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LETTER

A high-pressure micro-Raman spectroscopic study of copper cyanide, CuCN

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Introduction

There has been growing interest in materials that exhibit negative thermal expansion properties [1]. The largest magnitudes described so far involve metal cyanide complexes such as Prussian Blue analogues in which metal atoms at the corners of cubes are linked by cyanide groups along the edges [2–4], and the interpenetrating tetrahedral (diamond-like) lattices of zinc, and cadmium cyanides [5–10]. Although the same atomic sequence M–C–N–M occurs in the cyanides of copper, silver, and gold, these compounds do not form a three-dimensional lattice but consist of infinite chains in the solid state [11–14]. Furthermore, the structure of copper cyanide is polymorphic with a low-temperature (LT-CuCN) form that transforms irreversibly to a second form (high-temperature; HT-CuCN) upon heating above 550 K. In LT-CuCN, the infinite chains are not linear and show a wave-like structure, whereas HT-CuCN is linear. The chain structures are disordered with respect to the carbon and nitrogen atom positions [15].

The negative thermal expansion arises from thermally activated transverse vibrations of the M–C–N–M groups, which increase in amplitude with increasing temperature leading to a decrease in the M…M distance. In chain systems, the transverse cyanide vibrational modes would shorten the unit cell in one direction and lengthen it in another, causing an anisotropic thermal expansion. In the case of HT-CuCN, the X-ray diffraction measurements of the trigonal unit cell dimensions as a function of temperature showed that a normal positive increase occurs along the *a*-axis and there is a small decrease along the *c*-axis of the unit cell [12].

A property of particular interest for negative thermal expansion materials is the mode Grüneisen parameter, γ_i, which represents the volume dependence of the mode frequency and can be written as $B_0 \mathrm{d}(\ln(\nu_i))/\mathrm{d}P$, where B_0 is the bulk modulus. A negative value of a mode Grüneisen parameter is shown by a negative value of the pressure dependence of the vibrational frequency and this provides a method of determining which vibrational modes contribute to the negative thermal expansion.

Experimental

Copper cyanide was purchased from Alfa Aesar (Ward Hill, MA, USA) as a white powder with a very faint greenish tinge and was used without further treatment. Raman spectra were measured with a Renishaw inVia Raman spectrometer using the 514.5 nm excitation line from an argon ion laser. The spectra were curve-fitted using the WiRE 2.0 software package by Renishaw. The samples were contained in a 300-µm hole drilled into stainless steel gasket mounted in a commercial diamond anvil cell from High Pressure Diamond Optics, Tucson, AZ, USA. The pressure was determined by the ruby fluorescence method [16]. Photo-acoustic infrared (PAIR) spectra were recorded using a Bio-Rad FTS6000 spectrometer equipped with a MTEC 300 PA detector in rapid scan mode at 4 cm^{-1} resolution.

Results and discussion

Previous work has shown that the vibrational spectra of LT-CuCN and HT-CuCN are identical [12] and consist of

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peaks at 183 and 320 cm^{-1}, assigned as the Cu–C–N–Cu bending motions, at 593 cm^{-1} assigned as the Cu–C/N stretch, and the very strong C–N stretching peak at 2171 cm^{-1} [17]. In this study, the Cu–C–N–Cu bending region of the Raman spectrum was resolved into three peaks, namely 315, 326, and 358 cm^{-1}, and the C–N stretch, which is slightly asymmetric, can be fitted as two peaks at 2169 and 2175 cm^{-1}, possibly due to the symmetric and asymmetric C–N stretching modes that separate as the pressure increases. A weak broad peak at 587 cm^{-1}, observed in the infrared spectrum but not previously reported for the Raman spectrum, is assigned as the Cu–C/N stretching motion [17]. In addition, the ^{13}C^{14}N stretching mode at 2121 cm^{-1} [15] and the transverse bending motion at 184 cm^{-1} were observed in the ambient pressure spectrum. The PAIR spectrum showed peaks at 591, 2122, and 2168 cm^{-1}.

The changes in vibrational energy of all peaks with pressure were linear over the range from ambient pressure to 3.7 GPa (Figs. 1 and 2), so no pressure-induced phase transitions occur over this range. The three components of the transverse bending modes were closely spaced and merged together as the higher wavenumber peak has a negative pressure dependence. Unusually, the C–N stretching modes also exhibit a negative dependence, as does the Cu–C/N stretch at 587 cm^{-1}. The dν/dP values are given in Table 1. The mode Grüneisen parameters are given by $\gamma_i = B_0 d(\ln(\nu_i))/dP$, but the bulk modulus, B_0, of copper cyanide is not known. Hence, the pressure dependences of ln(ν_i) for each vibration (Table 1) are expressed as γ_i/B_0 and negative Grüneisen parameters occur for the 358 cm^{-1} transverse vibration and the Cu–C/N and C–N stretching modes. Since the stretching modes have lower amplitudes than bending and are less thermally accessible, these modes do not contribute significantly to the negative expansion and only the 358 cm^{-1} vibration and, probably, that at 184 cm^{-1}, are responsible for the modest contraction along the *c*-axis.

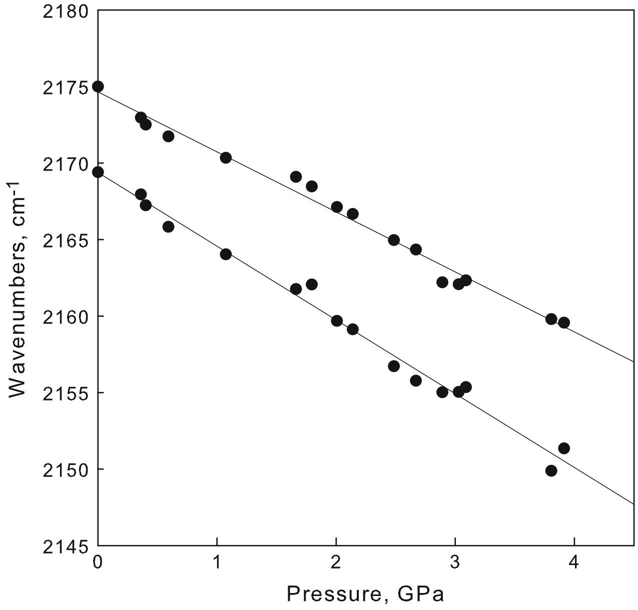

Fig. 1 Pressure dependence of the C–N stretching modes. *Lines* are least squares fits

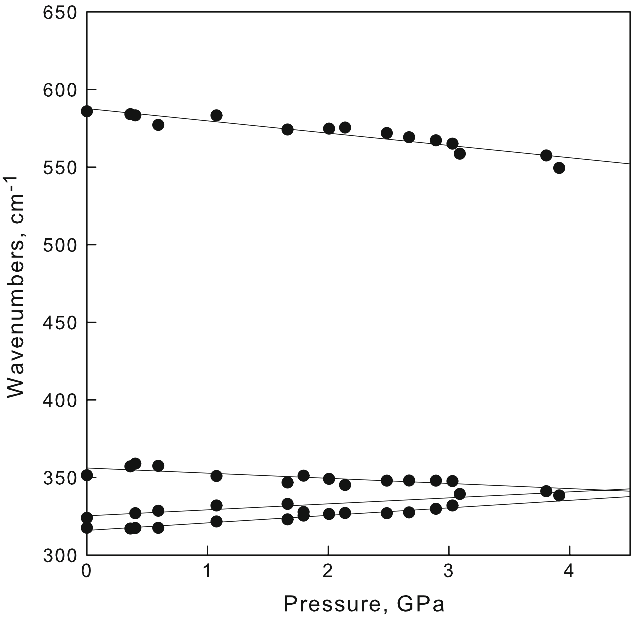

Fig. 2 Pressure dependence of the peaks in the region 300–600 cm^{-1}. *Lines* are least squares fits

Table 1 Raman wavenumbers (cm^{-1}), pressure dependence (cm^{-1} GPa^{-1}), and pressure dependence of ln(ν) (=γ_i/B_0) of copper cyanide

ν	dν/dP	$\gamma_i/B_0 \times 10^3$
315	4.9(2)	15.8(9)
326	3.9(5)	10.9(2)
358	−3.3(6)	−11.7(2)
587	−7.9(8)	−10.6(2)
2169	−4.8(1)	−2.22(1)
2175	−3.7(1)	−1.79(1)

Standard errors are given in parentheses

The local atomic arrangement, M–C–N–M, also occurs in zinc cyanide for which the pressure dependence of the Raman spectrum has been reported [9]. The spectrum [18] consists of modes at 216, 342, and 2221 cm^{-1} with dν/dP values of 4, −7.5, and 5.7 cm^{-1} GPa^{-1}, respectively. The 342 cm^{-1} peak is actually a doublet (339 and 343 cm^{-1}) and the C–N stretch dependence, dν/dP, while positive at low pressures, becomes negative above 2 GPa but there is no evidence of a phase transition at this pressure. The negative pressure dependence observed for the CN stretching mode in this study is not without precedent and might be due to backbonding from filled Cu d-orbitals to antibonding C/N π orbitals. Thus, there are strong similarities between copper and zinc cyanides both in the spectra and their pressure dependences, even though the crystal and molecular structures are so different.

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