Density Functional Studies Reveal Anomalous Lattice Behavior in Metal Cyanide, AgC₃N₅

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We have investigated anomalous lattice behavior of metal organic framework compound AgC₃N₅ on application of pressure and temperature using ab-initio density functional theory calculations. The van der Waals dispersion interactions are found to play an important role in structural optimization and stabilization of this compound. Our ab-initio calculations show negative linear compressibility (NLC) along the c-axis of the unit cell. The ab-initio lattice dynamics as well as the molecular dynamics simulations show large negative thermal expansion (NTE) along the c-axis. The mechanism of NLC and NTE along the c-axis of the structure is governed by the dynamics of Ag atoms in the a-b plane. The NLC along the c-axis drives the NTE along that direction.

Keywords: Phonons in crystal lattice, Thermal properties of crystalline solids, Pressure effects, Smart materials, Ab-initio

The understanding of atomic level mechanisms responsible for various functional properties [1-8] of materials is very important to improve their performance. By intuition, material should contract (or expand) on application of hydrostatic pressure (or temperature), yet a small number of crystals show opposite behaviour in a few directions. This type of anomalous behaviour with pressure (or temperature) is called negative linear compressibility (or negative thermal expansion) behavior[9]. Materials with a negative linear compressibility (NLC) and negative thermal expansion (NTE) could have interesting technological applications[9-11] in body muscle systems (as actuators), in marine optical telecommunication, components of aviation, sensors, and devices working in high pressure-temperature surroundings.

So far, few studies have been performed to realize the origin of NLC and NTE in crystalline solids[9, 12]. This type of behaviour is predicted in open framework structure with high unit cell volume per atom and low density (Table I). Many cyanide based metal organic flexible framework structure[4, 5, 13-15] like ZnAu₂(CN)₄, M₃Co(CN)₆, MAux₂(CN)₂, where M=H, Au, Ag, Cu and X=CN, Cl, Br etc. show anomalous NLC and NTE behaviour. It seems that the occurrence of NLC is closely related to the NTE behaviour in these compounds[2]. Moreover, there is a very strong link between NLC, NTE and geometry of the material[3, 4, 8, 16].

The NLC and NTE in ZnAu₂(CN)₄ arise from anharmonic nature of low energy optic phonon modes involving bending of the -Zn-N-C-Au-CN-Zn- linkage[2]. This bending produces the effects of a compressed spring upon heating and an extended spring[17] under hydrostatic pressure in specific spring like topology of ZnAu₂(CN)₄. In many cases like MFM-133(M) (M=Zr, Hf), L- tartrate, M₃Co(CN)₆ (M=H, Ag, Cu), the anomalous lattice behavior has been observed to arise from deformation mode of wine-rack-like geometries which is contributed from molecular strut compression and angle opening mechanism[3, 5, 6, 9, 13, 14, 18, 19] in anisotropic framework. In M₃Co(CN)₆, the intense and quicker response of phonon group velocity along c-axis than in a-b plane upon heating and compression facilitate c-axis to be a carrier of anomalous lattice behavior[20]. In a framework material, NLC can be effectively tuned by varying the inorganic component of the framework without changing the network topology and structure[18]. For 2-D layered framework compounds like Co(SCN)₂(pyrazine)₂, the layer sliding mechanism is found to be responsible for the observed NLC behaviour[21]. Framework hinging mechanism leads to an extreme NLC in InH(BDC)₂, which is much higher than CN based metal organic framework compounds[22]. Large NLC is observed in frameworks composed of rigid linear ligands and flexible framework angles[2, 4, 23]. The NTE behaviour along c-axis in linear chain structure like MCN (M=Ag, Au, Cu) is caused by the chain sliding phonon modes and –C≡N– bond flipping in the chain[24].

On the basis of current understanding of the mechanisms responsible for NLC, different approaches to design and fabricate new structures with NLC and NTE behaviour are being studied[25, 26]. High-pressure and high-temperature X-ray and neutron diffraction techniques are used to experimentally determine the anisotropic linear compressibility and linear thermal expansion coefficients of crystalline materials[3-5, 7-9, 16, 23]. However, ab-initio quantum mechanical calculations are well established to understand the microscopic mechanism governing these phenomena[2, 12, 24, 27, 29]. The compressibilities and expansion coefficients as calculated using ab-initio DFT and phonon calculations are found to reproduce fairly well the experimental values. These calculations, from the analysis of eigen vectors, provide the insight about the anharmonic phonon modes responsible for anomalous lattice behaviour in the material[2, 24, 27, 29].

The metal organic framework compound, AgC₃N₅ has comparatively lower density[30] (Table I) than its family compounds[16, 24] like AgCN and AgC₂N₃. This motivated us to study the anomalous lattice behaviour of AgC₃N₅ using ab-initio density functional theory. The details of the calculations are given in supplementary information[31].

As per our knowledge, there are no temperature/pressure dependent experimental or theoretical studies reported on this compound regarding its anomalous lattice behavior. The crystal structure (Fig. 1) of AgC₃N₅ contains the C₃N₅planer ligand and AgC₃N₅ tetrahedral units. Both, the planer and polyhedral units are distorted. The planer sheets of C₃N₅ are vertically placed along c-axis with small tilting in the a-b plane. These sheets are well separated along b-axis (distance ≈ 3 Å) in a-b plane. Therefore, these sheets must be weakly interacting through weak dispersion interaction to make the stable structure. The structure optimizations done without...
considering these weak interactions is found to highly overestimate (Table II) the b-lattice parameters. However, when van der Waals interactions are considered between these planar sheets the calculated structure is found to match with the experimental structure[30], within the limitations of GGA (Table II). It seems van der Waals interactions play a very important role in governing the structure stability of AgC$_3$N$_5$. The weak dispersion interactions acting in a-b plane (especially along b-axis) make the structure flexible in a-b plane as compared to that along c-axis. The structure with presence of van der Waals dispersion interactions is considered for all further calculations.

The elastic constants of AgC$_3$N$_5$ are derived from the strain-stress relationships obtained from finite distortions of the equilibrium lattice. The elastic constants are used to get the Bulk modulus and elastic compliance matrix, $S$=$C^{-1}$ (in 10$^3$ GPa$^{-1}$ units) as:

\[
\begin{pmatrix}
162.95 & -99.12 & -42.81 & 0 & 0 & 0 \\
-99.12 & 143.22 & 7.97 & 0 & 0 & 0 \\
-42.81 & 7.97 & 30.81 & 0 & 0 & 0 \\
0 & 0 & 0 & 435.16 & 0 & 0 \\
0 & 0 & 0 & 0 & 202.80 & 0 \\
0 & 0 & 0 & 0 & 0 & 203.79
\end{pmatrix}
\]

For negative compressibility along the crystallographic axes[32], in an orthorhombic crystal, the following inequalities should hold

\[X_a=S_{11} + S_{12} + S_{13}<0, X_b=S_{12} + S_{22} + S_{23}<0 \& X_c=S_{23} + S_{33} + S_{31}<0\]

Where $X_i$ (i=a, b, c) are the compressibilities of crystal along various crystallographic axes. It is observed that only the last inequality holds, implying that compound exhibits negative linear compressibility along the c-axis. To quantify this property, the crystal structure is relaxed under application of isotropic pressures and corresponding lattice parameters are calculated. The calculated lattice parameters as a function of pressure are shown in Fig 2. It is observed that the lattice parameters ‘a’ and ‘b’ decrease with increasing pressure and show normal behavior. The ‘b’ lattice parameter shows a larger decrease as compared to ‘a’ lattice parameter. This arises from the soft nature of van der Waals dispersion interaction acting among the planer sheets of C$_5$N$_5$ along b-axis. However, the ‘c’ lattice parameter shows an increase with increasing pressure. This confirms the negative linear compressibility along the c-axis. Overall volume is found to decrease with increase in pressure. Bulk modulus is calculated from the pressure dependence of unit cell volume. The PV equation of state is fitted with the well-known Birch–Murnaghan (2$^{nd}$ ordered) isothermal equation of state to get the value of bulk modulus. The calculated bulk modulus using this approach has the value of 14.5 GPa. This is consistent with that calculated from the elastic compliance (14.48 GPa) matrix. At ambient pressure, the calculated linear compressibilities are found to have the values of $X_a=21.0\times10^3$, $X_b=52.1\times10^3$ and $X_c=4.0\times10^3$ GPa$^{-1}$.

We observe that atomic coordinates of Ag atoms show major change on application of pressure. The displacement corresponding to this change is indicated as vectors in Fig 1. The displacement vector shows that the Ag atoms displace along the a-axis of the crystal. Further we found significant displacement of C=N unit, as a single rigid unit, attached to the corresponding Ag atoms. We found that C=N units only connected to Ag atoms are displaced in the a-b plane. Therefore, a hinging movement of rigid C=N units occurs about Ag atoms. On application of pressure, this gives rise to an expansion of the framework along c-axis and contraction in a-b plane.

As pressure increases above 4GPa, the structure becomes unstable and undergoes an unusual change. Around this pressure there are sudden jumps in lattice parameters, total energy and bond lengths of the compound (Fig 2). A sudden decrease in volume gives a signature of high pressure phase transition of the crystal. As indicated above, we found an anomalous change in the Ag atomic coordinate at this pressure. Above 4.0 GPa, AgN$_4$ tetrahedra are found to change the coordination and converts to AgN$_5$. This pressure may correspond to some phase transition of the structure; however, detailed high-pressure diffraction would be needful to identify the resultant structure of new phase.

The calculated structure as a function of pressure shows that the C≡N bond remains unchanged with a value of about 1.16Å. Moreover, various C-C bonds (Fig 4) in -C$_5$N$_5$- planer units do not show any significant changes (less than 1-2 %) with increase in pressure. The Ag-N bonds of AgN$_4$ tetrahedral units show (Fig 4) a variation of 5-6 %. This change would be due to the flexible nature of Ag-N bonds. There are significant changes (up to 6% of original bond angle) in the C≡C≡N bond angle (Fig 4) present on the periphery of C$_5$N$_5$ structural units. To understand these structural changes and the mechanism for negative and positive linear compressibility along c-axis and in the a-b plane respectively, we have calculated the difference in atomic coordinates of all the atoms corresponding to ambient pressure structure and 4GPa structure.

The primitive unit cell of AgC$_3$N$_5$ contains 168 atoms and has 504 phonon modes of vibrations. The calculation of complete phonon spectra in the entire Brillouin zone is computationally expensive for such a large system. We have calculated the zone centre phonon spectra in conventional unit cell with 336 atoms using linear response density functional perturbation theory (DFPT). These 1008 phonons at the zone- centre of the conventional unit cell correspond to 504 phonons each at the zone- centre and the (111) zone-boundary point of the Brillouin zone of the body centred orthorhombic structure. Leaving 3 acoustic branches, we have calculated the phonon spectrum for 1005 phonon modes.

The calculated partial density of states of C, N and Ag atoms show that these atoms contribute in different energy regions (Fig 3) of the spectra. The very high energy peaks around 270 meV in the spectra of C and N is related to the vibrational stretching modes associated with very strong C≡N bonds. The spectra in the 100-200meV range is highly contributed by C atoms and is related to stretching vibrations of strong C-C bonds in the -C$_5$N$_5$- planer structural units. The lower energy modes in spectra of C and N atoms are associated with bending vibrations of constructing -C$_5$N$_5$-units. It is interesting to note that the Ag atoms only contribute to the
vibrational spectra in very low energy up to 40 meV. Hence, the vibrational modes associated with Ag atoms would be populated at low temperatures and would give rise to interesting structural and dynamical properties. This also confirms, on application of pressure, the dominant role of Ag in giving rise to NLC and phase transition in AgC₃N₅.

The stress dependence of phonon energies is used for the calculation of anisotropic Grüneisen parameters of AgC₃N₅. An anisotropic stress of 5 kbar is implemented by changing only one of the lattice constants and keeping the others fixed. The calculated mode Grüneisen parameters as a function of phonon energy along different crystal directions are shown in Fig. 4(a). The Grüneisen parameters along a and b axes show normal positive behavior. However, the Grüneisen parameters along c-axis have large negative values. The calculated anisotropic Grüneisen parameters and elastic compliance matrix are used to calculate the anisotropic thermal expansion coefficients. The calculated temperature dependence of anisotropic thermal expansion coefficients and lattice parameters are shown in Fig 4 (c,d). Negative thermal expansion is found along c-axis while positive along a and b axes. The change with temperature along a-axis is more pronounced than that along b-axis. This is contrary to the calculated behavior as a function of pressure. The volume shows normal positive thermal expansion behaviour. The quantitative thermal expansion behavior is obtained from the calculated temperature dependence of linear thermal expansion coefficients (Fig 9). At 300K, the values of linear and volume thermal expansion coefficients are found to be $\alpha_a=105.4\times10^{-6}$K⁻¹, $\alpha_v=32.3\times10^{-6}$K⁻¹, $\alpha_c=-98.1\times10^{-6}$K⁻¹ and $\alpha_{\text{v}}=39.6\times10^{-6}$K⁻¹ respectively. These values are comparable to those reported for the highly anomalous thermal expansion cyanides[3, 7, 16] like AgC₃N₅, Ag₃Co(CN)₆, ZnAu(CN)₃ etc. The quasi-harmonic approximations has been proven very good for studying the NTE materials like[2, 12, 24, 28, 29] LiAlSiO₄, V₂O₃, MCN (M=Ag, Cu, Zn), and ZnAu(CN)₃. The compound AgC₃N₅ may be very useful for strong armour applications due to its anomalous lattice behaviour.

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**TABLE I.** The experimental unit cell volume per atom, density and linear thermal expansion coefficients ($\alpha_l$) at 300K of metal cyanides from literature. The values of $\alpha_l$($l=a, b, c$) for AgC₃N₅ are obtained from our ab-initio calculations.

| Compound | V/atom (Å³) | Density (g/cm³) | $\alpha_a \times 10^4$ K⁻¹ | $\alpha_b$ | $\alpha_c$ |
|----------|-------------|----------------|--------------------------|---------|---------|
| AgCN[36] | 13.6        | 4.07           | 66                       | 66      | -24     |
| AgC₃N₅[16] | 15.5       | 2.63           | -48                      | 200     | -54     |
| AgC₃N₅     | 16.3        | 2.00           | 105                      | 32      | -98     |
| Ag₃Co(CN)₆[3] | 19.1       | 2.93           | 132                      | 132     | -130    |
| ZnAu(CN)₃[4] | 19.3      | 4.37           | 37                       | 37      | -58     |
| KMnAg₃(CN)₆[23] | 19.8   | 2.83           | 61                       | 61      | -60     |

**TABLE II.** The comparison of calculated and experimental lattice parameters of AgC₃N₅.

| Optimization Scheme | a (Å) | b (Å) | c (Å) | V (Å³) |
|---------------------|-------|-------|-------|--------|
| DFT-GGA (0K)        | 12.46 | 15.91 | 32.27 | 6392   |
| DFT-GGA+ vdW (0K)   | 12.26 | 13.25 | 32.61 | 5297   |
| Experimental (300K) | 12.43 | 13.62 | 32.30 | 5466   |
FIG 1 (Colour online) (Top) The crystal structure of AgC$_8$N$_5$ containing AgN$_4$ (Blue) tetrahedra connected through C (Red) and N (Green) atoms. (Bottom) The calculated displacement pattern giving rise to negative linear compressibility along c-axis of AgC$_8$N$_5$. The arrow represents the displacement vector for Ag as obtained from the difference in atomic coordinates of all the atoms corresponding to ambient pressure and 4 GPa structure.

FIG 2 (Colour online) The calculated pressure dependence of lattice parameters ($l$), bond lengths and total energy/atom for AgC$_8$N$_5$.

FIG 3 (Colour online) The calculated total and partial phonon density of states for various atoms of AgC$_8$N$_5$.

FIG 4 (Colour online) (a) The calculated energy dependence of anisotropic Grüneisen parameters, $\Gamma$ for AgC$_8$N$_5$. (b) The contribution of phonon mode of energy $E$ to the linear thermal expansion coefficients. (c, d) The calculated temperature dependence of linear thermal expansion coefficients and lattice parameters of AgC$_8$N$_5$.

FIG 5 (Colour online) The displacement pattern of optic phonon modes projected in a-b plane of AgC$_8$N$_5$. The arrow represents the displacement vector for Ag atoms. The displacement vectors for C and N atoms are negligible and are not shown for clarity.
