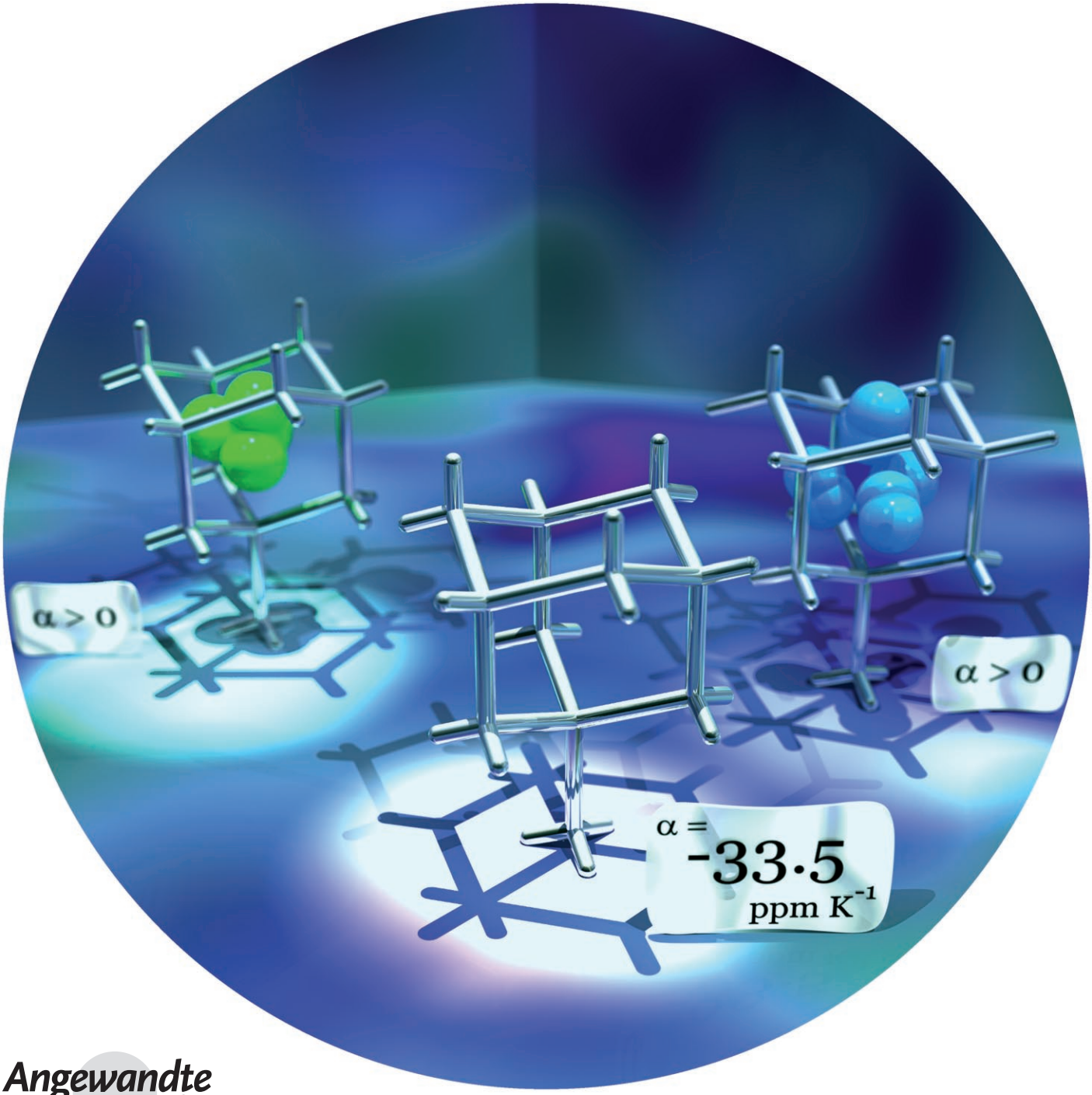

Although most solids expand on heating, a few display negative thermal expansion (NTE), the opposite effect, owing to magnetic or electronic transitions[1–4] or because of their vibrational structure.[5–9] Such materials are potentially useful in engineering systems sensitive to thermal expansion or stress. In particular, ZrW_2O_8 has attracted considerable attention, because its NTE behavior, which is attributed to transverse vibration of the oxide bridges between metal atoms, is large, approximately constant, and isotropic over a wide temperature range.[10]

More recently, the NTE behavior of several cyanide-bridged frameworks has been investigated.[11–17] NTE in this family is attributed to transverse vibrations of the cyanide bridges, which draw adjacent metal sites closer together. These vibrations are analogous to the transverse oxide vibrations in ZrW_2O_8 and related systems, except that the more flexible two-atom linkage in CN-bridged compounds allows freer vibration and hence greater NTE. Indeed, the greatest previously reported isotropic NTE is that of $Cd(CN)_2$, which has a linear coefficient of thermal expansion $\alpha = dl/ldT = -20.4(4) \times 10^{-6}\ K^{-1}$ over the temperature range 150–375 K, where l is length.[12] Evidence for the proposed vibrational model has been drawn from a variety of complementary experimental results. Pair distribution function analysis of $Zn(CN)_2$ demonstrates that Zn–CN bond lengths increase with temperature, while Zn···Zn separations decrease;[13] sorption of H_2O guests, which sterically hinder these transverse modes, into $ZnPt(CN)_6$ prevents negative thermal expansion in this compound;[14] and very low-energy vibrational modes have been observed in the phonon density of states of both of these systems by inelastic neutron scattering.[16]

In addition to its high-NTE, doubly-interpenetrated diamondoid structure, cadmium cyanide forms a wide variety of clathrates in which molecular guests replace one of the two diamondoid frameworks (Figure 1).[18,19] According to the model outlined above, removing one network may allow the other more transverse vibrational freedom, hence decreasing the coefficient of thermal expansion still further. Herein we report the desolvation of $Cd(CN)_2{\cdot}CCl_4$ to form a novel family of partially solvated cubic clathrates $Cd(CN)_2{\cdot}x\,CCl_4$, $0 \le x \le 1$, in which α varies monotonically with x down to a negative α of unprecedented magnitude for completely desolvated single-network $Cd(CN)_2$.

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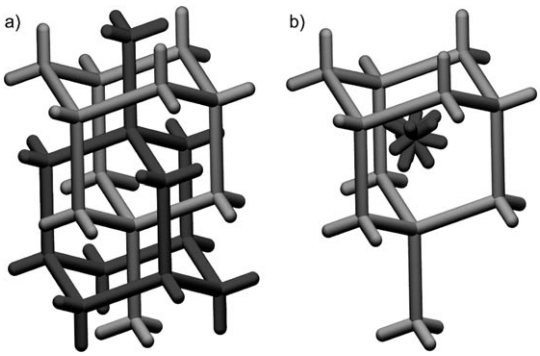

Figure 1. Crystal structures of a) $Cd(CN)_2$ and b) $Cd(CN)_2{\cdot}CCl_4$ (with crystallographically disordered guest), showing that in this clathrate, the guest displaces one of the two interpenetrating $Cd(CN)_2$ frameworks.

The coefficients of thermal expansion of $Cd(CN)_2{\cdot}x\,CCl_4$ were determined using single crystal X-ray diffraction to monitor the unit cell parameter as a function of temperature. Single crystals of $Cd(CN)_2{\cdot}CCl_4$ were mounted in a capillary at 100 K and heated slowly to 375 K. Above 300 K, the structural parameters revealed that the compound began to lose guest molecules while the framework remained intact. Complete removal of CCl_4 (b.p. 350 K) was effected by holding the crystal at 375 K for several hours in the nitrogen cryostream (see Figure S1 in the Supporting Information). The time taken for desolvation varied substantially; some crystals were completely desolvated after 2 h while others remained partially solvated after 24 h. Thus, single crystals of $Cd(CN)_2{\cdot}x\,CCl_4$ with a given value of x were obtained by holding the temperature constant until the desired desolvation had occurred. The value of x was obtained by refinement of a full data set collected at 300 K using atomic displacement parameters constrained to be equal to those from a full structural solution of the fully solvated framework. The temperature was then slowly returned to 100 K. Figure 2 shows the unit cell parameters of the solvated and completely desolvated frameworks as a function of temperature.

$Cd(CN)_2{\cdot}CCl_4$ displays positive thermal expansion from 100 to 240 K with $\alpha = +10.0(2) \times 10^{-6}\ K^{-1}$ (Table 1). Above approximately 300 K, the unit cell parameter begins to decrease; refinement of the guest occupancy at these temperatures showed that this effect is due to guest desorption rather than thermal expansion behavior intrinsic to the framework itself. Complete desorption at 375 K results in a decrease in the unit cell parameter and a substantial change in the coefficient of thermal expansion, which at $\alpha = -33.5(5) \times 10^{-6}\ K^{-1}$ is constant, negative, and of unprecedented magnitude over the temperature range 170–375 K. Below 170 K, this coefficient becomes positive owing to sorption of dinitrogen from the cryostream. The presence of unmodeled electron density in the pores is confirmed by the significantly higher refinement indices at these temperatures (see Table S2 in the Supporting Information). The unmodeled density was visualized with the program MCE,[20] which showed that the N_2 does not occupy the vacant CCl_4 sites at the center of the pores (diameter 9.6 Å). Rather, it adsorbs into the centers of the windows (dimensions 7.4×6.0 Å^2) between these sites and

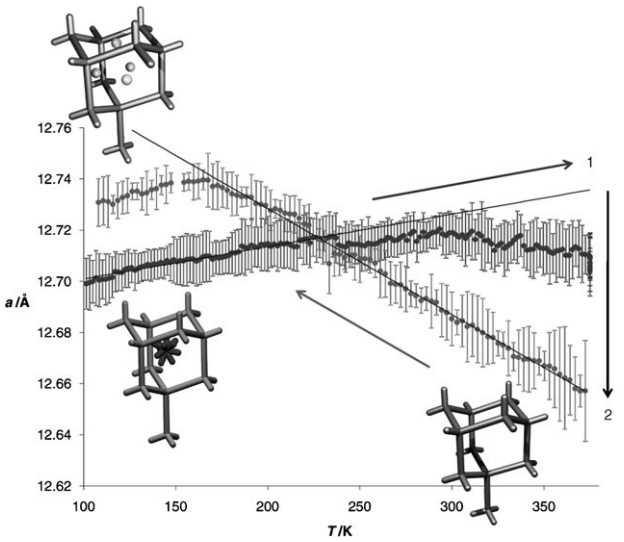

Figure 2. Unit cell parameter of $Cd(CN)_2 \cdot CCl_4$ (curve 1) and of single-network $Cd(CN)_2$ (curve 2) as a function of temperature. Insets are generated from structural solutions and show the disordered CCl_4 molecule in the pores (bottom left), the desolvated apohost structure (bottom right), and the difference electron density peaks arising from nitrogen sorption into the pore windows (top left; see also Figure S3 in the Supporting Information).

Table 1: Coefficients of thermal expansion of single-network $Cd(CN)_2$ with varying fractional CCl_4 occupancies. See also Figure S2 in the Supporting Information.

CCl_4 occupancy [%]	α [10^{-6} K^{-1}]	T [K]
0(4)	−33.5(5)	170–375
64(4)	−16.9(3)	240–375
75(4)	−5.7(3)	200–375
100(4)	+10.0(2)	100–240

is dynamically disordered (Figure 2 and Figure S2 in the Supporting Information). The difference in sorption site is clearly commensurate with the difference in size between the CCl_4 and N_2 molecules. Refinement using SQUEEZE[21] gave a void volume of 64% and a value of 216 unmodeled electrons per unit cell. This value corresponds to 96% occupancy of the pore window sites with dinitrogen molecules and hence a composition $Cd(CN)_2 \cdot 1.92\,N_2$. Some nitrogen sorption was also apparent for 64% CCl_4 occupancy, although none was observed in the system with 75% CCl_4. We note that, perhaps counterintuitively, the unit cell parameters of the $Cd(CN)_2 \cdot G$ system below 220 K decrease as G varies from $1.92\,N_2$ to CCl_4 to $Cd(CN)_2$ (double-network $Cd(CN)_2$ has $2a = 12.6498(16)$ at 150 K, where the factor of 2 is necessary to compare the networks of different symmetry). This result emphasizes the importance of interactions between frameworks (or between the framework and guests) in this system, although the exact nature of such interactions remains unclear.

The coefficients of thermal expansion of these systems (Table 1) vary monotonically with the guest occupancy. These results are readily interpretable in terms of the basic steric dampening model described previously for the hydration and dehydration of $ZnPt(CN)_6$.[14] Put simply, the presence of CCl_4 molecules impedes the vibrational motion responsible for NTE in the host $Cd(CN)_2$ framework. NTE requires vibrational modes with negative Grüneisen parameters, that is, modes whose energies decrease with a decrease in the unit cell parameter. As we have stated, a contraction in the $Cd(CN)_2$ cell involves displacements of C and N atoms away from the Cd···Cd axis and hence into the framework cavities. If these cavities are empty, then the energy of these transverse modes decreases with these displacements, as might be expected. Steric interactions in a solvated framework, on the other hand, act to increase the energy of these displacement patterns, thus producing a concomitant increase in the associated Grüneisen parameters and in turn a more positive overall thermal expansion behavior. We note also that the CCl_4 guest itself will vibrate with increased amplitude at higher temperatures, which may enhance this dampening effect further.

This steric dampening model is supported by the temperature and guest-occupation dependence of the atomic displacement parameters for transverse motion of the cyanide atoms (Figure 3 and Figure S3 in the Supporting Information). The mean square transverse displacement of these atoms from their equilibrium positions decreases with guest occupation at all temperatures, demonstrating that the amplitudes of the transverse modes are greatest in the absence of guest molecules. Moreover, the rates at which these displacements increase with temperature are themselves dependent on guest occupancy, with lower occupancies corresponding to greater increases with temperature. Since the transverse vibrational modes compete with longitudinal modes to influence the thermal expansion properties of the framework (see Figure S4 in the Supporting Information), negative thermal expansion behavior is observed when the former, through high dU/dT values, outweigh the latter in influence.

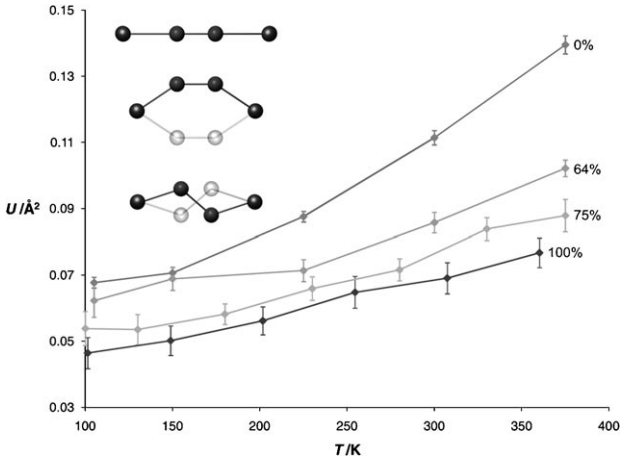

Figure 3. Transverse vibrational parameters of the cyanide C and N atoms in single-network cadmium cyanide with varying fractional CCl_4 occupancies. Inset shows the transverse Cd–C≡N–Cd vibrational modes dampened by the guest molecules. See also Figure S4 in the Supporting Information.

This model is also consistent with previous work on $Zn(CN)_2$, in which both the change in the transverse atomic

displacement parameter with temperature $dU_{\perp}/dT$ and the coefficient of thermal expansion α are lower ($Zn(CN)_2$: $dU_{\perp}/dT = 1.58(2)\times10^{-4}$ Å^{2}K^{-1}, $\alpha = -16.9(2)\times10^{-6}$ K^{-1};[12] single-network $Cd(CN)_2$: $dU_{\perp}/dT = 3.24(9)\times10^{-4}$ Å^{2}K^{-1}, $\alpha = -33.5(5)\times10^{-6}$ K^{-1}). This qualitative agreement is encouraging, despite the fact that the relationship between $dU_{\perp}/dT$ and α is insufficiently robust to allow a quantitative comparison to be made.

It is particularly noteworthy both that single-network $Cd(CN)_2$ exhibits a negative coefficient of thermal expansion more than 50% larger than the previously reported maximum[12] and that the variation of α with guest occupancy is exceptionally large, almost ten times that of previously reported examples.[14] We attribute this second effect to the greater relative steric influence of the bulky CCl_4 guest in this system. Importantly, the variation in thermal expansion properties and unit cell size between the double- and single-network compounds implies that interframework interactions play a significant role in the lattice enthalpy and lattice dynamics of double-network $Cd(CN)_2$ (and presumably those of $Zn(CN)_2$ by analogy). A similar conclusion was reached in lattice dynamical studies of the isostructural NTE material Cu_2O, for which interframework interactions were found necessary to reproduce the observed phonon dispersion relations.[22]

In summary, we have shown that single-network $Cd(CN)_2$ exhibits stronger NTE behavior than any previously reported material. The coefficient of thermal expansion of $Cd(CN)_2{\cdot}x\,CCl_4$, $0 \le x \le 1$, varies monotonically with x, thus supporting the model in which transverse vibrational modes are responsible for this material's NTE behavior. We aim to investigate this phenomenon further by adsorbing different guests into the desolvated framework.

Experimental Section

$Cd(CN)_2{\cdot}CCl_4$ was prepared from solutions of $K_2[Cd(CN)_4]$ (210 mg in 5 mL water) and $CdCl_2{\cdot}2.5\,H_2O$ (180 mg in 5 mL water), which were mixed and allowed to stand for 1 h, then filtered. 1–2 mL of the filtrate was added to a large vial in which a smaller vial containing carbon tetrachloride (1 mL) was placed. The larger vial was sealed to allow the clathrate to form by gas-phase diffusion of carbon tetrachloride. Octahedral crystals formed over two to three days.[19]

Single crystals were secured with a thin film of grease inside a 0.5-mm glass Lindemann capillary and mounted on a brass pin. Diffraction data were collected on a BrukerAXS SMART 1000 CCD diffractometer using an Oxford Cryosystems nitrogen cryostream. Graphite-monochromated $Mo_{K\alpha}$ radiation was generated from a sealed tube. Variable-temperature unit cell determinations were performed in situ while increasing the temperature over an appropriate range at a rate of 15 K h^{-1}.

Supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by quoting the CCDC reference numbers provided in Tables S2, S3 and S5 in the Supporting Information.

Received: September 26, 2007
Published online: December 19, 2007

Keywords: cyanides · materials science · metal–organic frameworks · microporous materials · negative thermal expansion

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