Volume Dependence of Raman Frequencies in α-N_2†

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(Received 17 October 1973)

The volume dependence of the Raman frequencies ω_i in α-N_2 has been measured yielding the following values of the Grüneisen parameter $\gamma_i \equiv -\partial \ln\omega_i/\partial \ln V$ at 8°K: 2.09 ± 0.12, 1.74 ± 0.10, and 1.70 ± 0.10, where i refers to the E_g, low-frequency T_g, and high-frequency T_g modes, respectively. These values are insensitive to temperature within experimental errors. The broad feature between 70 and 100 cm^{-1} is identified as a two-libron band.

The Raman spectrum of α-N_2 has been measured by several workers[1-4] who obtained librational frequencies which differ by as much as 6%. The librational frequencies in α-N_2 have also been the subject of an impressive number of classical and quantum mechanical calculations[5-14] aimed at elucidating the form of the orientation-dependent part of the intermolecular potential. Quantum mechanical calculations using the quadrupolar interaction potential[11,14] yield the best agreement with experimental results. We report here measurements of the volume dependence of the librational frequencies in α-N_2.

We have studied samples of α-N_2 using a novel method of sample preparation by growth of solid N_2 within a cell at high pressures on the melting curve and cooling isochorically to the temperature of observation. The optical cell is equipped with sapphire windows[15,16] so that the sample may be studied *in situ* within its high-pressure jacket. The method has been used in inelastic neutron studies of neon[17,18] and krypton.[19] The method has a number of advantages in addition to permitting measurements to be made as a function of density. Among the advantages are these: (1) The high pressure prevents sample cracking and the resultant loss of optical quality in the samples; (2) for the same reason the external optical surfaces remain flat and of high optical quality; (3) the shifts of spectral lines with temperature directly represent temperature-dependent anharmonic self-energies $\partial\omega/\partial T|_V$. In customary isobaric measurements, the derivative measured is $\partial\omega/\partial T|_P$ which is usually dominated by spectral shifts induced by the change of volume with temperature.

Samples of the high-temperature β phase of solid N_2 were grown at three different sets of melting temperature and pressure: 151°K and 6.0 kbar, 131°K and 4.3 kbar, 112°K and 3.8 kbar—corresponding to molar volumes of 25.1, 26.0, and 26.9 cm^3/mole for the solid. Data of Cheng[20] and of Schuch and Mills[21] were used to determine the molar volumes. The optical cell was attached to the cold finger of a cryostat allowing the temperature to be controlled within 0.1°K. After growth each sample was annealed. The temperature was then lowered slowly—while the volume stayed essentially constant—until the α-phase field was reached.

The Raman spectra were excited by the 5145-Å line of an argon-ion laser, analyzed by an Interactive Technology 0.5-m double monochromator, detected photoelectrically, and displayed on a photon counter. Figure 1 shows the Raman spectrum in the lattice region of an α-N_2 sample having a molar volume of 26.9 cm^3/mole at 8°K.

The features observed, including the splitting

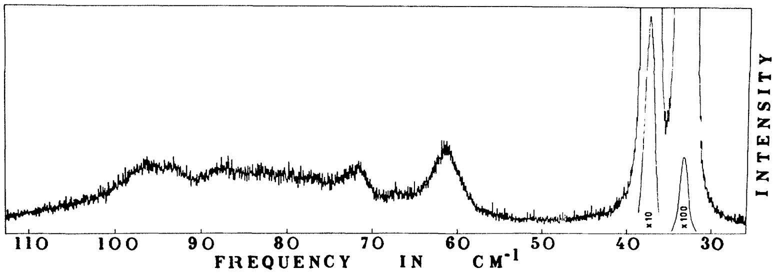

FIG. 1. Raman spectrum of α-N_2 at 8°K for a sample with a molar volume of 26.9 cm^3/mole. Instrumental resolution is 1 cm^{-1}.

TABLE I. Volume dependence of Raman spectrum in α-N_2.

T (°K)	Frequency (full width at half-height) (cm^{-1})			Relative peak intensities	Molar volume (cm^3/mole)
	E_g	T_g	T_g	E_g:T_g:T_g	
8	33.3[a]	37.5[a]	61.3(4.5)	3.6:1: 0.05	26.9
	35.6(0.8)	39.7(0.8)	65(5)	3.6:1: 0.05	26.0
	38.2(0.8)	42(0.8)	69(5)	4.2:1:< 0.05	25.1
18	33(1.7)	37.2(1.7)	61(5.5)	4.7:1: 0.05	26.9
	35.5(1.7)	39.5(1.7)	64.8(6)	5.2:1:< 0.05	26.0
	38(1.7)	42(1.7)	68.6(6)	5.5:1:< 0.05	25.1
35	32.3(8)[b]	...	...	...	26.9
	34.6(8)[b]	...	...	...	26.0
	37(8)[b]	...	...	...	25.1

[a] These lines are very narrow and the widths cannot be resolved from the instrumental widths.

[b] These are rough estimates since at this temperature the E_g line has merged with the low-frequency T_g line.

of the N_2 stretch, agree with previous results.[3] However, it is worth noticing that the peak near 70 cm^{-1} could coincide with one of the infrared-active lattice modes.[22,23] Coincidence between Raman and infrared frequencies has been recently observed in the infrared spectrum of α-N_2.[24] The observed coincidences between Raman and infrared frequencies support the x-ray studies[25,26] and the piezoelectric studies[27] which assign to α-N_2 a $P2_13$ structure in which each molecule is displaced from a center of inversion.

Table I contains the frequency ω (cm^{-1}) of each librational mode for different molar volumes V (cm^3/mole) and temperatures. Because of broadening of the lines we could determine only the frequencies of the E_g line at 35°K. Full widths at half-height and relative peak intensities of the lines are also included in Table I.

The frequencies of the Raman lines decrease slightly as the temperature is increased from 8 to 18°K. The frequency of the E_g line decreases by ~3% as we further increase the temperature to 35°K, in contrast to previous results[1] where the frequency was observed to change by as much as 15% in increasing the temperature from 12 to 35°K. Small changes are to be expected in our work since the frequency changes are almost entirely due to explicit temperature dependence under near isochoric conditions.

In Fig. 2, $\ln\omega$ is plotted versus $\ln V$ for the low-frequency T_g mode at 8°K. The experimental points fall nearly on a straight line. The negative slope of this line is the Grüneisen parameter for the T_g mode $\gamma_{T_g} = -(\partial \ln\omega_{T_g}/\partial \ln V)$. The Grüneisen parameter is critically dependent on the form of the intermolecular potential, especially on the short-range repulsive part.

Table II contains the Grüneisen parameters obtained from the data in Table I. The errors in these values are mainly due to uncertainties in the molar volumes. The resulting Grüneisen parameters are rather insensitive to temperature and are substantially higher than the result of $\frac{5}{6}$ expected for a quadrupolar interaction potential in the harmonic approximation. The expected result of $\frac{5}{6}$ follows from the relation $\omega^2 \sim r^{-5}$ between the librational frequency ω and the intermolecular distance r.

Our spectroscopic values are closer to the value $1.0 \leq \gamma \leq 1.5$ obtained by Brookeman, McEnnan, and Scott[28] using nuclear quadrupole resonance methods. For an orientational potential of the

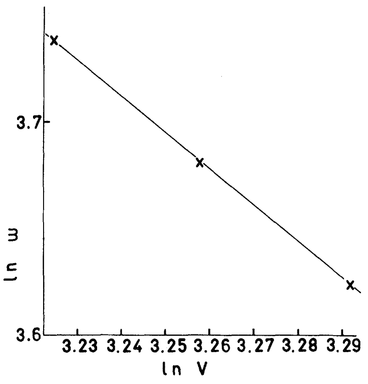

FIG. 2. Plot of $\ln\omega$ versus $\ln V$ for the low-frequency T_g mode of α-N_2 at 8°K where the frequency ω is in cm^{-1} and the molar volume V is in cm^3/mole.

TABLE II. Grüneisen parameters of the librational modes in α-N_2.

Temperature (°K)	E_g	Low-frequency T_g	High-frequency T_g
8	2.09 ± 0.12	1.74 ± 0.1	1.70 ± 0.1
18	2.10 ± 0.12	1.76 ± 0.1	1.77 ± 0.1
35	2.03 ± 0.12		

form Ar^{-n} our measured values of the Grüneisen parameter would yield $8 < n < 9$ for the T_g modes and $10 < n < 11$ for the E_g mode, in the harmonic approximation. However, anharmonic contributions to the Grüneisen parameters should be significant.

It is also possible that the quadrupole moment Q of the nitrogen molecule depends on the volume. Decreasing the molar volume may distort the molecules and possibly increase the quadrupole moment, which would explain the large volume dependence of the librational frequencies in α-N_2. An increased quadrupole moment would also improve the agreement between experimental and calculated librational frequencies for the high-pressure γ phase recently obtained in this laboratory.[29]

The librational frequencies can be extrapolated to zero pressure using the measured Grüneisen parameters and the molar volumes at zero pressure from Ref. 16. The calculated zero-pressure librational frequencies are 32.8, 37.0, and 60.5 cm^{-1} at 8°K and 32.1, 36.4, and 59.7 cm^{-1} at 18°K to be compared to 31.5, 36.0, and 59.8 cm^{-1} measured by Mathai and Allin[4] at 4°K and 32, 36.5, and 60 cm^{-1} measured by Anderson, Sun, and Donkersloot[3] at 18°K.

The feature between 70 and 100 cm^{-1} in Fig. 1 seems to consist of a series of broad lines, the most pronounced of which are near 70 cm^{-1} and near 95 cm^{-1}. The above frequencies lie close to the sums of the E_g and each of the T_g librational frequencies. The volume dependencies of the 70- and 95-cm^{-1} lines yield Grüneisen parameters 1.8 ± 0.3 and 2.1 ± 0.3, respectively. The error in these Grüneisen parameters is large because of the uncertainties in the frequencies. However, the Grüneisen parameters obtained for the 70- and 95-cm^{-1} lines are reasonably close to those obtained for the librations and seem to support the identification[13] of the broad band between 70 and 100 cm^{-1} as a two-libron band.

We would like to acknowledge the help of Paul Fleury, Paul Lazay, and John Worlock in the initial phases of assembling our Raman scattering equipment.

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†Research supported in part by the National Science Foundation under Grant No. GH-32491-X and by the Unidel Foundation of the University of Delaware.

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Dynamics of an $S=\frac{1}{2}$, One-Dimensional Heisenberg Antiferromagnet

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We report a detailed neutron-scattering study of the spin dynamics in $CuCl_2 \cdot 2N(C_5D_5)$, a physical realization of the one-dimensional $S=\frac{1}{2}$ Heisenberg antiferromagnet. At $T=1.3$ K well-defined excitations are observed over the whole zone with energies given by $E(q)=\pi J_{nn}\sin(qc)$, the celebrated des Cloizeaux–Pearson exact solution for the spectrum of first excited states, but with intensities approximately those expected from classical spin-wave theory. At $T=8$ K the excitations are broad and ill defined.

The one-dimensional (1D), nearest-neighbor (nn), $S=\frac{1}{2}$ Heisenberg antiferromagnet is one of the few nontrivial many-body problems with interesting dynamics for which exact solutions exist. In 1931, Bethe[1] found the ground-state eigenfunction, and he showed that no long-range order exists even at 0 K. Somewhat later, Hulthén[2] derived the ground-state energy $E_0=-|J|N(2\ln 2-\frac{1}{2})$. In 1962, des Cloizeaux and Pearson[3] (dC-P) found that the first excited states obey the simple dispersion relation

$$E(q)=\pi J|\sin(qc)|, \tag{1}$$

where c is the nn separation, and they identified these excitations as "spin waves." They noted that, quite remarkably, the dispersion relation, Eq. (1), has a double periodicity of π just as in standard spin-wave theory[4] starting from an assumed Néel ground state. However, the coefficient of J in Eq. (1) is equal to π, compared with 2 for classical spins.[4] It has not proven possible, however, to go from the exact dC-P calculation to a response function $\chi''(\vec{q},\omega)$. In order to elucidate this problem, we have carried out a detailed inelastic neutron scattering study of the spin dynamics in $CuCl_2 \cdot 2N(C_5D_5)$, dichlorobis pyridine copper II (CPC). As discussed below, CPC is a good physical approximation to the idealized 1D nn $S=\frac{1}{2}$ Heisenberg antiferromagnet. We find that at $T=1.3$ K there are sharp excitations with a dispersion relation given precisely by Eq. (1); this work thence constitutes the first experimental observation of the dC-P states.

We first discuss the crystal structure[5] and the consequent magnetic properties[6] of CPC. As shown in Fig. 1, CPC is body-centered monoclinic, with space group $P2_{1/n}$. Each Cu^{++} ion is located at the center of a rhombus of chlorine and nitrogen atoms which are stacked along the c axis, thence giving rise to a linear chain structure. The chains are kept well separated by the large intervening pyridine molecules; the ratio of in-