New insights into the compressibility and high-pressure stability of Ni(CN)$_2$: a combined study of neutron diffraction, Raman spectroscopy, and inelastic neutron scattering

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Abstracts
Nickel cyanide is a layered material showing markedly anisotropic behaviour. High-pressure neutron diffraction measurements show that at pressures up to 20.1 kbar, compressibility is much higher in the direction perpendicular to the layers, c, than in the plane of the strongly chemically bonded metal-cyanide sheets. Detailed examination of the behaviour of the tetragonal lattice parameters, $a$ and $c$, as a function of pressure reveal regions in which large changes in slope occur, for example, in $c(P)$ at 1 kbar. The experimental pressure dependence of the volume data is fitted to a bulk modulus, $B_0$, of 1050 (20) kbar over the pressure range 0–1 kbar, and to 124 (2) kbar over the range 1–20.1 kbar. Raman spectroscopy measurements yield additional information on how the structure and bonding in the Ni(CN)$_2$ layers change with pressure and show that a phase change occurs at about 1 kbar. The new high-pressure phase, (Phase PII), has ordered cyanide groups with sheets of $D_{4h}$ symmetry containing Ni(CN)$_4$ and Ni(NC)$_4$ groups. The Raman spectrum of phase PII closely resembles that of the related layered compound, Cu$_{1/2}$Ni$_{1/2}$(CN)$_2$, which has previously been shown to contain ordered C≡N groups. The phase change, PI to PII, is also observed in inelastic neutron scattering studies which show significant changes occurring in the phonon spectra as the pressure is raised from 0.3 to 1.5 kbar. These changes reflect the large reduction in the interlayer spacing which occurs as Phase PI transforms to Phase PII and the consequent increase in difficulty for out-of-plane atomic motions. Unlike other cyanide materials e.g. Zn(CN)$_2$ and Ag$_3$Co(CN)$_6$, which show an amorphization and/or a decomposition at much lower pressures (~100 kbar), Ni(CN)$_2$ can be recovered after pressurising to 200 kbar, albeit in a more ordered form.

Keywords: neutron diffraction, crystallographic aspects of phase transformations, neutron inelastic scattering, Raman spectroscopy, phonons in crystal lattice

(Some figures may appear in colour only in the online journal)
I. Introduction

Metal cyanides, formed by linking together M(C≡N)n building blocks, can exhibit 1-, 2- and 3 dimensional (D) structures. Disorder of carbon (C) and nitrogen (N) atoms within the C≡N groups is common, as both these atoms can occupy the same crystallographic positions due to their similar size and coordination preferences. For example, at ambient pressure, Zn(CN)2, which is constructed from corner sharing Zn(CN)2−(NC)1 tetrahedra, possesses a 3D structure with cubic symmetry which can be described in either space group Pn-3m (for a model with C/N disorder) [1–3] or P43m (for an ordered model) [4]. AgCN and AuCN consist of linear [M(C≡N)M−] chains, again with head-to-tail disorder in the cyanide groups, packed into 3D hexagonal structures [5, 6]. Nickel cyanide, Ni(CN)2, however, has a layered structure which is formed from linked square-planar Ni(CN)4−(NC)2 units, with long-range order only in two dimensions (within the a-b plane) and no true periodicity along c [7–9]. Due to the 2D nature of Ni(CN)2, it has been proposed as an inorganic analogue of graphene, and is predicted to form nanotubular structures [10]. It is known to form intercalates and clathrates if molecular species are inserted between the layers [11]. The structure of one layer of Ni(CN)2 is shown in figure 1(a), and the spatial relationship between adjacent layers is shown in figure 1(b).

The analysis of the powder x-ray diffraction data indicates that at ambient pressure the compound crystallizes with a tetragonal unit cell with a = 4.857 Å and c = 12.801 Å [7]. Ni(CN)2 exhibits anomalous thermal expansion over the temperature range 28–300 K [7]. The thermal expansion coefficient is found to be negative within the two-dimensionally connected sheets (in the a-b plane, αa = −6.5 × 10−6 K−1) and has a high positive value perpendicular to the sheets (αc = 61.8 × 10−6 K−1). The net result is an overall positive volume thermal expansion coefficient (αV = 48.5 × 10−6 K−1).

In a previous study, we explored the origins of the thermal expansion behaviour of Ni(CN)2 by measuring the temperature dependence of the phonon spectra using inelastic neutron scattering [3]. The results were analysed and interpreted using \textit{ab initio} calculations. It was found that the experimental phonon spectra of Ni(CN)2 do not show any significant temperature dependence, and the phonon modes of energy ~2 meV are the principal contributors to the negative thermal expansion (NTE) observed within the Ni(CN)2 layers. At 1 bar, the interactions between the layers appear to be weak but not entirely negligible since no soft modes are observed in the phonon spectra. These interlayer interactions might be expected to increase on application of pressure and the layered nature of the material makes it a suitable candidate for studying anisotropic compression with pressure. Thus high-pressure neutron diffraction experiments, along with inelastic neutron scattering and Raman measurements were carried out to understand the structural and dynamical behaviour of Ni(CN)2 and gain new insights into its compressibility and stability under pressure.

II. Experimental details

A polycrystalline sample of Ni(CN)2 was prepared by heating Ni(CN)2.3H2O (sold by Alfa Aesar as Ni(CN)2.4H2O) under vacuum at 473 K for 48 h. Powder x-ray diffraction and IR spectroscopy showed that the hydrated nickel cyanide had been completely converted to anhydrous nickel cyanide and that Ni(CN)2 was the only crystalline phase present. The resulting yellow powder was stored in a sealed glass ampoule prior to use, to prevent rehydration.

Neutron powder diffraction data for Ni(CN)2 were measured at room temperature under pressures of up to 20.1 kbar using the high-flux D20 diffractometer [12] at the Institut Laue-Langevin (ILL), France. Low-pressure measurements (up to 2.7 kbar) were performed under hydrostatic conditions in a gas pressure cell, with argon gas as the pressure-transmitting medium, using neutrons of wavelength of 1.12 Å. For high-pressure measurements a Paris-Edinburgh (P-E) device [13] was employed using neutrons of wavelength of 2.41 Å. The sample, mixed with Pb metal as the pressure manometer, was loaded into an encapsulated Ti-Zr gasket filled with a 4:1 mixture of methanol-ethanol as the pressure medium, before pressing in the P-E device. The structural refinements were performed on the neutron diffraction data using the Rietveld refinement program FULLPROF [14]. In all the refinements, the background was defined by a sixth-order polynomial in 2θ. A Thompson-Cox-Hastings pseudo-Voigt function with axial divergence asymmetry was chosen to define the profile shape for the neutron diffraction peaks.

Room-temperature Raman spectroscopy measurements at high pressure were carried out on the polycrystalline sample of Ni(CN)2 in a diamond anvil cell (Diaccell B-05) fitted with culets of 400 microns diameter, with a 4:1 methanol-ethanol mixture as the pressure-transmitting medium. It is important to notice that methanol-ethanol mixture is not hydrostatic in the entire region of investigation up to 200 kbar; it remains hydrostatic up to 105 kbar beyond which the medium solidifies and becomes non-hydrostatic [14]. At 200 kbar, the non-hydrostaticity is expected to be of about 20 kbar. The pressure was measured using the ruby fluorescence technique. The sample was excited using a 532 nm excitation from a diode-pumped, frequency doubled solid-state laser with a power of ~15 mW. Scattered light was analysed using a home-made 0.9 m single monochromator, coupled with an edge filter and detected by a cooled CCD. Thus, Raman data could not be collected between 0 and 1 kbar, due to the low accuracy of pressure determination in this pressure range.

Inelastic neutron scattering measurements were carried out at pressures up to 2.7 kbar on Ni(CN)2 using the cold neutron, time-of-flight, time-focusing spectrometer, IN6, at the Institut Laue-Langevin (Grenoble, France) operating with an incident neutron wavelength λi = 5.12 Å (Ei = 3.12 meV), with a resolution of 80 μeV at the elastic line. About 7 grams of the polycrystalline sample of Ni(CN)2 were compressed using argon in
In order to measure the temperature dependence of 
\[ \frac{\partial \ln E}{\partial P} \left( = \frac{\Gamma i}{E i} \right) \] (where \( \Gamma i \), \( E i \), \( P \) and \( B \) are Grüneisen parameters, phonon energy, pressure and bulk modulus, respectively), the inelastic neutron scattering data of Ni(CN)\(_2\) were collected at 200 and 300 K at a number of pressures up to 2.7 kbar. The measurements were first performed at 300 K, and the data were collected at 1 bar and 0.3, 1.9, and 2.7 kbar. After completing the measurements at 2.7 kbar, the pressure was released to ambient conditions. The temperature was then decreased to 200 K, and similar measurements were performed at the same pressures. The inelastic neutron scattering data were averaged over a scattering angle range of 10° to 113° and corrected for the contributions from argon at the respective pressures and for the background (including empty-cell measurements). A standard vanadium sample was used to calibrate the detectors. The data reduction and treatment were performed using standard ILL software tools. The neutron cross-section weighted phonon densities of states were extracted from the measured scattering function, \( S(Q, E) \), using the incoherent approximation [15], in similar way as in a previous work [3].

### III. Results and discussion

#### III.A. High-pressure neutron diffraction study

Figure 2(a) shows the neutron diffraction pattern of Ni(CN)\(_2\) in a vanadium sample holder at ambient conditions. The diffraction pattern contains a mixture of sharp and broad peaks. The presence of well-defined sharp peaks reveals information about the periodic nature of the material; however, the broadening of certain reflections indicates stacking disorder. Similar diffraction patterns have been reported previously in other publications [7, 8].

Figure 2(b) shows the pressure evolution of the diffraction patterns of Ni(CN)\(_2\) in the gas pressure cell up to a pressure of 2.7 kbar. The diffraction patterns contain contributions from the sample and the aluminium (Al) container (marked with arrow). The anisotropic nature of the compressibility of Ni(CN)\(_2\) is revealed by the separation of reflections which are coincident at ambient pressure. For example, above 1.2 kbar, the peaks with indices (3 0 0), (3 0 1), (2 0 6) and (0 0 8) at around \( Q = 4 \) Å\(^{-1}\), separate. The separation is due to the easier compressibility in the \( c \) direction as confirmed by the shift in the (103/004) reflection at \( Q = 2 \) Å\(^{-1}\) to a higher \( Q \) value on application of pressure.

The maximum pressure achievable in the gas pressure cell is about 2.7 kbar. Further measurements at higher pressures were carried out using a Paris–Edinburgh (P–E) device. In addition, some of the measurements, below 2.7 kbar, were also repeated in the P–E device and the results are in good agreement with those from the gas pressure cell. Figure 2(c) shows the evolution of the neutron diffraction patterns of Ni(CN)\(_2\) in the P–E device. Peak shifts become even more obvious over this greater pressure range. In particular, above 0.5 kbar, the (004) reflection, at around \( Q = 2 \) Å\(^{-1}\), moves towards higher \( Q \) values. We notice also that the intensity of the peaks decreases with increasing pressure.
Although the presence of a large number of stacking faults in Ni(CN)$_2$ precludes the determination of accurate atomic parameters, the variation of the lattice parameters with pressure can be determined from the diffraction data using Le Bail fitting. The quality of the fitting of the diffraction data is good (figure 3). This method of obtaining the lattice parameters was shown to be reproducible by carrying out the fitting using data sets in successive cycles of increasing and decreasing pressure cycle.

Figure 4 depicts the evolution of the lattice parameters extracted from the refinement of the high-pressure diffraction data, collected using both the gas pressure cell and the P–E device. The value of the $a$ lattice parameter, 4.835 Å, does not show an appreciable change up to 2.7 kbar. Further increase in pressure up to 20.1 kbar, which is the maximum pressure achieved, leads to a decrease in the $a$ lattice parameter to 4.803 Å. The $c$ lattice parameter also decreases as the pressure is raised to 20.1 kbar, and does so in a number of stages. The $c$ lattice parameter first decreases slowly, up to just below 1 kbar and then falls more rapidly over the range 1 to 1.6 kbar (from 12.69 to 12.46 Å). There must be a change in the nature of the interactions between the layers because there is a
sudden and substantial change in the compressibility at 1 kbar. Lattice parameter \( c \) continues to decrease up to 20.1 kbar (11.55 Å). The pressure dependence of the unit-cell volume shows a decrease over the entire pressure range of our study up to 20.1 kbar. It is notable that high-pressure Raman scattering measurements also change dramatically over the same range of pressure (see below).

Figure 4 highlights the strongly anisotropic response under pressure of the lattice parameters with the variation of the interlayer spacing, \( c \), reflecting a significantly larger axial contraction compared to the contraction in the \( a-b \) plane. In order to determine the bulk modulus at zero pressure, \( B_0 \), and its pressure derivative, \( B' \), the pressure-volume data were fitted by a third-order Birch–Murnaghan equation. A least-squares fit to the measured pressure dependence of the volume data in the range 0–1 kbar yields a bulk modulus, \( B_0 \), of 1050 (20) kbar, while over the remaining pressure range, 1–20.1 kbar, the \( B_0 \) value is 124 (2) kbar. The pressure derivative, \( B' \), was kept fixed at 4. The variation of the lattice parameters with pressure can be converted into compressibility values using the relationship: \( K_i = -\left[\ln(l - \ln l_0)/(P - P_0)\right] \), where \( l_0 \) is the lattice parameter \( l \) (\( a \) or \( c \)) at pressure \( P \), and \( l \) is the lattice parameter \( l \) at \( P_0 \). Over the pressure range 0–1 kbar, this leads to \( K_a = +2.0 \times 10^{-4} \) kbar\(^{-1} \) and \( K_c = +3.5 \times 10^{-4} \) kbar\(^{-1} \). Beyond the phase transition, over the pressure range 1–20.1 kbar, the values are \( K_a = +3.5 \times 10^{-4} \) kbar\(^{-1} \) and \( K_c = +4.5 \times 10^{-3} \) kbar\(^{-1} \). The magnitudes of \( K_a \) and \( K_c \) are comparable to those reported recently for layered silver(I) tricyanomethanide, although the latter material shows negative compressibility in two dimensions on application of pressure [16].

For a proper understanding of the properties of the materials, the structural information, as obtained from diffraction techniques, should be supplemented and supported by other techniques. Inelastic neutron scattering offers a unique opportunity to reach a comprehensive conclusion on the dynamics. With this aim in mind, we performed Raman spectroscopy measurements and high-pressure inelastic neutron scattering experiments, which are discussed in the following sections.

**III. B. High-pressure Raman scattering measurements**

Figure 5 shows the pressure evolution of the Raman spectra of Ni(CN)\(_2\) up to ~200 kbar. At 1 bar, for Phase PI, the bands at ~2200 cm\(^{-1}\) correspond to C≡N stretching modes and bands in the region 200–650 cm\(^{-1}\) comprise Ni–CN/NC bending modes together with Ni–CN=N stretching modes. On increasing the pressure from ambient to 1 kbar, dramatic changes are observed in all regions of the Raman spectra which indicate that a phase transition has occurred. These changes include a large decrease (of about 40 cm\(^{-1}\) ) in the C≡N stretching-mode frequencies (red shift) (Figure 5(b)), accompanied by an increase in separation of the two principal peaks and a reduction in their FWHM. In the low energy portion of the Raman spectrum, the relative intensities of the bands at ~275 cm\(^{-1}\) and ~330 cm\(^{-1}\) comprise Ni–C=N bending modes together with Ni–C=N=N stretching modes. With this aim in mind, we performed Raman spectroscopy measurements and high-pressure inelastic neutron scattering experiments, which are discussed in the following sections.

After releasing the pressure from 200 kbar, the Raman spectrum of the recovered sample was measured at ambient pressure. The spectrum resembles those observed at 1–3 kbar, indicating that Phase PII has formed and that it is stable at 1 bar. It is notable that, in contrast to other cyanide materials, e.g. Zn(CN)\(_2\) and Ag\(_2\)Co(CN)\(_6\) [18, 19] which show an amorphization and/or a decomposition at much lower pressures
Ni(CN)\(_2\) can be recovered after pressurizing to 200 kbar, albeit in a more ordered form. An interesting observation is that when the pressure is only raised as far as 4 kbar (figure 5(c)), Phase PII is formed, which then reconverts to Phase PI on the release of pressure back to 1 bar. Presumably in the initial transformation of PI to PII, defects remain and conversion is not wholly complete.

The spectra (figure 5) were fitted to Lorentzian line shapes to yield a good fit to determine the mode frequency, full width at half maximum (FWHM) and integrated intensity for each mode. It may be noted that during spectral analysis we have adopted the standard strategy to use the minimum number of peaks that yield a good fit to obtain peak centers. This procedure was followed consistently for all pressures. The pressure dependence of the Raman shifts of the modes are shown in figure 6. The variation of FWHM of the most intense mode (2215 cm\(^{-1}\) at 1 bar) in the C≡N stretching region as a function of pressure is shown in figure 6(c). Errors from different experimental runs are less than 10% of the FWHM of the Lorentzian. There is a sharpening of C≡N stretching modes across the first transition on increasing the pressure from ambient to 1 kbar (figure 6(c)).

The PI to PII phase change on application of pressure can be ascribed to a change in C≡N order within the nickel-cyanide layers. In the monometallic transition-metal cyanides so far studied, definitive results, available for example in the cases of Zn(CN)\(_2\) [1], CuCN [20, 21], AgCN [6] and AuCN [5], reveal that in the normal forms prepared at atmospheric pressure there is head-to-tail cyanide disorder. Thus it is reasonable to suppose that head-to-tail cyanide disorder also occurs in Ni(CN)\(_2\) in its low-pressure form, Phase PI, and this is supported by the Raman spectrum (vide infra). The strongest interactions, i.e. chemical bonds, occur within the nickel-cyanide layers and it is changes in the chemical bonding within the layers that have the greatest effect on the vibrational states that are sampled using Raman spectroscopy. Interactions between layers will slightly perturb these vibrational frequencies and may be expected to become more important as pressure increases. Thus the large changes which occur in the Raman spectrum at

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**Figure 5.** Room-temperature Raman spectra of Ni(CN)\(_2\) at various pressures in the region of (a) the Ni–CN/NC–Ni bending and Ni–C/ Ni–N stretching and (b) the C≡N stretching modes (note: The Raman spectra labelled ‘p-released’ are measured at ambient pressure after releasing the pressure from 200 kbar). (c) The Raman spectra of a fresh sample of Ni(CN)\(_2\) after compression up to 4 kbar, followed by decompression to ambient pressure.
about 1 kbar, a relatively low pressure, are ascribed to changes in bonding within the nickel-cyanide layers. The sharpening of the $\nu$($C\equiv N$) bands at $\sim$2200 cm$^{-1}$ is ascribed to the formation of layers in which the cyanide groups are ordered. Possible ordering schemes within Ni(CN)$_2$ layers, which may be applicable to Phase PII, have been discussed by Mo and Kaxiras [10], who, in their work on metal-cyanide nanotubes, determined the energies of individual nickel-cyanide sheets for three different ordered arrangements (figure 7). Density functional theory (DFT) calculations found that the sheet...
Figure 8. Room temperature Raman spectra of Ni(CN)\(_2\) (Phase PI) (black line) and Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) [22] (blue line) at ambient pressure. Note the similarity of the spectrum of Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) to that of Ni(CN)\(_2\) at 1 kbar (Phase PII) (red line).

Figure 9. Pressure dependence of the phonon spectra of Ni(CN)\(_2\) from inelastic neutron scattering measurements using the IN6 spectrometer at 200 K (left) and 300 K (right).

of C\(_{2v}\) symmetry assembled from cis-Ni(CN)\(_2\)(NC)\(_2\) units lies lowest in energy. The D\(_{4h}\) sheet built from Ni(CN)\(_4\) and Ni(NC)\(_4\) units has a slightly higher calculated energy (0.07 eV per Ni(CN)\(_2\) unit) than the cis-Ni(CN)\(_2\)(NC)\(_2\) modification whilst the D\(_{3h}\) sheet containing trans-Ni(CN)\(_2\)(NC)\(_2\) units has the highest calculated energy (0.17 eV per Ni(CN)\(_2\) unit above the cis form). As we show below, it is the D\(_{4h}\) sheet structure which forms at about 1 kbar (Phase PII). It should be noted that the calculated relative energies [10] are for individual sheets, whereas in the solid, the interactions between sheets may be sufficient to change the energy order of the three different forms. There is clearly a significant change in the interactions between the layers on going from phases PI to PII as seen in the large change in the c lattice parameter (figure 4).

Although there are no known examples of M(CN)\(_2\) sheets containing M(CN)\(_2\)(NC)\(_2\) units, there is a recently reported example containing M(CN)\(_4\) and M(NC)\(_4\) units [22]. The copper-nickel cyanide, Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\), is isostructural with Ni(CN)\(_2\) with both metal centres having square-planar coordination, but has been shown unequivocally to contain ordered Ni(CN)\(_4\) and Cu(NC)\(_4\) groups within the M(CN)\(_2\) layers to form sheets with D\(_{4h}\) symmetry [22] (figure 1(a)). Comparison of the Raman spectrum of Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) with those found for the PI and PII forms of Ni(CN)\(_2\) (figure 8) is highly suggestive that pressure has induced a phase transition in Ni(CN)\(_2\) in which a disordered layer transforms to one with D\(_{4h}\) symmetry. The clear splitting of the two ν(C≡N) Raman active stretches and the low-energy region in the Raman spectrum of Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) bear very close resemblance to the features seen for Ni(CN)\(_2\) in its PII form. The spectra of PII and Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) also show an absence of modes in the region 550–650 cm\(^{-1}\), which are seen for Ni(CN)\(_2\) in its PI form.

Group theoretical analysis of the three sheets shown in figure 7 predicts for the C\(_{2v}\) structure: 12 Raman active bands (3A\(_1\) + 3A\(_2\) + 2B\(_1\) + 4B\(_2\)); for the D\(_{3h}\) structure: 12 Raman active bands (4A\(_g\) + 4B\(_{1g}\) + 2B\(_{2g}\) + 2B\(_{3g}\)); and for the D\(_{4h}\) structure: 8 Raman active bands (2A\(_{1g}\) + 2B\(_{1g}\) + 2B\(_{2g}\) + 2E\(_g\)). For an isolated Ni(CN)\(_2\)\(^{-}\) unit with D\(_{4h}\) symmetry [23], 7 Raman active bands are predicted (2A\(_{1g}\) + 2B\(_{1g}\) + 2B\(_{2g}\) + E\(_g\)). Using the relative positions and intensities from the Raman spectrum of this isolated unit, six bands for Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) and hence Ni(CN)\(_2\)-PII can be assigned as shown in figure 8. A very weak peak seen at ~400 cm\(^{-1}\) in PI and Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) probably arises because of the loss of the centre of symmetry when the layers are stacked together. It is notable that a very intense band with E\(_g\) symmetry is predicted at ~400 cm\(^{-1}\) in the Ni(CN)\(_2\)\(^{-}\) unit [22]. The remaining two bands, B\(_{3g}\) (predicted for the isolated unit to be at 109 cm\(^{-1}\)) [23] and the additional e.g. (predicted when the square-planar units are connected into a D\(_{4h}\) sheet) might be expected to lie below 200 cm\(^{-1}\) and hence are not observed. It is difficult to reconcile the observed Raman spectrum with the group theoretical predictions for the C\(_{2v}\) and D\(_{4h}\) structures.

Pressure-induced ordering of C≡N groups has been observed previously. For example, Zn(CN)\(_2\) undergoes a phase transition at about 10 kbar from a cubic to an orthorhombic structure [17, 24], and it has been suggested that this orthorhombic phase is likely to show CN ordering, unlike the ambient-pressure phase [1]. In addition, over the pressure range 0–1200 kbar in the Prussian Blue analogue,
K$_3$Fe$_4$(Cr(CN)$_6$)$_{2.8}$H$_2$O, in which Cr$^{III}$–CN–Fe$^{II}$ linkages isomerise to the Cr$^{III}$–NC–Fe$^{II}$ form [25]. This isomerization is reversible on releasing the pressure when low pressures are applied, but after pressing at ~12 kbar, a metastable phase is formed which does not re-isomerise to the original form.

**III.C. High-pressure inelastic neutron scattering measurements**

The phonon spectra of Ni(CN)$_2$, measured at ambient pressure, 0.3, 1.5 and 2.7 kbar, at 200 K and 300 K are shown in figure 9. The large amount of scattering from the high-pressure cell only allowed measurement of the phonon spectra up to 40 meV. The spectra consist of broad peaks centred on 7, 9, 17, 21 and 30 meV. The intensity of the broad peaks decreases and the peaks below 20 meV shift significantly towards higher energies with increasing pressure; the others do not change by a significant amount. These observations are consistent with our previous assignment of these low-energy modes to motions involving out-of-plane atomic motions [3].

These motions become more constrained under pressure as the layers are squeezed together.

Our previous ab-initio calculations [3] for Ni(CN)$_2$ show that the contributions from Ni atoms extend up to 75 meV, while C and N atoms contribute in the whole phonon spectra range up to 280 meV. The Ni atoms provide the main contribution to the low-energy phonon spectra up to 40 meV. It is found that all the modes shift towards higher energies as pressure increases. This is what would be expected for compounds exhibiting positive thermal expansion behaviour. The experimental data (figure 9) allow extraction of the mode Grüneisen parameters $\Gamma / B = (\partial \ln \Theta / \partial \ln P)$ (where $B$, $\Theta$ and $P$ are the bulk modulus, phonon energy and pressure, respectively). As shown in figure 9, the Grüneisen parameters, as extracted for Ni(CN)$_2$, from the pressure dependence of the phonon spectra (0 to 2.7 kbar) at 200 K and 300 K, are found to have significantly different values. The difference seems to be significant in the low-energy region below 10 meV.

We have previously reported [26] high-pressure inelastic neutron scattering measurements of Zn(CN)$_2$ up to 2.8 kbar at 165 K and 225 K. In contrast to Ni(CN)$_2$, the Grüneisen parameters for Zn(CN)$_2$, as extracted from the high-pressure data up to 2.8 kbar, were found to be very similar at 165 and 225 K (figure 10) illustrating that although the two cyanide materials both contain M–C≡N–M units, the way that these are further connected has a profound effect on the lattice dynamics and their pressure and temperature dependence.

The volume thermal expansion coefficient, $\alpha_V$, for Ni(CN)$_2$ is $48.5 \times 10^{-6}$ K$^{-1}$, while Zn(CN)$_2$ has an isotropic NTE coefficient, $\alpha_V$, of $-51 \times 10^{-6}$ K$^{-1}$. Although the signs of the volume thermal expansion coefficients for the two compounds are different, the values have similar magnitude, $|\alpha_V|$ ~ $50 \times 10^{-6}$ K$^{-1}$ and hence the average values of $\Gamma'(\Theta)/\Theta$ are expected to be nearly the same in both compounds. However, on comparing $\Gamma'(\Theta)/\Theta$ for both compounds (figure 10), it can be seen that $\Gamma'(\Theta)/\Theta$ for Ni(CN)$_2$ has twice the magnitude of...
CN stretching modes soften by about 50 cm\(^{-1}\) in the neutron diffraction pattern of Ni(CN)\(_2\). This is despite the fact that ordering produced only very small changes in the powder neutron diffraction measurements, with values of about 1 kbar. Yet further evidence of a phase transition at moderate pressure is the change in the slope of the lattice parameters, as well as in the variation of the \(\Gamma(E)/B\) obtained from the two different pressure regimes are found to differ significantly.

The neutron diffraction experiments we report here. For Ni(CN)\(_2\), our measurements (figure 11) show a change in the neutron diffraction pattern occurring on CN ordering is extremely small. The changes occurring in the diffraction patterns on CN ordering in Ni(CN)\(_2\) with stacking disorder, the situation here, will be even smaller, and certainly too small to be observed in the neutron diffraction experiments we report here. For Ni(CN)\(_2\), Raman spectroscopy, combined with monitoring changes in lattice parameters rather than monitoring changes in diffraction intensities, provide the appropriate techniques to monitor phase changes occurring as a function of pressure.

IV. Conclusions

In summary, we report the high-pressure evolution in the structure and dynamics of Ni(CN)\(_2\) using a combination of neutron diffraction, inelastic neutron scattering and Raman spectroscopy.

That the powder diffraction pattern of Ni(CN)\(_2\) does not change drastically at moderate pressures and that the inter-layer spacing of Ni(CN)\(_2\) above 1kbar is similar in value to that measured for the recently characterised compound, Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\) (at 1 bar) [22], provides compelling evidence for retention of the simple layered structure under these conditions. A change in geometry around some or all of the nickel from square planar to tetrahedral on application of pressure would be accompanied by significant changes in the diffraction pattern, rather than the gradual evolution of the pattern and the lattice parameters as observed here. Indeed polymorphs of ZnNi(CN)\(_4\) which contain tetrahedral Zn(NC)\(_4\) square-planar Ni(CN)\(_4\) units and consequently have 3D framework structures have very different diffraction patterns [27, 28].

Overall, the response of the lattice parameters of Ni(CN)\(_2\) to applied pressure is strongly anisotropic with a significantly larger contraction occurring along the c axis than in the a-b plane. This behaviour is as a result of the existence of strong chemical bonding within the Ni(CN)\(_2\) layers, parallel to the a-b plane (the relatively incompressible part of the structure), and no chemical bonding between the layers. Above 1 kbar, the diffraction measurements show a change in the slope of the variation of the c lattice parameter with pressure, which is the signature of a phase transition. From high-pressure Raman measurements and, by comparison with, Cu\(_{1/2}\)Ni\(_{1/2}\)(CN)\(_2\), we ascribe this phase transition (Phase PI to Phase PII) to a change in CN ordering within the nickel-cyanide layers with retention of square-planar coordination around nickel.

The pressure dependence of the phonon spectra of Ni(CN)\(_2\) from the inelastic neutron scattering measurements, also highlights the occurrence of the pressure-induced phase transition, PI to PII, at about 1 kbar and supports the conclusion from our previous work [3] that motions perpendicular to the layers are major contributors to the density of states at low energies.

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