Anomalous Behavior of the Vibrational Spectrum of the High-Pressure δ Phase of Nitrogen: A Second-Order Transition

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In a careful Raman spectroscopic study on the high pressure δ phase of nitrogen we have observed an anomalous break in the slope of the vibrational Raman shift as a function of temperature. We interpret this as a second-order phase transition due to an orientational localization of the molecules, a phenomenon which has not previously been detected experimentally. Our results explain the change above 12 GPa in the experimental compressibility at room temperature measured by Olijnyk. The interpretation is consistent with the results of computer simulations.

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Numerous studies have been reported in the literature on the static behavior of molecular systems at high pressures [1]. Much less information is available on the dynamics, e.g., the orientational behavior of the molecules, although this may have a considerable influence on the phase diagram and the properties of the system, since it may give rise to orientationally ordered or disordered phases. This behavior is reflected in the vibrational properties, that are sensitive to the local environment and that are conveniently probed by Raman spectroscopy. Nitrogen is one of the simplest anisotropic molecules and is considered to be a molecular model system [1–8]. Therefore, we have performed a careful high pressure investigation of the behavior of the vibrational spectrum of the orientationally disordered δ phase of nitrogen. We have observed a peculiar behavior of the Raman shift as a function of temperature along a quasi-isobar. Figure 1 shows a plot of the Raman shift of the two modes of δ nitrogen at about 6 GPa. The frequency of the upper mode is gradually changing as the temperature is decreased but suddenly the change is more pronounced at about 210 K. It should be noted that the anomaly takes place within the stability range of δ nitrogen (Fig. 2) in which no structural changes have been reported [5]. Therefore it is proposed that the orientational behavior of the molecules is changing as discussed below.

Investigations using x-ray diffraction [4–6] revealed the structure of δ-N_2 to be disordered cubic with space group $Pm3n$. The unit cell consists of eight molecules, two of which (the corner and body-centered ones) have a spherically symmetric orientational distribution [4] (spherical molecules). The six other molecules are situated in pairs at the faces of the cube and they possess a random orientation in a planar disk normal to the unit cell face [4] (disklike molecules). The experiments could not reveal whether the molecules are rotating or are statically disordered. This peculiar structure also exists in O_2, F_2, and CO [4,5]. At low temperature a structural phase transition occurs to the ϵ phase, which is an ordered modification of the δ phase.

The same optical setup and diamond anvil cell (DAC) were used as in previous investigations [9]. The pressure scale of Mao, Xu, and Bell [10] has been used; the temperature correction was taken from Ref. [11]. After each measurement the double monochromator was calibrated, resulting in an accuracy of 0.2 cm^{-1}.

We first determined at room temperature the isothermal pressure dependence of the Raman shifts, while increasing the pressure. Then at a predetermined pressure only the temperature was varied and the Raman spectrum was determined in steps of 15 K. After each

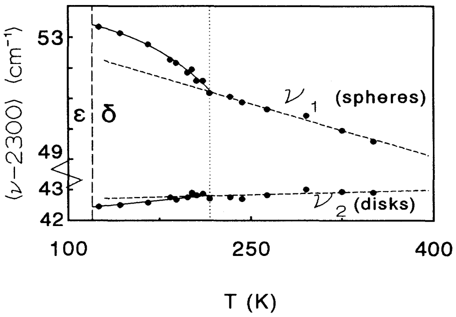

FIG. 1. ν_1 and ν_2 vs T corrected to the isobar at 5.9 GPa; dotted line marks transition; dashed and full lines are guides to the eye.

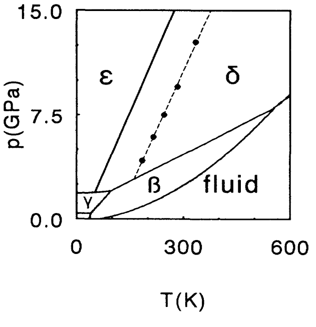

FIG. 2. Phase diagram of N_2; dots are p-T points of breaks in the slope of $\nu_1 - \nu_2$ vs T; dashed line is a linear fit.

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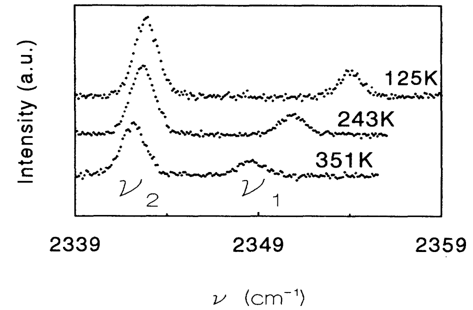

FIG. 3. Raman spectra of δ-N_2 at about 5.9 GPa.

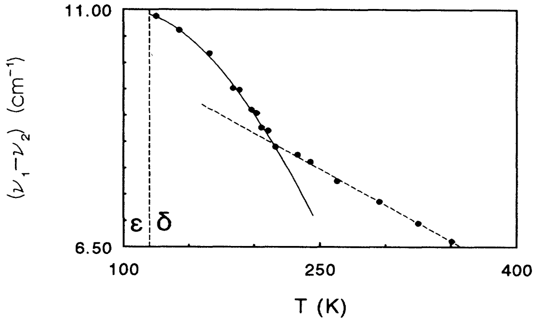

FIG. 4. $\nu_1-\nu_2$ vs T corrected to the isobar at 5.9 GPa; the lines are the fits giving T of intersection.

step the system was equilibrated for at least 1 h to get a well-defined temperature. A technically unavoidable aspect of our DAC is the fact that the pressure usually increases when the temperature is lowered. Over 100 K this change could amount from 0.1 GPa for the lowest up to 0.5 GPa for the highest pressures. Therefore, the measurements were performed along quasi-isobars.

A series of vibrational Raman spectra of δ-N_2 along quasi-isobars around 4.2, 5.9, 7.5, 9.5, and 12.7 GPa have been obtained in the temperature range from 120 to 400 K. Some typical spectra at 5.9 GPa are shown in Fig. 3. The low frequency high intensity peak is called ν_2 and is due to the disk molecules [12]. The higher frequency peak, called ν_1 is about 3 times lower in intensity and is due to the sphere molecules [12]. In general, the scatter is decreased if the difference in peak positions ($\nu_1-\nu_2$) is plotted. Figure 4 shows the result for 5.9 GPa. A break in the slope of $\nu_1-\nu_2$ versus the temperature at about 210 K can be clearly noticed. The same behavior has also been observed at the four other quasi-isobars.

It is convenient for the interpretation and discussion to have the data along a well defined thermodynamic path, e.g., an isobar. Corrections for the experimental pressure deviations have been made in the following way. An estimate of the pressure and temperature of the kink in the curves (Figs. 1 and 4) was made graphically. The total collection of data points (more than 100) was divided in points below and above the kinks. Fits were made for the two data sets of ν_1 (standard deviation $\sigma=0.15$ cm^{-1}), the two sets of ν_2 ($\sigma=0.15$ cm^{-1}) and for those of $\nu_1-\nu_2$ ($\sigma=0.10$ cm^{-1}). Using these fits the data on a quasi-isobar were corrected to the estimated pressure of the kink.

In fact the data in Figs. 1 and 4 have been corrected in this way. We notice that at high temperatures $\nu_1-\nu_2$ is a linear function of T whereas below the break it has a significant curvature which is mainly due to ν_1 (see Fig. 1). The curvature levels off in the neighborhood of the ϵ-δ phase transition line. This is also the case at the other isobars.

Finally, to get more precise values for the temperature of the break in the slope, fits were made for $\nu_1-\nu_2$ through both parts of each isobar separately (Fig. 4). It was assumed that the intersection gives the correct temperature. The resulting values corresponding to the five pressures mentioned above are respectively 185, 216, 246, 283, and 335 K. These points have been plotted in Fig. 2 together with a linear fit: $p(\text{GPa})=0.0568T(\text{K})-6.37$ ($\sigma=0.14$ GPa). This curve has a positive slope and now serves as a transition line for the process to be discussed hereafter.

Before interpreting the experiments we have to outline the physical origin of the temperature dependence of the Raman shifts along an isobar. The change of the Raman shift is mainly due to the *axial* components (F_{ax}) of the intermolecular forces. Therefore, the frequency will change if the molecules change their orientations with respect to their nearest neighbors (orientation effect) or their distance (configuration effect). At high densities the pressure is a measure for the average force on the molecules and so it is to be expected that along an isobar the configuration effect is smaller than the orientation effect. The Raman shift will also change by the vibration-rotation (VR) coupling if the molecules can rotate. For the motionally narrowed lines of N_2 the effect is negative and linear in temperature: $\omega_{\text{VR}}(\text{cm}^{-1})=-6\times10^{-3}T(\text{K})$ [13].

The main reason that ν_1 is larger than ν_2 is the fact that for the spheres the axial forces (heart on tail configuration, denoted by T) are dominant as shown by the simulations of Belak [14]; for the disks the perpendicular forces are dominant, e.g., by body to body orientations (denoted by X and P). The axial and perpendicular forces will become more alike at higher temperatures due to the thermal averaging. Therefore, ν_1 will in general decrease at increasing T and ν_2 will increase. The orientations of the disks are more or less restricted to a plane, even at higher temperatures. The disks have fewer possibilities for changing their orientation and, therefore, the orientation effect is smaller than that of the spheres. For the disks the orientation effect and the VR coupling will have opposite directions, also causing the change of ν_2 to be smaller than that of ν_1.

For the interpretation of the results we propose that at low temperature in the δ phase the molecules are orientationally localized and at high temperature more or less freely rotating. The orientational order parameter for the spheres is then $O_r = 0.5[3\langle(\hat{\mathbf{a}}\cdot\hat{\mathbf{e}})^2\rangle - 1]$, where $\hat{\mathbf{a}}$ and $\hat{\mathbf{e}}$ are unit vectors giving the orientations of the molecule and one of the body diagonals, respectively. O_r is in the order of 1 in the ϵ phase, it is nearly 0.25 just above the ϵ-δ phase transition and zero at the new transition. The changes in the disk are minor: from a few degenerate planar orientations to rotation.

At high temperatures the molecules are probably more or less freely rotating. The VR coupling is present for all the molecules but the orientation effect will be modest. It turns out that the combined result is the almost linear temperature dependence of ν_1 and ν_2 (Fig. 1).

At low temperatures the situation is essentially different. In the ϵ phase the molecular orientations are fixed and so ν_1 and ν_2 hardly change as a function of T [9]. At the structural transition to the δ phase the molecules obtain some orientational freedom and librate around a few equally probable orientations: orientational localization. Note that the initial slopes of ν_1 and ν_2 versus T are modest (Fig. 1). On further heating a rapid decrease of ν_1 is observed. We interpret this as a cascade process in which the localization vanishes rapidly: If on heating the librational amplitude of an arbitrary molecule is increasing, it simultaneously facilitates the libration of its neighboring molecules and an acceleration of the orientation effect and possibly of the VR coupling effect will occur (vibration-libration coupling cannot explain the effect since then a librational energy of 1000 cm^{-1} is needed [15]). The end of this delocalization process causes the break in the slope for ν_1 (Fig. 1): This break represents a phase transition. The general picture is supported by the fact that at higher pressures (higher densities) the process starts at higher temperatures (at the ϵ-δ phase line). The new transition curve is nearly parallel to the ϵ-δ phase transition line suggesting a relation between the processes at the transitions.

The next question is whether the transition is of second order. Mills, Olinger, and Cromer [5] and Olijnyk [6] have performed x-ray experiments in δ-N_2 in the low as well as in the high temperature phase of δ-N_2. The diffraction patterns showed that the structure of both parts of δ-N_2 is that already determined by Cromer *et al.* [4]: disordered cubic with space group $Pm3n$. Also no pressure jump was detected using the sensitive method of scanning isochorically the pressure as a function of temperature [16]. Therefore, it is reasonable to assume that there is *no* first-order phase transition within δ nitrogen. The interpretation of a second-order transition is supported by the x-ray diffraction work of Olijnyk [6]. It is known from general thermodynamic arguments that at a second-order phase transition with a positive slope in the pT plane, the thermal expansion and the compressibility of the ordered phase are larger than those of the disordered phase [17]. Olijnyk [6] has performed pV measurements at room temperature using x-ray diffraction and found at higher pressures (about 12 GPa) a softening of the isotherm. This can be explained by a positive jump in the compressibility at the localization transition at $p = 10.5$ GPa. There is an interesting analogy with the low pressure orientational disordering in α-N_2, which is triggered by argon as spherical diluent [18,19]. Although the fcc lattice is preserved, the transition is of first order and occurs only in the mixture. In α-N_2 the orientation of the molecules do not flip from one body diagonal to the other as in δ-N_2.

A second-order transition due to orientational ordering has also been observed in ionic systems like NH_4Cl (Ref. [17]). Here the NH_4^+ ions are orientationally localized in both phases: In the high temperature phase the ions are randomly distributed over two orientations, whereas in δ nitrogen the molecules are almost uniformly distributed over all orientations.

Nitrogen has also been investigated extensively by computer simulations. Nosé and Klein [7] performed a molecular dynamics (MD) study, using a Lennard-Jones potential, on δ-N_2. They found a first-order phase transition at 7.0 GPa and 230 K. In the low temperature phase the disks were orientationally ordered and the spheres disordered. Later Belak, LeSar, and Etters [8] performed a Monte Carlo (MC) study, using the sophisticated potential of Etters *et al.* [3]. They found a change in the thermal expansion at about 200 K and 7.0 GPa. As the temperature was lowered from 300 to 200 K, they observed that a degree of orientational localization occurred. On further cooling the localization increased until it was complete at about 120 K, where a structural phase transition occurred. However, the low temperature phase did not have the experimentally determined structure.

Because of the large amount of stray light in the forward scattering geometry we could not observe the phonons. Determination of the profiles of the spectra was not possible due to the signal to noise ratio. For the rotational phonons (with symmetry F_{2g} [12]) we expect a gradual transformation from a rotonic to a libronic character at decreasing T. We expect that the linewidths could reveal interesting effects. The localized molecules will have an increasing orientational correlation time (τ_{cor}) on cooling due to the increasing time scale on which the molecules have fixed orientation (τ_{fix}). The corresponding broadening of the line might come in the slow modulation regime resulting in a Gaussian contribution to the profile of the spectrum [20]. This point needs further investigation with time resolved techniques, but in order to make an estimate on the order of magnitude of the effect we have made a series of 20 measurements of the full width at half maximum on ν_2 around the ϵ-δ phase transition at 9.0 GPa and 173 K. From the average results (0.90 ± 0.03 cm^{-1} in δ-N_2, 0.78 ± 0.03 cm^{-1} in ϵ-N_2), obtained with an instrumental resolution of 0.7 cm^{-1}, we estimate a broadening of 0.4 cm^{-1} in δ-N_2 compared to ϵ-N_2. The dephasing time corresponding to this broadening is 30 ps and is in the slow modulation case much smaller than τ_{cor} [20] and probably also τ_{fix}. Therefore, we indeed expect τ_{fix} to be much larger than the free rotation period which is 1 ps for N_2 at 173 K.

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