PHYSICAL REVIEW B **76**, 052102 (2007)

Phonon dispersion and Grüneisen parameters of zinc dicyanide and cadmium dicyanide from first principles: Origin of negative thermal expansion

J. W. Zwanziger*
Department of Chemistry and Institute for Research in Materials, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

(Received 23 May 2007; revised manuscript received 23 July 2007; published 27 August 2007)

Zinc dicyanide, $Zn(CN)_2$, and the isostructural cadmium dicyanide show negative thermal expansion over a broad range of temperatures. By the use of density functional theory calculations, we determine the phonon dispersion curves of these materials and show that the transverse acoustic modes give rise to a relatively sharp feature at about 2–4 meV in the phonon density of states. In addition, we compute the Grüneisen parameters of these modes and show that they have large negative values, indicating that they are the primary contributors to the negative thermal expansion in this material. Our results are in broad agreement with recent neutron scattering experiments on $Zn(CN)_2$ and the rigid unit mode analysis of these materials.

DOI: 10.1103/PhysRevB.76.052102 PACS number(s): 65.40.De, 71.15.Nc

I. INTRODUCTION

Zinc dicyanide, $Zn(CN)_2$, and the isostructural cadmium analog are examples of negative thermal expansion (NTE) materials, meaning that they contract with increasing temperature over a broad range. In $Zn(CN)_2$, the value of the thermal expansion coefficient $\alpha = d\ln V/dT$ is about -16×10^{-6} K^{-1} over the range 25–375 K,[1,2] over two times larger than the value in ZrW_2O_8.

These compounds have particularly simple structures.[1,3] The unit cell is primitive cubic, with metal ions at the corners and the center, bridged by four cyanide anions to form an interpenetrating network of tetrahedrally connected tetrahedra. If all the cyanides are oriented the same way, as in Fig. 1, the space group is $P\bar{4}3m$, while if orientationally disordered, the symmetry is $Pn\bar{3}m$. It is likely that synthetic samples typically have the disordered structure.[1]

It has been argued based on the rigid unit mode (RUM) model that the NTE behavior in these compounds originates from the topology of the tetrahedral connections.[2,4] RUM's involve librations of groups of atoms around a metal center such that the metal coordination geometry is preserved, and should occur at low energy (according to Ref. 2, less than about 8 meV). In $Zn(CN)_2$ and $Cd(CN)_2$, the extra degrees of freedom imparted by the cyanide anions, as compared to the same structures linked by monatomic anions, allow the metal-centered tetrahedra to undergo rigid local twisting librations with respect to one another. This freedom leads to an enhancement in the number of RUM's, and it has been conjectured that these modes are, in turn, responsible for the striking NTE behavior. A detailed x-ray diffraction study indicated that in $Zn(CN)_2$, the important structural change involves lateral displacement of the cyanide anions together with contraction of the zinc-zinc distances.[5] In addition, recent inelastic neutron scattering experiments on $Zn(CN)_2$ determined the phonon density of states and reported a strong low-frequency peak at about 2 meV.[6] This peak correlated well as a function of temperature with the thermal expansion and was suggested to represent the motional process giving rise to the NTE behavior. Because the experiment was performed on a powdered sample, detailed phonon dispersion curves and assignments could not be obtained. On the other hand, a recent Raman and IR study reported no observation of any modes in $Zn(CN)_2$ below about 18 meV.[7]

A microscopic understanding of the NTE behavior requires the phonon dispersion curves as well as the Grüneisen parameters. The RUM model provides a very helpful framework for understanding the relationship between network topology and dynamical behavior, but does not provide such microscopic details. In addition, the experimental evidence on the low-frequency modes appears to be in conflict.[6,7] In order to provide microscopic details on the low energy modes and their contribution to the NTE in $Zn(CN)_2$ and $Cd(CN)_2$, we used first-principles calculations to determine the phonon dispersion curves as a function of volume and, hence, to obtain both the phonon assignments in terms of atomic displacements as well as the Grüneisen parameters. Our results are broadly in accord with the neutron scattering data and the RUM model in that we find the transverse acoustic modes to appear in a nearly dispersionless band at about 2–4 meV and to exhibit large negative Grüneisen parameters.

II. METHODS

The present results have been obtained using the ABINIT code,[8,9] a density functional theory code implemented with

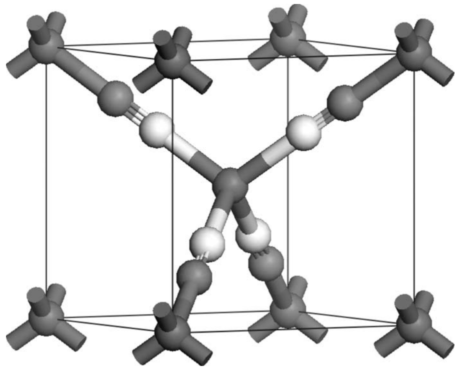

FIG. 1. Crystal structure of $Zn(CN)_2$ in the ordered phase. The zinc ions are at the centers of the tetrahedra, linked by cyanide anions along four of the body diagonals. The result is an interpenetrating network of tetrahedrally coordinated tetrahedra.

pseudopotentials and plane waves. It is a common project of the Université Catholique de Louvain, Corning, Inc. and other contributors.[16] Optimized norm-conserving pseudopotentials were used,[10] generated with the OPIUM code[17]. The Perdew-Burke-Ernzerhof exchange and correlation functionals[11] were used both in the creation of the pseudopotentials and in the subsequent density functional theory calculations. Technical details on the computation of responses to atomic displacements and homogeneous electric fields can be found in Ref. 12 while Ref. 13 presents the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants.

We carried out our study on the ordered model because its higher symmetry greatly simplifies the calculations without significantly altering the low-frequency part of the phonon spectrum. The cyanide anions as linker groups can be viewed as nearly rigid rods because their internal stretch frequency (about 275 meV, Ref. 7) greatly exceeds the other frequencies in the cell. The short distance of the CN bond and its small dipole moment both suggest that the librational forces that are the main interest here are likely to be nearly identical, whether two tetrahedra are linked by CN or NC. As a check on this assumption we computed the phonon dispersion curves for $Zn(CN)_2$ using the virtual crystal approximation (VCA), in which the carbon and nitrogen atoms were replaced by 50/50 blends of the carbon and nitrogen pseudopotentials.[14] Such a calculation mimics disorder in a simple way without the computationally expensive (but ultimately more accurate) process of generating an optimized disordered supercell. Within the VCA, the dispersion curves, including the acoustic modes, showed essentially no difference to those of the ordered model. We conclude from this agreement that a detailed study of the simplified ordered models is justified in this case.

The computation of the phonon responses proceeded as follows. First, the experimental crystal structure[3] was optimized such that no force in the unit cell exceeded 2.0×10^{-5} a.u., which resulted in an internal pressure on the order of ±0.002 GPa and a lengthening of the cell constant by less than 2% [0.5% in the $Zn(CN)_2$ case]. Next, the ground state electron density and responses to electric fields and atomic displacements were computed using a cutoff energy of 25 hartree, 36 bands (30 occupied, 6 unoccupied), and a $4\times4\times4$ shifted Monkhorst-Pack grid.[15] This grid corresponded to a spacing of about 0.04 Å^{-1}. Responses on a matching grid of phonon wave vectors were computed in order to determine the interatomic force constants; this set was then interpolated to determine the dispersion curves at arbitrary phonon wave vectors. The determination of the Grüneisen parameters was accomplished by computing the phonon dispersion curves at two additional unit cell volumes, derived from the optimized ones by straining the lattice parameter by −1% and +1% and reoptimizing the ion positions.

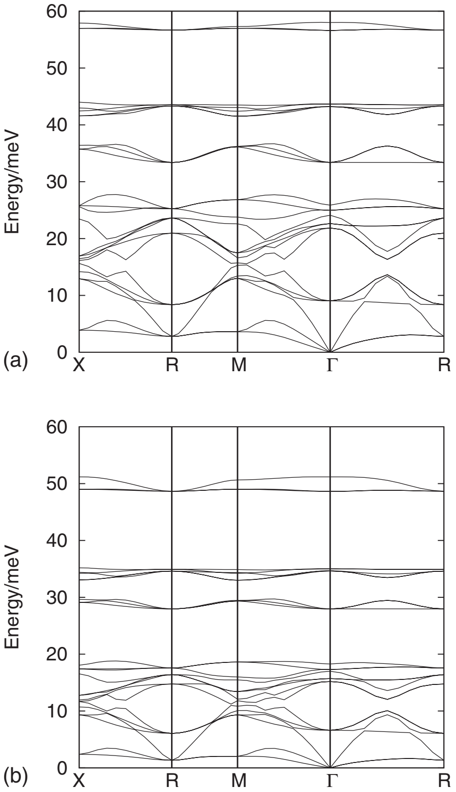

FIG. 2. Phonon dispersion curves for (a) $Zn(CN)_2$ and (b) $Cd(CN)_2$. In order to expand the scale, the cyanide anion stretch modes, a set of four essentially dispersionless bands at about 273 meV is not shown.

III. RESULTS AND DISCUSSION

The calculated phonon dispersion curves for $Zn(CN)_2$ and $Cd(CN)_2$ are shown in Fig. 2 and the phonon densities of state in Fig. 3. Of particular importance in the present context is the dispersion of the two lowest acoustic modes, which are remarkably flat as a function of wave vector. These modes have average energies in the 2–4 meV range. Although somewhat higher in energy than the value measured by neutron scattering (2 meV, Ref. 6), we believe that

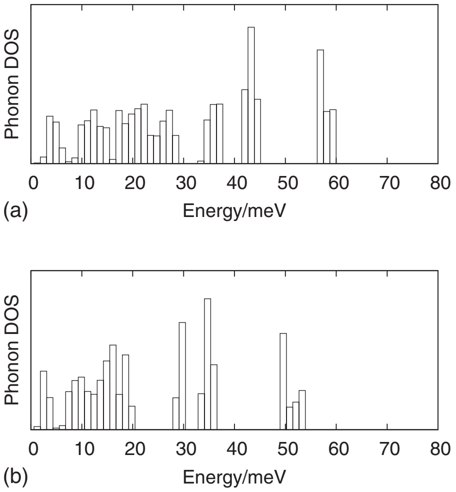

FIG. 3. Phonon density of states for (a) $Zn(CN)_2$ and (b) $Cd(CN)_2$. The data are binned in 10 cm^{-1} increments, and the cyanide stretch modes at 2200 cm^{-1} (273 meV) are not shown.

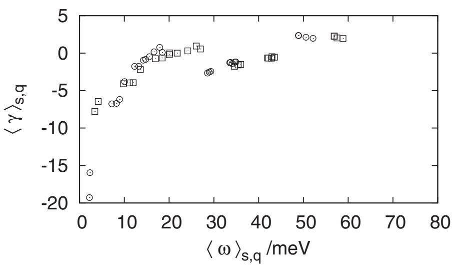

FIG. 4. Grüneisen parameters $\langle \gamma \rangle_{\mathbf{q}}$ as a function of mode energies $\langle \omega \rangle_{\mathbf{q}}$ in units of meV. Each quantity was averaged over a $4 \times 4 \times 4$ grid of wave vectors in order to obtain average values for each mode. Results for $\mathrm{Zn(CN)_2}$ are plotted with squares, and results for $\mathrm{Cd(CN)_2}$ are plotted with circles. The cyanide stretch modes at 273 meV are not shown; they have Grüneisen parameters of 0.25.

these modes correspond to those observed experimentally. As in the experiment, they give rise to well-isolated peaks in the phonon density of states (Fig. 3). The $\mathrm{Cd(CN)_2}$ curves [Fig. 2(b)] are very similar to the $\mathrm{Zn(CN)_2}$ curves [Fig. 2(a)] although lower in energy due to the greater mass of Cd versus Zn.

The Grüneisen parameters were calculated for all the modes by a linear fit to the dispersion curves computed at three cell volumes. The Grüneisen parameter expresses the volume dependence of the mode frequency and is defined for mode s and wave vector $\mathbf{q}$ as

$$\gamma_{s,\mathbf{q}} = -\frac{V}{\omega_{s,\mathbf{q}}} \frac{\partial \omega_{s,\mathbf{q}}}{\partial V}. \tag{1}$$

Shown in Fig. 4 are the Grüneisen parameters averaged over a $4 \times 4 \times 4$ grid in reciprocal space, plotted as a function of the mode energies averaged in the same way. The acoustic modes, particularly the lowest two, have large negative Grüneisen parameters, a necessity to exhibit negative thermal expansion behavior.

The thermal expansion coefficient itself can be written in terms of the Grüneisen parameters as

$$\alpha = \frac{1}{BV} \sum_{s,\mathbf{q}} \hbar \omega_{s,\mathbf{q}} \gamma_{s,\mathbf{q}} \frac{\partial n_{s,\mathbf{q}}}{\partial T}, \tag{2}$$

where B is the bulk modulus and $n_{s,\mathbf{q}}$ the phonon occupation number. We computed the bulk modulus of $\mathrm{Zn(CN)_2}$ using the perturbation theory approach within ABINIT and obtained a value of 59 GPa. Using this value and the above equation, we compute α for $\mathrm{Zn(CN)_2}$ as $-12 \times 10^{-6}\ \mathrm{K}^{-1}$ at 5 K, in fair agreement with experiment.[2] However, this agreement is only good at low temperature because our model is based on a 0 K structure that does not account for dynamical processes and distortion, which must be present at higher temperatures (and pressures). In making this calculation, all the modes were included, but at these low temperatures only the acoustic modes contribute beyond the 1% level. Majority of the modes have negative Grüneisen parameters (Fig. 4) and are expected to contribute in the real material; the acoustic modes should still dominate, however.

In $\mathrm{Cd(CN)_2}$, α would be even larger in magnitude due to the larger predicted Grüneisen parameters, and this is again in agreement with experiment.[2] However, the cadmium data extend down only to 150 K, at which point there is a phase transition; thus, comparison with our 0 K model of the $P\bar{4}3m$ structure is only qualitatively, not quantitatively, valid.

In both compounds, the acoustic modes involve translational motion of all the atoms, trivially at Γ and less so at other points in reciprocal space. An examination of the atomic displacements of the acoustic modes at X and R shows that both lowest modes involve translation of the cyanide anions and the metal cations in one direction, together with translational displacement of the cyanide anions in the other two directions. This finding is in qualitative agreement with the finite-temperature experimental results presented in Ref. 5.

IV. CONCLUSIONS

Our results indicate that the isolated low-frequency band in $\mathrm{Zn(CN)_2}$ observed by neutron scattering[6] is due to the transverse acoustic modes. These modes are nearly dispersionless and arise from the translation of the zinc and cyanide anions together in one direction coupled with cyanide translation in the other two directions. Majority of the modes show negative Grüneisen parameters, with the lowest frequency modes showing the largest effect. The energies and anharmonicities of these modes are sufficient to account for the negative thermal expansion of this material, particularly at low temperature. The isostructural cadmium analog shows the same trends, although more pronounced, in accord with the larger NTE effect observed in this compound.

ACKNOWLEDGMENTS

We thank Karena Chapman and Peter Chupas of Argonne National Laboratory and Mary Anne White of Dalhousie University for helpful discussions. Financial support from the Natural Sciences and Engineering Research Council of Canada through the Canada Research Chairs program and the Canada Foundation for Innovation is gratefully acknowledged.

---

*jzwanzig@dal.ca

[1] D. J. Williams, D. E. Partin, F. J. Lincoln, J. Kouvetakis, and M. O'Keeffe, J. Solid State Chem. **134**, 164 (1997).

[2] A. L. Goodwin and C. J. Kepert, Phys. Rev. B **71**, 140301(R) (2005).

[3] B. F. Hoskins and R. Robson, J. Am. Chem. Soc. **112**, 1546 (1990).

[4] A. L. Goodwin, Phys. Rev. B **74**, 134302 (2006).

[5] K. W. Chapman, P. J. Chupas, and C. J. Kepert, J. Am. Chem. Soc. **127**, 15630 (2005).

[6] K. W. Chapman, M. Hagen, C. J. Kepert, and P. Manuel, Physica B **385-386**, 60 (2006).

[7] T. R. Ravindran, A. K. Arora, and T. N. Sairam, J. Raman Spectrosc. **38**, 283 (2007).

[8] X. Gonze *et al.*, Comput. Mater. Sci. **25**, 478 (2002).

[9] X. Gonze *et al.*, Z. Kristallogr. **220**, 558 (2005).

[10] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B **41**, 1227 (1990).

[11] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[12] X. C. Gonze, Phys. Rev. B **55**, 10337 (1997).

[13] X. C. Gonze and C. Lee, Phys. Rev. B **55**, 10355 (1997).

[14] Ph. Ghosez, D. Desquesnes, X. Gonze, and K. M. Rabe, AIP Conf. Proc. **535**, 102 (2000).

[15] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[16] http://www.abinit.org

[17] http://opium.sourceforge.net