

High-pressure Raman studies of a nitrogen - helium mixture up to 40 GPa

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 11219

(<http://iopscience.iop.org/0953-8984/9/50/022>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 11:51

Please note that [terms and conditions apply](#).

High-pressure Raman studies of a nitrogen–helium mixture up to 40 GPa

H Olijnyk and A P Jephcoat

Department of Earth Sciences, University of Oxford, Oxford OX1 3PR, UK

Received 11 August 1997

Abstract. A He–N₂ mixture of 0.8 mole fraction He was investigated by high-pressure Raman spectroscopy. The N₂ vibron in fluid He–N₂ is observed up to ≈ 9 GPa. Spectra of external and internal modes of the van der Waals compound He(N₂)₁₁, which is formed above 9 GPa, were obtained up to 40 GPa. The similarities of the spectral features to those of ε -N₂ imply a close relationship between the structures of He(N₂)₁₁ and ε -N₂. The enhanced ν_2/ν_1 -intensity ratio suggests that He may substitute or displace N₂ molecules from the *a* site in the ε -phase. The observed splitting of the main vibron of isotopic species ¹⁴N–¹⁵N indicates that in addition to factor-group interactions site effects are responsible for the observed splittings of the ¹⁴N₂ main vibron of He(N₂)₁₁.

1. Introduction

High-pressure studies of dense gas mixtures are of particular interest if the components show mutual solubility resulting in the formation of solid solutions [1, 2]. The first study of the solubility of a fluid in a solid, which was performed on the system He–N₂ [3], showed that about 2 mol% He can be dissolved in δ -N₂ at high pressures and low temperatures and about 9 mol% in the ε -phase [3]. The transition from δ -N₂ to ε -N₂ was found to be shifted to lower pressures in the mixture and was attributed to the high solubility of He in nitrogen [3]. A subsequent study revealed that the ‘9% phase’ of the He–N₂ system is a stoichiometric solid compound of composition He(N₂)₁₁, which forms at 7.7 GPa at room temperature [4]. X-ray diffraction studies are consistent with a hexagonal unit cell containing 24 particles, though the correct space group has not yet been determined, and the pressure–volume curve was measured between 9 and 14.5 GPa [4]. Raman-spectroscopic studies showed that the main vibron is shifted with respect to that of pure N₂ for a given pressure by 1–2 cm⁻¹, but neither spectra nor frequency data were reported [4].

The formation of solid stoichiometric compounds at high pressure has also been reported in the systems He–Ne [5], Ar–H₂ [6] and O₂–H₂ [7]. These compounds are held together by van der Waals forces. Vibrational studies of such compounds give valuable information on the interactions between unlike molecules, which cannot be determined from knowledge of the forces between like molecules [2]. Understanding of compound phases and their properties may be important for modelling the interiors of the outer planets and their satellites, which may be a reservoir of such solids.

In this paper we report on high-pressure Raman studies of a He–N₂ mixture with an initial composition of 80% He and 20% N₂. Raman spectra of both internal and external modes were obtained up to 40 GPa for the van der Waals compound He(N₂)₁₁.

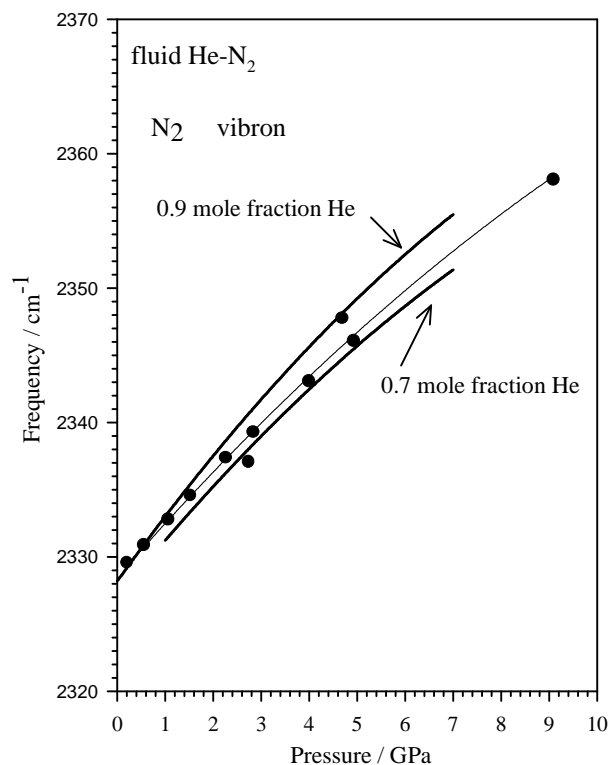


Figure 1. Raman shift of N₂ in He-N₂ as a function of pressure at room temperature at various mole fractions. Upper and lower heavy curves are for 0.9 and 0.7 mole fraction He, respectively, from [11]; full circles: this study; the light curve serves as a guide for the eye through the data points of this study. The uncertainty in frequency corresponds to the symbol size.

2. Experimental

A ternary gas mixture of 7% CO₂, 18% N₂ and 75% He (high-purity laser gas) was filled into the gasket hole of a high-pressure diamond-anvil cell at 0.2 GPa using a high-pressure gas-loading technique [8]. Pressure was determined with the ruby fluorescence method [9]. Pressure inhomogeneities in the investigated pressure range were negligible: pressure differences of only 1 GPa were measured over the total gasket hole of 100 μm in diameter at 30 GPa. Raman spectra were excited by the 514.5 nm line of an Ar⁺ laser. Scattered light was collected at an angle of 135° with respect to the incoming laser beam and analysed using a 0.6-m triple spectrograph and a liquid-nitrogen-cooled CCD multichannel detector.

3. Results

By visual inspection three phase separations were observed with increasing pressure at room temperature. The first occurred at 1.5 GPa, where CO₂ freezes out, which was confirmed by the observation of external and internal Raman spectra of solid CO₂ at this pressure and above. The Raman spectra from the solid CO₂ phase of the sample were identical to those of pure CO₂ [10] giving no indications for the formation of a solid solution or van der Waals compound of CO₂ with either He or N₂.

From those parts of the sample containing no CO₂ one Raman peak was observed in the vibronic region up to ≈ 9 GPa in the loading cycle. Its Raman shift as a function of pressure is shown in figure 1 by full circles. Raman studies on fluid He-N₂ mixtures have previously been performed up to 7 GPa for different compositions [11]. Comparison

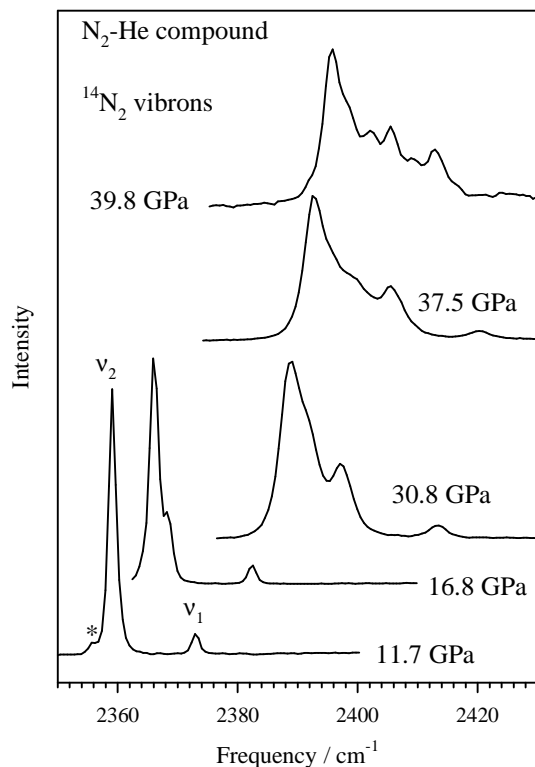


Figure 2. Raman spectra of the vibrons of the van der Waals compound $\text{He}(\text{N}_2)_{11}$ at various pressures.

with the present data shows that the Raman shift with pressure of our single vibron data lies between the curves with He mole fractions of 0.7 and 0.9, which agrees well with the nominal composition of 0.8 mole fraction He relative to N_2 of the sample under study, if the CO_2 portion is disregarded.

Near 9 GPa a further phase separation was observed visually. The Raman spectrum from this phase consists of two bands, an intense low-frequency band with an asymmetry on the high-frequency side and a small high-frequency band (see figure 2). The occurrence of multiplet structure in the vibronic band of a diatomic molecule indicates solidification. By analogy with pure nitrogen the two main bands are labelled ν_1 and ν_2 . These Raman spectra are characteristic of the solid van der Waals compound of composition $\text{He}(\text{N}_2)_{11}$ which is known to form in this pressure range [4].

A third phase could be distinguished in the sample chamber above ≈ 10 GPa from which neither CO_2 nor N_2 Raman signals could be obtained. Since the composition of the van der Waals compound is $\text{He}(\text{N}_2)_{11}$, one can expect that in this sample all of the nitrogen is involved in forming the van der Waals compound. The third phase, from which no Raman signals could be obtained, was assumed to be excess He.

With increasing pressure quite distinct splittings of the lower frequency vibron of the van der Waals compound occur. In figure 2 the evolution of these spectral features is shown in the pressure range 10–40 GPa. At 40 GPa eight peaks can be distinguished in the vibronic region. On unloading the spectral changes occur reversibly and the single vibron spectra were observed only below 5 GPa indicating hysteresis in the formation of the van der Waals compound. The pressure shift of all these peaks is shown in figure 3.

In the frequency range a few tens of wavenumbers below these bands additional spectral

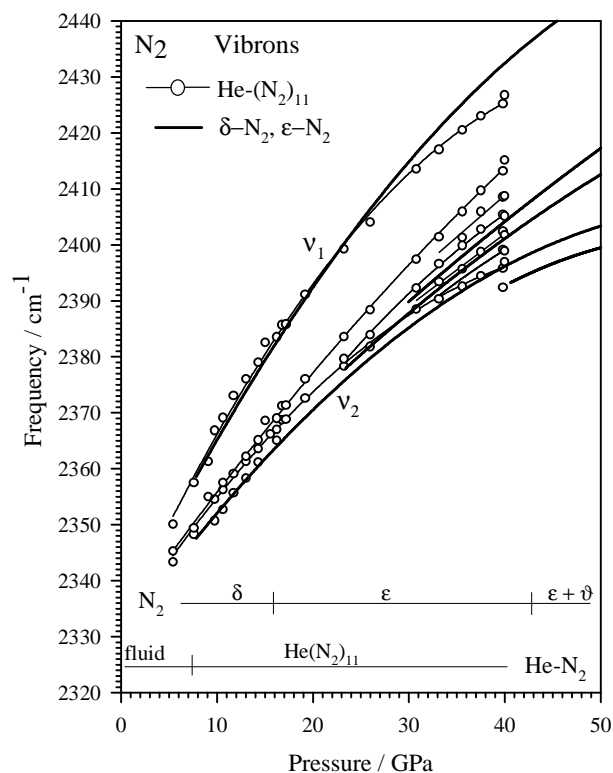


Figure 3. Pressure shift of the $^{14}\text{N}_2$ vibrons. Open symbols: van der Waals compound $\text{He}(\text{N}_2)_{11}$, this study. Full curves: $\delta\text{-N}_2$ and $\epsilon\text{-N}_2$ from [12]. The uncertainty in frequency corresponds to the symbol size.

features of very low intensity could be observed. Examples at two different pressures are shown in figure 4. These bands originate from isotopic species of nitrogen. In the harmonic approximation the frequency, ν , of a mode of a diatomic molecule can be expressed in terms of the force constant k and the reduced mass μ as

$$\nu \sim \sqrt{(k/\mu)}. \quad (1)$$

The force constants are invariant under isotopic substitution and for the corresponding mode frequency of a different isotopic species we obtain

$$\nu_i = \nu \sqrt{(\mu/\mu_i)}. \quad (2)$$

The natural abundance is 99.63% and 0.37% for ^{14}N and ^{15}N , respectively [13]. As shown in figure 5, the pressure shifts for $^{14}\text{N}\text{-}^{15}\text{N}$ vibronic modes calculated from the data of $^{14}\text{N}_2$ using equation (2) compare favourably with the frequencies and their pressure dependences of these weak features, and are in this way identified with vibrations of $^{14}\text{N}\text{-}^{15}\text{N}$ molecules. In the vibron, which corresponds to the high-intensity ν_2 band of $^{14}\text{N}\text{-}^{15}\text{N}$, splitting is observed at high pressure (see figures 4 and 5). Unusually, for the isotopic species the higher frequency component of the ν_2 vibron has higher intensity, which is the reverse case as for $^{14}\text{N}_2$.

Raman spectra of the lattice-mode region are shown in figure 6. The spectra are not well resolved and appear to be composed of rather broad bands. In the spectrum at 39.8 GPa shown in figure 6, one can distinguish by visual inspection four to five peaks, the pressure shift of which is shown in figure 7.

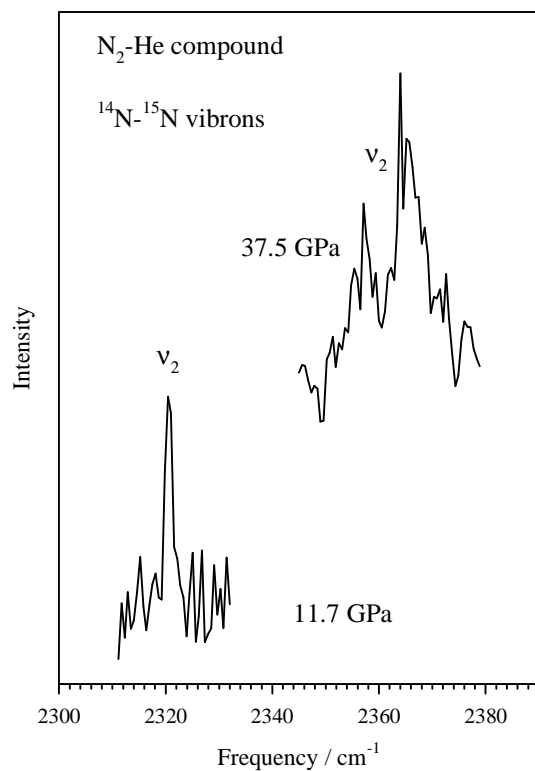


Figure 4. Raman spectra of ^{14}N - ^{15}N vibrons of the van der Waals compound $\text{He}(\text{N}_2)_{11}$ at different pressures.

4. Discussion

In figure 3 the pressure shifts of the vibrons of the van der Waals compound are compared with those of δ - N_2 and ε - N_2 . For the ν_1 -vibron the frequency–pressure curves nearly overlap, and only above 25 GPa an increasingly smaller Raman shift with respect to that of pure N_2 is observed. The ν_2 -vibron has slightly higher frequencies than the ν_2 -vibron of pure N_2 . As in the case of ε - N_2 splitting occurs with increasing pressure. There are three to four components in ε - N_2 whereas up to seven components can be recognized in $\text{He}(\text{N}_2)_{11}$. The pressure shift of the weak peak, which is located on the low-frequency side of the main vibron and labelled with an asterisk in figure 2, in fact coincides with the lowest frequency component of ν_2 of ε - N_2 , but due to the overlapping frequencies of the vibrons of $\text{He}(\text{N}_2)_{11}$ and ε - N_2 it is difficult to determine whether ε - N_2 is also present in the sample.

In figure 7 the pressure dependence of the lattice mode frequencies of $\text{He}(\text{N}_2)_{11}$ are compared with those of ε - N_2 . One can note that the discernible modes of $\text{He}(\text{N}_2)_{11}$ are located close to some modes of ε - N_2 .

The similarities of the internal and external modes of $\text{He}(\text{N}_2)_{11}$ to those of ε - N_2 suggest a close structural relationship between the van der Waals compound and ε - N_2 . The unit cell of ε - N_2 (space group $R\bar{3}c$) in the hexagonal notation contains 24 N_2 molecules, six on the a site and 18 on the f site [14]. In fact, a hexagonal unit cell with 22 N_2 molecules and two He atoms has been proposed for the crystal structure of the van der Waals compound [4]. The unit cell of the hexagonal van der Waals compound at 12.6 GPa has dimensions $a = 8.02 \text{ \AA}$ and $c = 9.46 \text{ \AA}$ [4], whereas for ε - N_2 extrapolation of the lattice parameters to the same pressure gives $a = 7.73 \text{ \AA}$ and $c = 10.76 \text{ \AA}$ [15]. Comparison of lattice parameters

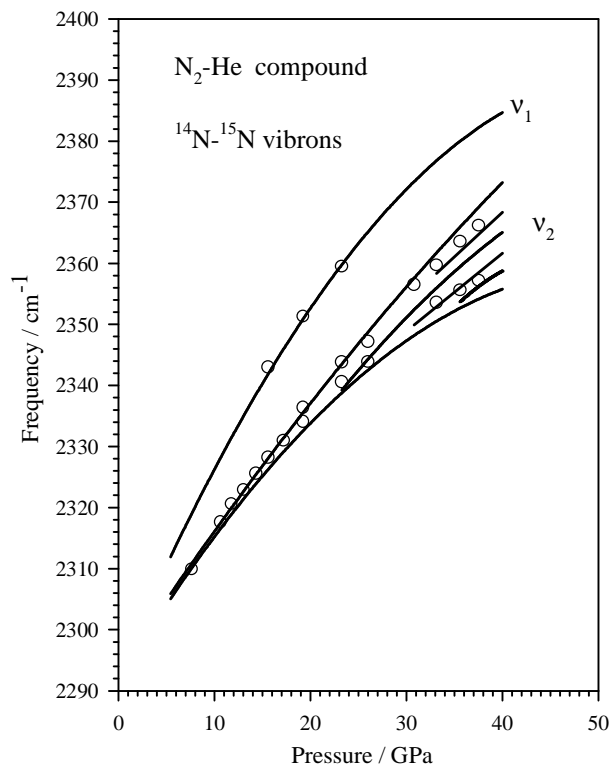


Figure 5. Pressure shift of $^{14}\text{N}-^{15}\text{N}$ vibrons of the van der Waals compound $\text{He}(\text{N}_2)_{11}$; open circles: experimental data; full curves: calculated from the pressure shift of $^{14}\text{N}_2$ vibrons of $\text{He}(\text{N}_2)_{11}$ using equation (2). The uncertainty in frequency corresponds to the symbol size.

at 12.6 GPa shows that for the van der Waals compound a is 2.5% larger and c is 13% smaller than in $\epsilon\text{-N}_2$, yielding a volume 5.4% smaller for the van der Waals compound.

The intensity ratio of ν_2 relative to ν_1 , which is ≈ 3 for $\epsilon\text{-N}_2$ [12], is a factor 4–5 larger for $\text{He}(\text{N}_2)_{11}$, as one can estimate from the spectra shown in figure 2. In $\epsilon\text{-N}_2$ this ratio reflects the difference in occupation of the two sites. If the N_2 molecules of the two sites are replaced randomly by He the intensity ratio in $\text{He}(\text{N}_2)_{11}$ should be approximately the same as in pure N_2 . If, however, the N_2 -molecules, which are substituted by the He atoms, originate from the a positions, one would expect an increase in the intensity ratio $I(\nu_2)/I(\nu_1)$ relative to that of $\epsilon\text{-N}_2$ in agreement with experiment.

For $\epsilon\text{-N}_2$ the splittings of the ν_2 -vibron have been explained by factor-group effects [16] and the onset of a phase transition above 40 GPa [12]. The space group of the hexagonal cell of $\text{He}(\text{N}_2)_{11}$ is not known, so that no predictions on the number of Raman allowed modes can be made. In this regard the results on the isotopic modes are informative. If the concentration of the isotopically substituted molecules is small, these are isolated in the host matrix, and the factor-group coupling effect is very small, because of the frequency difference between like vibrations of the two types of molecules. The splitting we observed in the main vibron of the isotopic species then clearly indicates that the observed splittings in the $^{14}\text{N}_2$ main vibron of the van der Waals compound are both due to factor-group interactions and site effects. In particular, this might indicate that the N_2 molecules, which contribute to the ν_2 spectral features in $\text{He}(\text{N}_2)_{11}$, are located on two different sites. A different population of these two sites by the $^{14}\text{N}_2$ and $^{14}\text{N}-^{15}\text{N}$ molecules would also explain the reversed intensity ratio observed for the components of the main vibron for the isotopic species $^{14}\text{N}-^{15}\text{N}$.

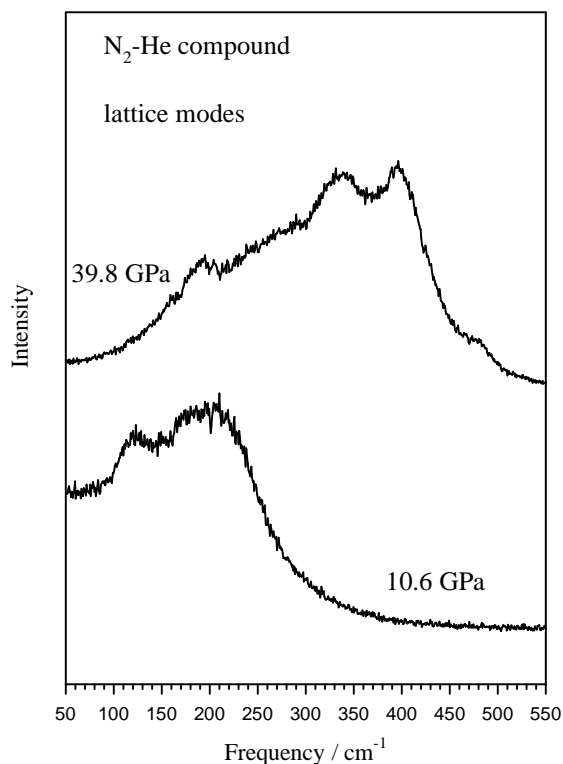


Figure 6. Lattice mode Raman spectra of the van der Waals compound $\text{He}(\text{N}_2)_{11}$ at different pressures.

In comparison with $\epsilon\text{-N}_2$ the spectral features of the lattice mode region are less structured and the individual bands appear broader for $\text{He}(\text{N}_2)_{11}$. In many cases such broadening is the result of orientational disorder. According to Vos and Schouten [3] orientational ordering is enhanced in solid N_2 by the admixture of He, but it is possible that positional disorder is introduced by the He atoms. The He atoms are thought to be bound only weakly by van der Waals forces. As a result of zero-point motion large fluctuations of the He atoms from their equilibrium positions are expected to occur, which introduce some amount of disorder in the local environment due to the randomness of this process.

5. Conclusion

A ternary gas mixture of 7% CO_2 , 18% N_2 and 75% He was investigated by Raman spectroscopy up to 40 GPa. In this gas mixture solid CO_2 freezes out at 1.5 GPa. Up to 9.5 GPa the vibron of N_2 in fluid He-N_2 is observed. At higher pressures the Raman spectra of external and internal modes of the solid van der Waals compound of composition $\text{He}(\text{N}_2)_{11}$ were recorded. The similarities of the spectral features of the internal and external modes to those of $\epsilon\text{-N}_2$ reveal a close relationship of the crystal structures of both phases. There is some evidence that the N_2 molecules, which are substituted by the He atoms, are removed from the a sites of the $\epsilon\text{-N}_2$ structure. The observed splitting of the ν_2 mode of isotopic species $^{14}\text{N}\text{-}^{15}\text{N}$ may indicate that three different sites, as compared with two in $\epsilon\text{-N}_2$, are occupied by the N_2 molecules in the lattice of the van der Waals compound.

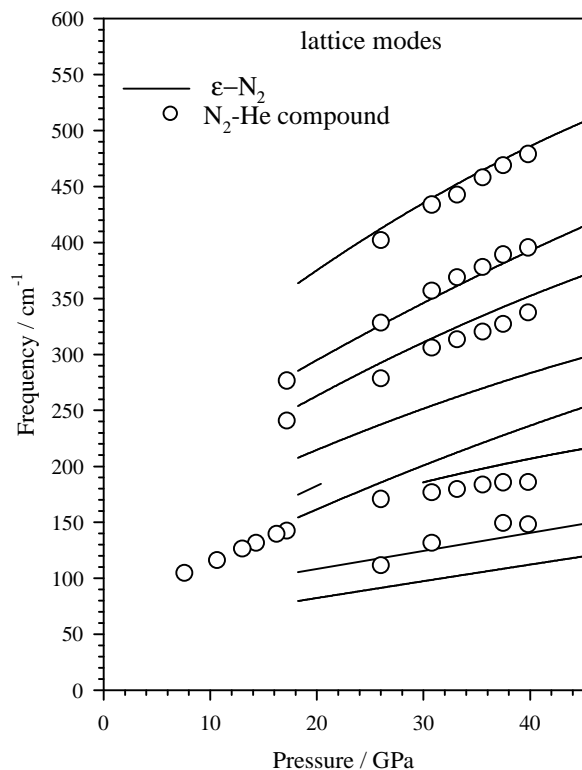


Figure 7. Pressure shift of lattice modes. Open circles: van der Waals compound He(N₂)₁₁; full curves: ε-N₂ from [12]. The uncertainty in frequency corresponds to the symbol size.

Acknowledgment

Support for this project was provided in part by the European Community under contract SCI*CT920802.

References

- [1] Meyer L 1969 *Adv. Chem. Phys.* **16** 343
- [2] Schouten J A 1989 *Phys. Rep.* **172** 33
- [3] Vos W L and Schouten J A 1990 *Phys. Rev. Lett.* **64** 898
- [4] Vos W L, Finger L W, Hemley R J, Hu J Z, Mao H K and Schouten J A 1992 *Nature* **358** 46
- [5] Loubeyre P, Jean-Louis M, LeToullec R and Charon-Gerard L 1993 *Phys. Rev. Lett.* **70** 178
- [6] Loubeyre P, LeToullec R and Pinceaux J P 1994 *Phys. Rev. Lett.* **72** 1360
- [7] Loubeyre P and LeToullec R 1995 *Nature* **378** 44
- [8] Jephcoat A P, Mao H-K and Bell P M 1987 *Hydrothermal Experimental Techniques* ed G C Ulmer and H L Barnes (New York: Wiley-Interscience) p 469
- [9] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673
- [10] Olijnyk H and Jephcoat A P 1997 *Phys. Rev. B* submitted
- [11] Scheerboom M I M and Schouten J A 1996 *J. Chem. Phys.* **105** 2553
- [12] Schneider H, Haefner W, Wokaun A and Olijnyk H 1992 *J. Chem. Phys.* **96** 8046
- [13] Weast R C (ed) 1980 *Handbook of Chemistry and Physics* (Boca Raton, FL: Chemical Rubber Company) p B-238
- [14] Mills R L, Olinger B and Cromer D T J 1986 *Chem. Phys.* **84** 2837
- [15] Olijnyk H 1990 *J. Chem. Phys.* **93** 8968
- [16] Schiferl D, Buchsbaum S and Mills R L 1985 *J. Phys. Chem.* **89** 2324