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High-pressure behavior of the alkali cyanides KCN and NaCN

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The C-N stretching vibration has been studied in both KCN and NaCN through the combination of Raman-scattering and infrared-absorption spectroscopy. Raman and infrared data were collected on KCN up to pressures of 20 and 40 GPa, respectively, and for NaCN the pressure range was limited up to 20 GPa for both techniques. Changes in the spectra of NaCN confirm a transition to a high-pressure polymorph at approximately 12 GPa. The combination of the two optical techniques has allowed for a determination of changes in the C-N bond anharmonicity as a function of pressure. [S0163-1829(99)01726-9]

I. INTRODUCTION

The group of four alkali cyanides, NaCN, KCN, RbCN, and CsCN, represent a class of compounds exhibiting properties of both ionic and molecular crystals. These compounds crystallize in either the NaCl or CsCl structure at room temperature and zero pressure,[1] with the CN^- molecule behaving roughly as an ion intermediate in size (radius ~1.9 Å) between Cl^- and Br^- (radii of 1.81–1.96 Å).[2] In contrast to the alkali halides, however, the cyanides display a rich degree of polymorphism that is expressed by a complex phase diagram. The difference between the cyanides and halides is primarily due to the elliptically shaped CN^-, which can distort the crystal structure. In addition to interest in the alkali cyanides, the C-N bond is of general interest in a number of areas, having implications for low-compressibility materials as well as astrophysical significance.[3–5]

KCN and NaCN are two of the prominent members of the alkali-cyanide family, an extensive amount of research having been carried out on the properties of both.[1,6–8] There has also been a great deal of interest on the effects of high pressure on these materials.[9–17] At zero pressure and room temperature, both cyanides are in the plastic phase, possessing a pseudocubic structure analogous to that of NaCl. This phase is characterized by rapid reorientation of the CN^- ions; when the rotations are time averaged the CN^- ions appear spherical, which accounts for their similarity to the alkali halides. Temperature, pressure, or a combination of the two can hinder the rotations. This effectively causes the CN^- ion to become significantly elliptical, and the departure from the time-averaged spherical shape distorts the crystal structure. At zero pressure, for example, there is a transition to an elastically ordered structure occurring at 168 K for KCN and at 288 K for NaCN.[8] At room temperature KCN undergoes a first-order phase transition, with a volume reduction of 11%, to a monoclinic distortion of the CsCl structure (KCN IV) at 1.97 GPa. This high-pressure phase is best thought of as first applying a small rhombohedral stretch to the CsCl cubic cell, followed by a monoclinic distortion.[11] In this phase the CN^- ions are no longer free to rotate. NaCN has also been found to undergo structural modifications with the application of pressure. At room temperature, NaCN first transforms to an orthorhombic phase (D_{2h}^{25}) at 0.2 GPa, at approximately 4 GPa to a phase with D_{2h}^{13} symmetry, and at 12.5 GPa there is a transition to a monoclinic structure (C_s').[17]

II. EXPERIMENT

For the infrared absorption measurements, reagent grade KCN or NaCN powder (Spectrum Chemical Mfg. Co., Gardena, CA) was mixed with 0–90% KBr powder and loaded into a gasketted diamond-anvil cell. All of the infrared spectra were obtained using a liquid-nitrogen-cooled InSb detector, a globar source, and a Bruker IFS-66V Fourier-transformed infrared spectrometer. Raman spectra were obtained from pure NaCN and KCN in a gasketted diamond-anvil cell, using a Dilor OMARS 89 micro-Raman spectrometer and a liquid-nitrogen-cooled charge-coupled device detector (OMA4). All Raman spectra were obtained in the backscattering geometry using the 514-nm line from an Ar^+ laser as the excitation source, and the incident laser power on the diamond cell was typically ~1 mW. For both types of experiments, pressure was determined with the ruby fluorescence technique.[18,19] KCN, NaCN, and KBr are relatively soft; over the pressure range of this study pressure inhomogeneities were typically ~10% of the average pressure. All spectra were collected at room temperature and with a resolution of 4 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Infrared data

The CN^- fundamental vibration has a strong infrared absorption at ~2100 cm^{-1} in both KCN and NaCN. However, this coincides with the two-phonon (first overtone) absorption of the diamond anvils, which surround the sample and

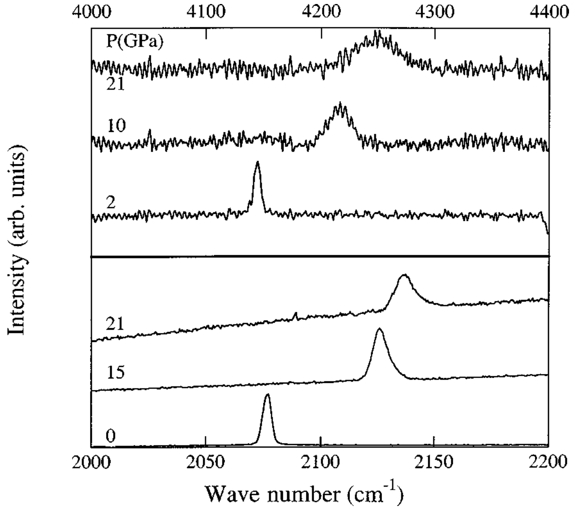

FIG. 1. Representative spectra of KCN. The bottom axis is associated with the three lower, Raman spectra (fundamental) while the upper axis is associated with the three upper, infrared spectra (first overtone).

interfere with the measurement. We were thus unable to obtain any reliable information on the fundamental vibration using infrared spectroscopy. However, we were able to obtain infrared-absorption spectra of the first overtone of the CN stretching vibration at ~4000 cm^{-1}, since it is relatively strong and is in a region where the diamonds are transparent (Figs. 1 and 2).

B. Raman data

The fundamental mode of the CN stretching vibration is also Raman active and, in the spectral region of the fundamental, Raman spectroscopy does not suffer from absorption through the diamonds as does infrared spectroscopy. Thus, measurements of the CN stretch fundamental mode were made using this technique (Figs. 1 and 2). However, due to the significant decrease in intensity of the first overtone as compared to the fundamental, we were unable to observe any Raman scattering from the first overtone.[8]

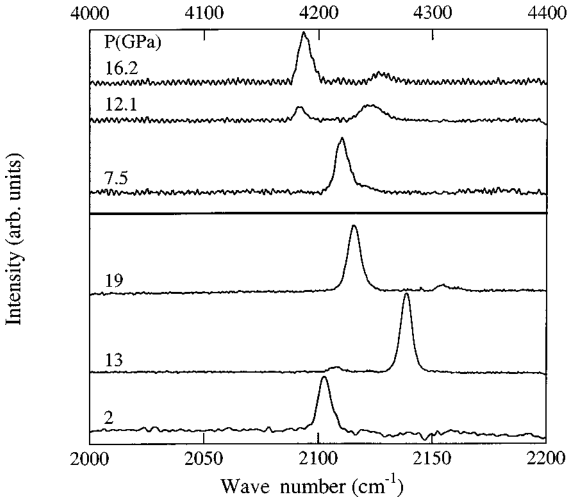

FIG. 2. Representative spectra of NaCN. The bottom axis is associated with the three lower, Raman spectra (fundamental) while the upper axis is associated with the three upper, infrared spectra (first overtone).

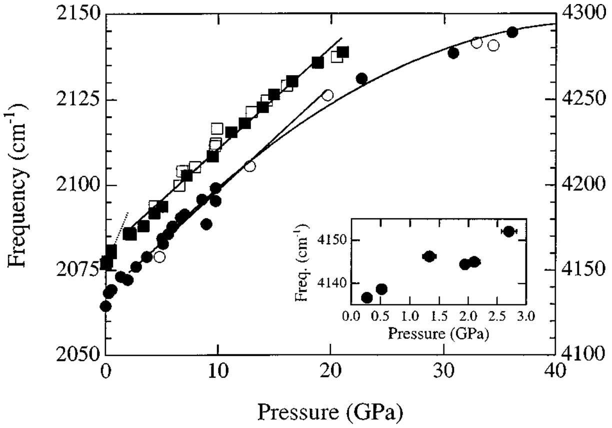

FIG. 3. The frequency shift of the fundamental (squares) and first overtone (circles) stretching CN vibration of KCN as a function of pressure. Closed symbols are on compression; open symbols on decompression. The lines are fits to the data.

C. KCN

Spectroscopy can be particularly useful in determining phase boundaries as well as providing insights about the changes in bonding and local environment of the species being probed. The frequency shift with pressure of both the fundamental mode and first overtone of the CN vibration in KCN is summarized in Fig. 3. The pressure dependence of the fundamental peak position is well fitted by two straight lines, with slopes of 7.8(±1) cm^{-1}/GPa for $P<2$ GPa and 3.0(±0.1) for $2<P<20$ GPa (Table I). The discontinuity in the peak position and the change in the pressure dependence of the fundamental at approximately 2 GPa are in good agreement with previous measurements, indicating the existence of a phase boundary between the low-pressure KCN structure and the high-pressure phase with a distorted CsCl structure (KCN IV).[12]

Over a pressure range of 0–20 GPa the frequency dependence of the first overtone can also be fit by two lines, with a break at ~2 GPa (Fig. 3). The fit to the low-pressure ($P<1.5$ GPa) data has a slope of 12(±2) cm^{-1}/GPa, and the fit to the high-pressure data ($3<P<20$ GPa) yields 6.0(±0.2) cm^{-1}/GPa. There is some nonlinearity in the region about 2 GPa, as has been noted earlier.[12] The break in the slope at ~2 GPa is consistent with the results obtained on the fundamental mode, and with the reported phase transition at this pressure.[12] Data on the first overtone were collected to a pressure of 40 GPa and clearly indicate that over this extended pressure range a linear fit is no longer adequate (Fig. 3), although a second-order polynomial can be well fit over the extended pressure range. It is possible to interpret the pressure dependence of the data from the first overtone in the high-pressure (>2 GPa) region as being composed of two linear regions, with a discontinuity in the slope at ~20 GPa. If true, this may indicate the occurrence of a transformation to another high-pressure polymorph. Additional structural data will be needed to establish if there is a transformation at ~20 GPa.

TABLE I. Mode shifts for the CN$^-$ stretch frequencies; all units are cm^{-1}/GPa.

	Fundamental		Second harmonic	
	This study	Previous study	This study	Previous study
KCN I	7.8(1)	7.2,[a] 6[b]	12(2)	
KCN IV (2–20 GPa)[c]	3.0(0.1)	5.6[b]	6.0(0.2)	
NaCN I	10.1(0.6)	10.0[d]		
NaCN (>5 GPa)	3.2(0.1)		5.1(0.4)	
NaCN (New phase)	1.2(0.1)		1.1(0.1)	

[a] Reference 12.

[b] As determined from Fig. 4 of Ref. 13, over a pressure range of 2–5 GPa.

[c] Assuming a linear fit over this pressure range.

[d] Reference 25.

Treating the CN$^-$ ion as an anharmonic oscillator and keeping the first two nonzero terms in the Taylor expansion of the potential energy gives[20]

$$V=(k/2)r^2-(g/3)r^3, \quad (1)$$

where k and g are positive constants and r is the magnitude of the atomic displacement from its equilibrium position. The energy (cm^{-1}) of the nth harmonic is then given by

$$E_n=\nu_e[(n+\tfrac{1}{2})-x_e(n+\tfrac{1}{2})^2], \quad (2)$$

where ν_e is the harmonic frequency and x_e is the anharmonicity constant. The frequency of the nth vibration (ν_n) is

$$\nu_n=\nu_e[(n+\tfrac{1}{2})-x_e(n+\tfrac{1}{2})^2]-\nu_0. \quad (3)$$

For the fundamental and the second harmonic (first overtone), this reduces to

$$\nu_1=\nu_e[1-2x_e], \quad \nu_2=\nu_e[2-6x_e]. \quad (4)$$

From the pressure dependencies of the fundamental and first overtone of the CN stretch, one can thus determine $\nu_e x_e$, as well as ν_e and x_e separately, as functions of pressure for both phases of KCN (Fig. 4). The low-pressure value for $\nu_e x_e$, 11.2(±1) cm^{-1} at $P=0$, is in good agreement with those previously reported for KCN I at zero pressure, 11.5 cm^{-1}.[8]

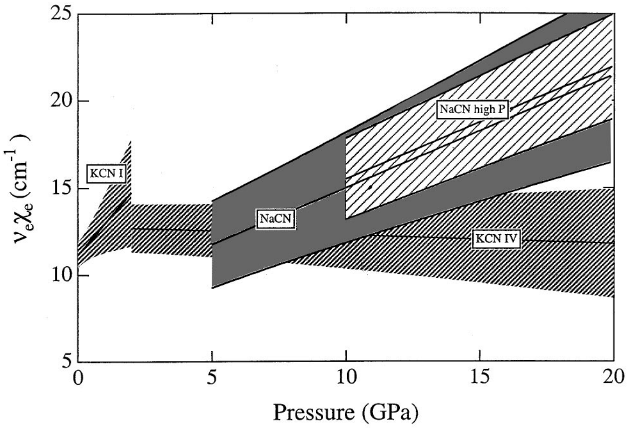

FIG. 4. The pressure dependence of the anharmonic correction ($\nu_e x_e$) for the CN potential for the two phases of KCN and NaCN.

Surprisingly, the anharmonic offset ($\nu_e x_e$) to the CN stretching frequency of KCN I increases with increasing pressure (Fig. 4). Although a decreasing anharmonic contribution is expected for matter under compression,[21,22] there has previously been little direct evidence of this expectation for specific phonon modes. In fact, in the case of hydroxyl bonds, increased anharmonicity with pressure, due to an increase in the O-H bond length, is to be expected and has been observed.[23,24] Thus, counter to what is expected in most cases, the C-N bond is becoming more anharmonic with increasing pressure from 0 to 2 GPa. As KCN transforms into KCN IV, there is a discontinuity in the anharmonic correction (Fig. 4). The decrease in the anharmonicity of the CN bond with pressure, for KCN IV, is in agreement with what one would expect for most bonds.

As pressure is increased through the transition from KCN I to KCN IV, there is a large decrease in the full width at half maximum (FWHM) of the infrared band (overtone), from ~35 cm^{-1} to under 10 cm^{-1} (Fig. 5). The large, zero-pressure FWHM is similar to previously reported values and is due to a coupling of the stretching modes with the C-N rotational bands.[8] Previous work has demonstrated that the decrease in the FWHM at low temperatures is due to a freezing out of the CN rotations.[8] We find the same to be true with increasing pressure. With increasing pressure, the rotational modes become increasingly hindered, and thus contribute less to the broadening of the vibrational mode, as probed with infrared spectroscopy.

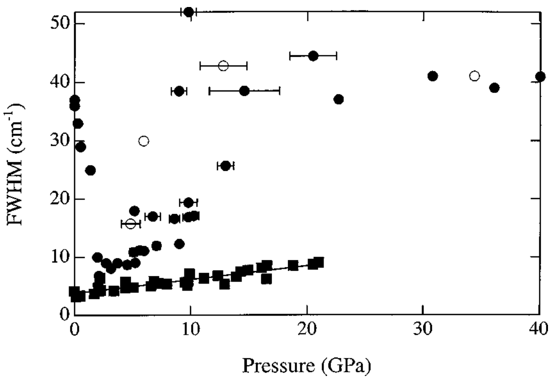

FIG. 5. The full width at half maximum (FWHM) of the Raman (squares) and infrared (circles) peaks of the CN stretch in KCN as a function of pressure. Closed symbols are on compression; open symbols on decompression.

With further compression, there is an increase in the FWHM to approximately the $P=0$ GPa value. It is difficult to conclusively determine the cause of the subsequent increase in FWHM of the first overtone. The change in FWHM observed for KCN IV may be due either to the occurrence of another phase transition at a pressure between 5–10 GPa or to increasing nonhydrostaticity. We consider the last explanation to be less plausible since we observed no significant variation in FWHM among our various experiments, which were repeated with different degrees of nonhydrostaticity (as quantified by spatial variations in ruby fluorescence spectra across the sample). Although there is presently no other evidence of a phase transition between 5 and 10 GPa (e.g., discontinuous changes in the peak positions of either the fundamental mode or the second harmonic), it is possible that the change in the FWHM may be due to an ordering transition, as has been observed in RbCN. Such a transition will result in a small, and with our resolution, undetectable shift in the peak position of the CN stretch.[8]

In contrast, there is no significant change in the FWHM of the Raman (fundamental) mode over this pressure range (Fig. 5). The FWHM has been measured previously, at 0 GPa to be 1.2 cm^{-1}. With instrumental resolution of ~4 cm^{-1}, we are not able to measure the FWHM of the Raman peak at low pressures and are instead measuring the instrument response function. With increasing pressure however, the width of the peak increases slightly, to greater than 4 cm^{-1}, and thus is no longer a result only of the resolution of the Raman spectrometer. This is most likely due to the added contribution of pressure inhomogeneity, which will result in an inhomogeneous broadening of the peak.

As just described the pressure dependence of the peak width of the Raman (fundamental) mode is markedly different from that of the infrared absorption peak (first overtone) (Fig. 5). This has been noted in a previous temperature study.[8] Since the IR absorption (first overtone) couples to the rotational modes, its FWHM will be strongly dependent upon the degree of CN rotation. However, the selection rule for the Raman mode, $\Delta v=\pm 1$, $\Delta J=0$ does not allow for coupling of the rotational bands to the stretching mode. This is the reason for the sharp 0 GPa Raman band in contrast to the broadened IR band, and also its insensitivity to the freezing out of the CN rotations.

D. NaCN

Previous high-pressure studies on NaCN have demonstrated that at room temperature there are three phase transitions, at 0.2 GPa, 4 GPa, and at 12.5 GPa.[17,25,26] The low pressure transitions are not readily observable in either Raman-scattering or infrared-absorption studies due to the subtle nature of the changes in the spectra across the transition. For example, there is less than a 1 cm^{-1} discontinuity in the peak position of the fundamental mode across the 0.2 GPa transformation.

In the present experiments, a second weak peak appears at ~12 GPa in both the infrared and Raman spectra (Figs. 2 and 6). In the Raman spectra, the new peak is at 29.1 cm^{-1} below the original peak, while in the infrared spectra the new peak is at 62.2 cm^{-1} below the original absorption peak. With compression beyond 12 GPa, the new peaks increase in intensity while the original peaks decrease in intensity. By ~17 GPa the original peaks vanish and the new peaks are all that are observable in both the Raman and infrared spectra, consistent with previous work.[17] Upon decompression the reverse happens, and by approximately 9–10 GPa the new peaks vanish. A small degree of hysteresis is evident (Fig. 6). The pressure dependence of all four of the peaks is given in Table I.

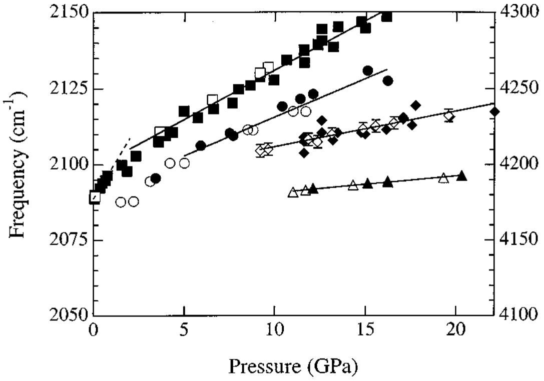

FIG. 6. The frequency shift of the fundamental (squares and diamonds) and first overtone (circles and triangles) stretching CN vibration of NaCN as a function of pressure. The squares and circles are for the low-pressure phase, and the diamonds and triangles for the high-pressure phase. Closed symbols are on compression; open symbols on decompression. The lines are fits to the data.

Because the frequency of the new peak observed by infrared spectroscopy is approximately twice the frequency of the new peak observed by Raman spectroscopy, and because both peaks appear and disappear at approximately the same pressure, one may infer that these represent the fundamental mode and first overtone of the same vibration. The new vibrations are clearly due to the C-N stretch, based upon their frequencies and the correlation with the C-N vibrations observed at low pressure.

Our results are consistent with there being a pressure-induced phase transformation at ~12 GPa, with the structural rearrangement manifesting itself as a large decrease in the frequencies of the fundamental mode and first overtone.[17]

As in the case of the CN vibration in KCN, the spectral data of NaCN allows one to determine the degree of anharmonicity present in the CN bond in NaCN. Due to the lack of reliable infrared data on the first overtone, the anharmonicity constant has not been determined at pressures below 4 GPa (Fig. 4). However, extrapolation of the anharmonicity constant yields a 0 GPa value of $\nu_e x_e$ of $8.5\pm 1.5\,\mathrm{cm}^{-1}$. This disagrees with the previously measured value of 11.3 cm^{-1} for 0 GPa.[8] Thus, although not directly measured, we can conclude that there must be a change in the anharmonicity value or slope at the low-pressure phase transitions.

The changes in the FWHM of the CN vibration in NaCN with pressure are significantly different from the CN behavior in KCN having no obvious correlation to phase transformations.

IV. CONCLUSION

The high-pressure behavior of KCN and NaCN has been observed through Raman and infrared spectroscopy. A large decrease in the FWHM of the infrared band of KCN at low pressures can be interpreted as a freezing out of the CN rotations due to compression. While no discontinuities in the peak positions of the Raman or infrared bands were observed beyond 2 GPa, the subsequent increase in the FWHM at ~10 GPa of the infrared mode and the observable break in the slope at ~20 GPa, of infrared peak with pressure, may be indications of phase transitions in KCN. The high pressure, monoclinic phase of NaCN has been observed using Raman and infrared spectroscopy. This phase is stable to at least 20 GPa and is not quenchable.

The combination of spectroscopic techniques has allowed for a determination of the pressure dependence of the anharmonic correction to the potential energy of the CN stretching vibration.

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