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Vibrational line broadening in the mixed solid N_2–Kr: A high-pressure Raman study of the phase diagram

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In this paper, the results of an experimental study on the spectral behavior of the Raman Q branch of nitrogen in the mixed solid N_2–Kr are presented. The experiments have been performed at ambient temperature as a function of pressure up to 15 GPa. On the basis of the results, the *p-x* cross section of the phase diagram is constructed. In the mixture, the β region extends to very high pressures. The maximum amount of krypton dissolving in β-nitrogen is about 85%. As a consequence, the regions where the fcc-Kr lattice and the δ lattice of nitrogen are stable are relatively small. In all phases, the vibrational frequencies of the nitrogen molecule are shifted to lower values compared with neat nitrogen. The most interesting aspect is that in the β solid the linewidth is extremely composition dependent, with maximum values for the mixture with equal mole fractions. It is suggested that the increase in the linewidth is mainly due to an increase in the correlation time rather than an increase of the amplitude of modulation.

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I. INTRODUCTION

In the past decade nitrogen has been the subject of an extensive program, both experimental and theoretical, concerning the spectral behavior of nitrogen molecules and the phase behavior of various binary nitrogen mixtures. The second component, always a noble gas, is chosen in such a way that the effect of the diameter ratio (α) of the components on the phase behavior and, in particular, on the crystal structure can be studied. It is obvious that insertion of a (spherical) molecule, with a smaller or larger diameter, will influence the rotational behavior of the nitrogen molecules. This is reflected in the spectra.

It is generally believed that geometrical aspects play an important role in the formation of compounds and mixed solids.[1–8] Theoretical calculations[9,10] on binary hard-sphere systems predict a monotonic incline of the fluid-solid phase line towards the component with the highest solidification pressure, if $\alpha > 0.94$. The well-known Hume-Rothary rule[11] for binary mixtures dictates mutual solubility if $\alpha > 0.85$, i.e., the molecules/atoms of the first component dissolve in the lattice(s) of the second component and vice versa. On the other hand, in case the diameters differ substantially, the formation of stoichiometric compounds is expected. For spherical molecules, this empirical rule is in good agreement with experiments and computer simulations.

Experimental studies on the binary systems nitrogen-neon[12] ($\alpha = 0.73$ with Ne the smaller component) and nitrogen-xenon[12] ($\alpha = 0.88$, but now N_2 is the smaller component) revealed that the homogeneous mixed fluid extends to high pressures compared to the pure systems, whereas in the nitrogen-argon[13] system ($\alpha = 0.94$; Ar is the smaller component) the melting pressure is almost linear with the composition. Further, in the systems N_2–Xe and N_2–Ne the region of the low-pressure β phase is very small, in contrast with N_2–Ar. In fact, in the latter case, the β phase is stable up to pressures almost twice as high as the β-δ transition pressure in the neat system and the maximum solubility of argon in β-nitrogen is about 75%. Probably related to this high solubility is the fact that, in the case of N_2–Ar, the vibrational linewidth is composition dependent in the β phase and higher than in pure solid nitrogen. In fluid mixtures, such a broadening is due to concentration fluctuations. These fluctuations do not result in a larger amplitude of modulation, as might be expected, but give rise to a longer vibrational relaxation time.[14] Thus, the origin is the local fluctuation in time, not in space. The question then is, what is the reason for line broadening in a solids?

In order to obtain more information about this phenomenon we studied the system nitrogen-krypton. Krypton fits better in the nitrogen lattice than argon, since it has an atomic diameter nearly equal to that of the nitrogen molecule ($\alpha \approx 1$). Therefore, the solubility in the orientationally disordered β phase is expected to be even higher than for N_2–Ar. The mixtures formed are not ideal, as the nitrogen molecule is not perfectly spherical. In this way, it is possible to study the effect of the nonspherical shape of the molecule on the solubility. Since the attractive well depth of the krypton potential is larger than that of argon, we expect broader vibrational linewidths in N_2–Kr than in N_2–Ar mixtures.

The results of the Raman experiments as a function of pressure at ambient temperature will be presented. Special attention has been paid to the linewidths and frequencies in the various high-pressure phases. Together with the information obtained from visual inspection, the spectra have been used to construct the phase diagram of the system.

II. EXPERIMENTAL METHODS

In order to study the phase behavior of the nitrogen-krypton system, mixtures with nitrogen mole fractions x of 0.06, 0.25, 0.50, 0.75, and 0.93 have been investigated by Raman spectroscopy, at elevated pressures and ambient temperature. The mixtures (research grade nitrogen and krypton with a purity of 99.999%) have been prepared in a gas compressor. The gasket was filled at 0.3 GPa, using a high-pressure gas-loading technique.[15] To provide for proper mixing, we waited at least 60 h before loading the sample cell. The pressure was generated in a diamond-anvil cell (DAC). The experimental setup has been described elsewhere.[13] We used the 488-nm line of an argon-ion laser at beam intensities of 400 mW for the Raman measurements. The pressure in the DAC was determined using the ruby fluorescence technique with the scale of Mao and Bell.[16] The absolute uncertainty in the pressure is estimated to be 0.03 GPa in the low-pressure range. At high pressures (above 10 GPa this value could possibly be a bit higher (up to 0.1 GPa). In order to prevent heating of the ruby chip, we used minimum laser intensity during the pressure measurements. All spectra have been recorded using forward scattering with an entrance slit width of 20 μm, resulting in an instrumental width (Lorentzian) of 0.15 cm^{-1} and an absolute accuracy of 0.1 cm^{-1}. The spectra have been recorded along an isotherm (296 K) in the pressure range from 0.3 to 15 GPa. We used 0.1–2 GPa pressure steps and time intervals of 1–3 h, depending on the size of the step.

To determine the peak positions and the full width at half maximum (FWHM), all Raman spectra in the fluid phase (Lorentzian line shape) have been fitted by a single Lorentzian curve. The FWHM was calculated by subtracting the instrumental width from that of the measured spectra. The spectra in the solid phases (Gaussian) have been fitted by one or two ($x=0.75$, up from 6 GPa, and $x=0.93$, up from 13 GPa) Gaussian curves.

III. RESULTS

The vibrational frequencies of the nitrogen molecule in the mixed system (symbols) are presented in Fig. 1. The corresponding widths are shown in Fig. 2. For comparison, the data of neat nitrogen (Refs. 17–19) are also given (solid lines). For pure nitrogen in the fluid phase up from 0.3 GPa, the frequencies increase almost linearly with pressure. The pressure dependence of the FWHM is also linear up from about 0.6 GPa. The solidification takes place at 2.4 GPa and can be observed both visually, through the microscope, and via a jump in the frequency of about 0.95 cm^{-1}. At the transition the linewidth decreases considerably and increases only slightly in the β phase. At 4.7 GPa the solid-solid β-δ transition takes place. This transition is easily detectable since in the δ phase two sites exist. Hence, we find two distinct vibrational modes, δ_1 and δ_2. The corresponding widths for both modes are about 0.4–0.5 cm^{-1}, slowly increasing with pressure.

A. The mixed systems

1. The mixed fluid region

For all mixed systems in the fluid phase, only a single mode was found. The frequencies are shifted to lower values compared with the pure system and the shift is dependent on the composition, with smaller N_2 fractions resulting in a stronger redshift. For $x=0.93$ the frequencies coincide within experimental uncertainty with those of pure nitrogen. Also the widths are dependent on the composition. While for $x=0.93$ the values coincide within experimental accuracy with those of pure nitrogen, for all other mixtures these are higher, with a maximum deviation for the 50-mole % mixture.

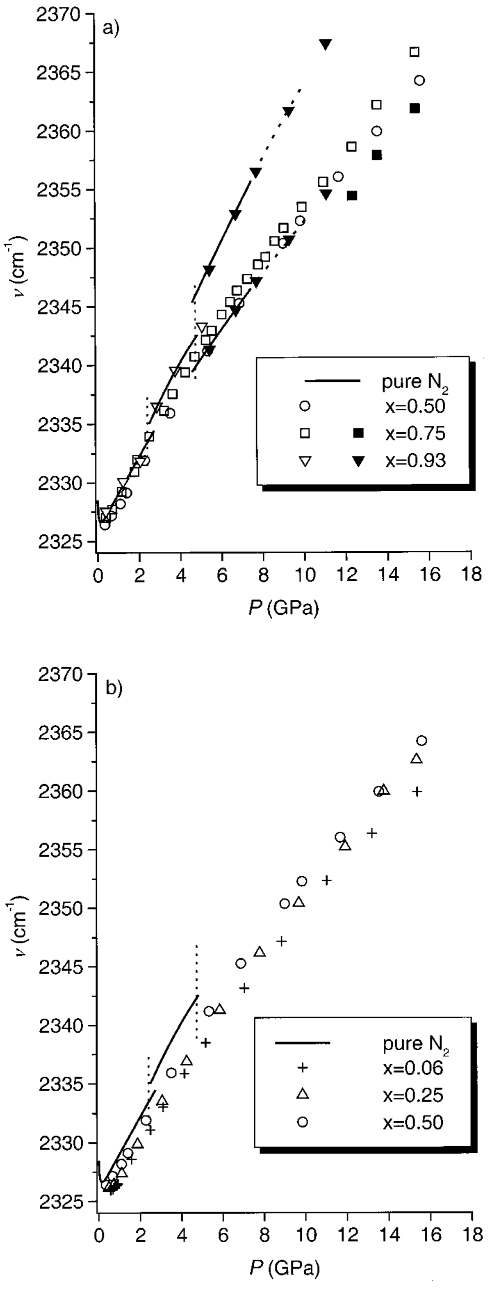

FIG. 1. Vibrational frequency of nitrogen in N_2–Kr versus pressure at 296 K. Symbols: mixtures, full symbols represent the δ^* phase; solid lines, pure nitrogen. The dashed vertical lines indicate the fluid-β and β-δ phase transitions in pure N_2.

2. Transition to the solid phases

To avoid misinterpretation, all solid phases in the mixed system are indicated with an asterisk (e.g., β^*, δ_1^*, etc.). The fluid-solid coexistence region is small for all compositions and is entered for increasing nitrogen mole fractions at 0.9, 0.9, 1.4, 1.8, and 2.2 GPa, respectively. The transition could clearly be detected by visual inspection. The frequency

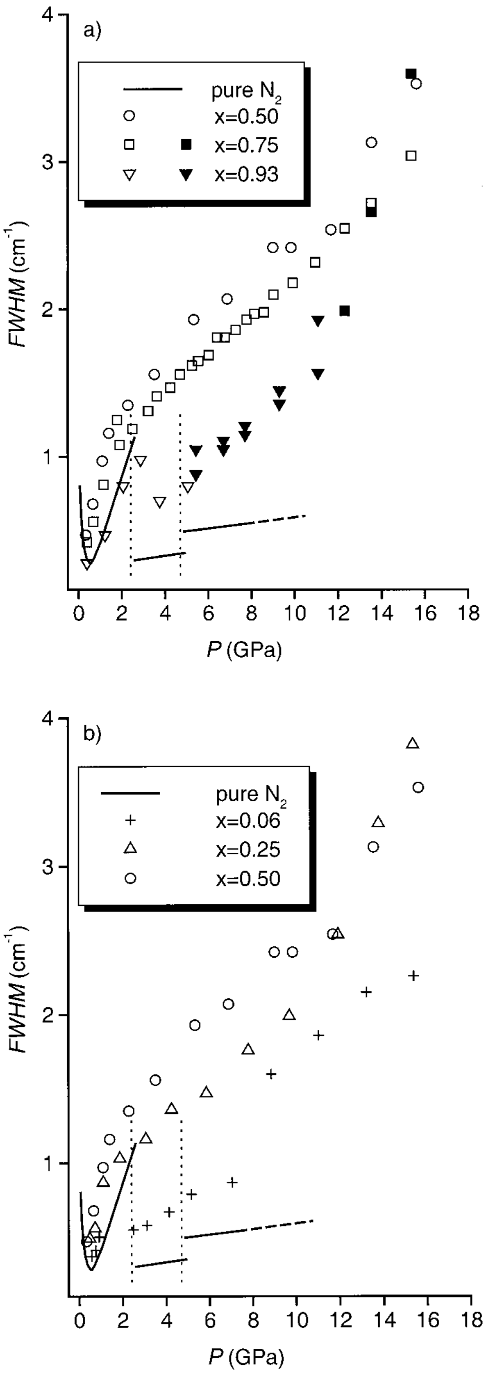

FIG. 2. FWHM versus pressure at 296 K. Symbols: see Fig. 1.

jump at the transition, which is characteristic for the fluid-solid transition in pure systems, is reduced in the mixed systems and is only detectable for $x=0.93$ and 0.75. For all other compositions no discontinuity in the frequency was found, however the transition is demonstrated visually and by a change in behavior of the FWHM. As in the fluid phase, the frequencies are shifted to lower values compared with the pure system and the shift is dependent on the amount of nitrogen.

For $x=0.93$ the frequencies coincide within experimental accuracy with those of pure β-N_2, as in the fluid phase. In the pressure region where for the pure system the β phase is the stable structure, for all mixtures the dependence is linear with pressure. The behavior of the width, however, is quite remarkable. First, there is a very strong composition dependence. For example, in the sample with 50% krypton, at 4.5 GPa, the width is five times larger than in pure nitrogen. Moreover, the pressure dependence is much stronger in the mixed system. Finally, the discontinuity in the width at the transition deviates considerably from that in pure N_2. Only for $x=0.93$ is there a relatively small discontinuity in the width. For all other mixtures, only a discontinuity in the slope of the width against pressure is observed at the transition.

3. The solid-solid transition

At still higher pressures, the most striking difference in the measured frequencies is the fact that for $x=0.75$ and 0.93, we find additional modes (see Figs. 3 and 4), while for the samples with lower x values no additional modes have been found up to the highest pressures investigated (15 GPa). In the case of low nitrogen concentrations, no discontinuity in the frequency was found. In all cases, the slope in the frequency against pressure shows a tendency to decrease with increasing pressure.

For $x=0.93$ the low-pressure solid mode is no longer present at pressures slightly higher (5.5 GPa) than the β-δ transition pressure in pure N_2, but instead we find two new modes, δ_1^* and δ_2^*. Both modes consist of double peaks, as can be seen in Fig. 3 (lower two spectra). At increasing pressure (upper two spectra), both modes broaden strongly and the double nature is less pronounced, but still present. Fitting both modes with just one curve, the main peak positions coincide within experimental accuracy with those of pure δ-nitrogen. The widths, however, are much higher than in the pure system and increase strongly with pressure.

Looking at the results of the $x=0.75$ mixture, at about 12 GPa a new mode appears at lower frequencies, while the low-pressure solid mode (β^*) continues to be present (see Fig. 4). When the laser is focused on a different spot in the sample space, the intensity ratio of the two signals changes. This shows that two different phases are present in the DAC. With increasing pressure, the intensity of the new mode slowly becomes stronger, although the signal broadens extremely with pressure. Due to the overlap with the β^* signal, it is not possible to ascertain whether the new mode consists of a double peak. Both signals stay present up to the highest pressures investigated. The frequencies of the new mode are about 2 cm^{-1} lower compared with the extrapolation of the δ_2^* mode ($x=0.93$) but the widths are comparable.

Finally, for $x<0.75$ the frequencies increase monotonically with pressure, without any discontinuity up to the highest pressures investigated. Hence, from Fig. 1(b) no information can be obtained concerning the location of possible phase transitions. Looking at the FWHM, for $x=0.50$ and 0.25 we find a sudden increase in the width above 12 and 10 GPa, respectively, while for $x=0.06$ a discontinuity occurs at about 9 GPa.

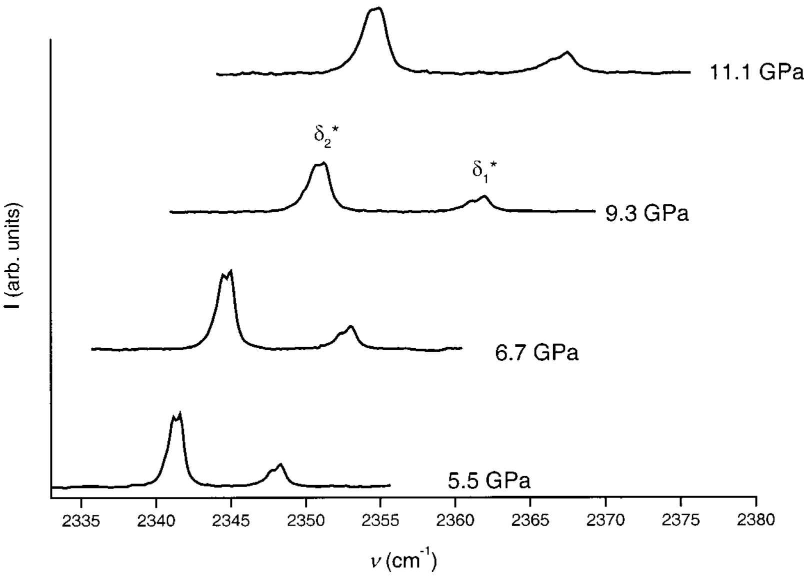

FIG. 3. Raman spectra of nitrogen in N_2–Kr at ambient temperature in the δ^* phase, $x = 0.93$.

4. Spectral line shape

It is interesting to notice that, while in pure nitrogen the line shapes are Lorentzian in all phases, in the mixed system with x values in the intermediate range ($x = 0.25–0.75$) the line shape changes at the fluid-solid transition from Lorentzian to almost Gaussian and remains almost Gaussian at higher pressures. Even for the 93 mole % sample, although the line shape is not completely Gaussian in the solid phases, we find a large Gaussian component up from the fluid-solid transition pressure.

In Fig. 5(a) the spectral linewidth is plotted against the mole fraction. The squares represent the FWHM in the fluid phase at 0.7 GPa. The figure shows clearly that the linewidth is strongly dependent on the concentration. The FWHM shows a maximum around $x = 0.50$. The width at this maximum is about twice that for pure N_2.

When comparing these experimental results with those in the solid phase at 5.0 GPa (circles) it is clear that the maximum in the width occurs at the same mole fraction but the concentration dependence of the width in the solid is even stronger, with a maximum value about five times that in the pure system.

IV. SUGGESTED PHASE DIAGRAM

From the experimental results, the p-x cross section of the phase diagram for the N_2–Kr system at ambient temperature is constructed (see Fig. 6). The following will also demonstrate the problems occurring in constructing the phase diagram.

A. The fluid-solid transition

From visual inspections, it is clear that for all mixtures, the fluid is homogeneous. The melting pressures for krypton and nitrogen at ambient temperature are 0.83 and 2.47 GPa, respectively. In the mixture, the two-phase-area fluid solid is entered at, respectively, 0.9, 0.9, 1.4, 1.8, and 2.1 GPa at increasing mole fractions, hence we find a monotonic incline

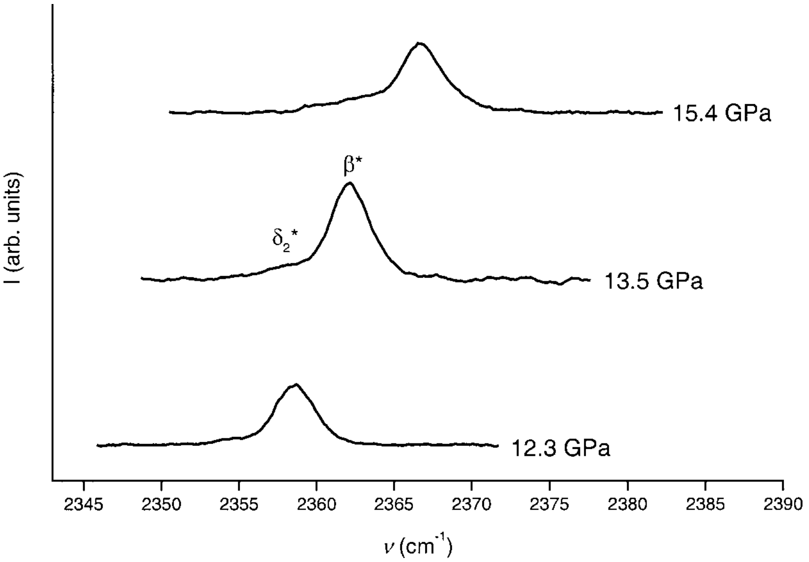

FIG. 4. Raman spectra of nitrogen in N_2–Kr at ambient temperature, in the β^*-δ^* coexistence region; $x = 0.75$.

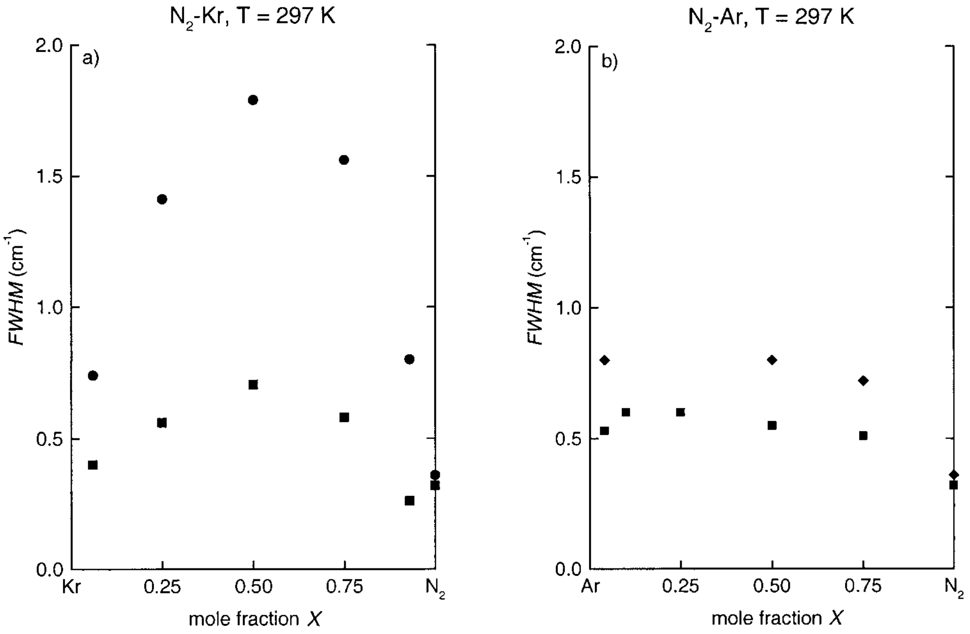

FIG. 5. FWHM against the nitrogen mole fraction for (a) nitrogen diluted in N_2–Kr and (b) nitrogen diluted in N_2–Ar in the low-pressure solid phase at 0.7 (squares) and 5.0 GPa (circles). All points except those for pure N_2 have been obtained by linear interpolation. Note that the experimental value of the frequency of pure β-N_2 has been obtained by linear extrapolation, since pure nitrogen is in the δ phase at this pressure.

of the two-phase line, which is in accordance with theoretical calculations mentioned earlier. From visual observations it is clear that, for all mixtures, the fluid-solid region is small (a few kilobar), but smallest for $x = 0.93$.

B. Solid-solid transitions

For $x = 0.93$ at 5.4 GPa a second two-phase area (β^* δ^*) is entered and the spectrum consists of three modes, one of which belongs to the β^* phase and the other two, δ_1^* and δ_2^*, correspond to the a and the c sites of the δ^* phase, respectively. At 5.5 GPa the lower boundary of the δ^* region is crossed since up from 5.5 GPa the β^* signal is no longer present and the spectrum consists of both delta modes only.

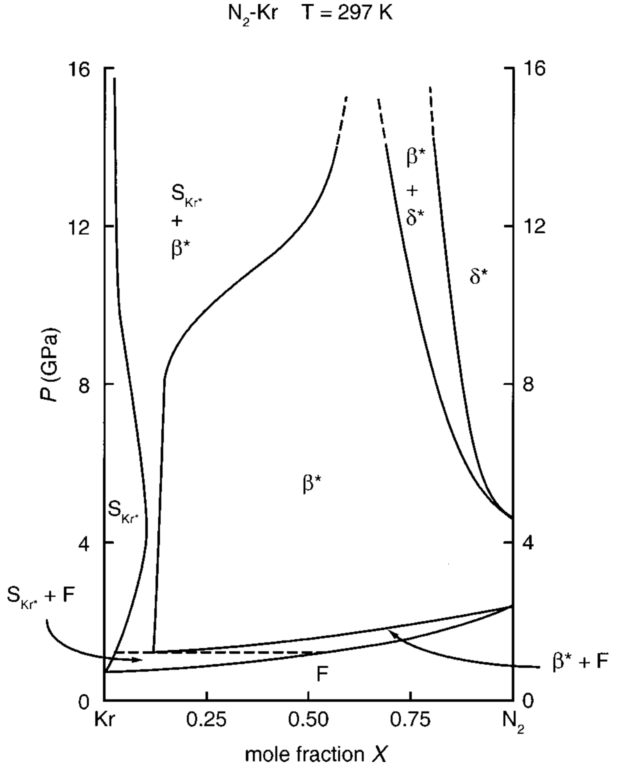

FIG. 6. Suggested p-x diagram at 296 K for the N_2–Kr system. Solid lines: two-phase lines, horizontal dashed line: three-phase line.

In the 75-mole % mixture, the transition to the $\beta^* - \delta^*$ region is more difficult to indicate. First of all, at the transition the intensity ratio slowly changes with pressure and secondly, the signals overlap due to the increasing broadness at high pressure. At 12 GPa, however, evidently the spectrum consists of two modes. Since α is nearly one, the formation of a van der Waals compound is very unlikely. Therefore, the most obvious possibility involves a transition to δ^*. The fact that the peak position of the new mode is shifted to lower values compared with δ_2^* in the 93-mole % sample is consistent with the fact that in the mixtures at decreasing nitrogen fractions all frequencies show an increasing redshift. Further, the absence of δ_1^* could be explained by realizing that, in the pure system, the integrated intensity of this mode is three times as small as that of δ_2^*, since the unit cell consists of six c and two a sites. In the mixture, this ratio could be different. For example, the krypton atoms exhibit a preference for one of the two sites, as is the case in the nitrogen-argon system.[20] However, in this system the intensity ratio is comparable with the pure system (as shown for $x = 0.93$), hence there is no evidence for any preference.

In conformity with experimental findings, Monte Carlo simulations on various binary mixtures with noble-gas atoms in solid nitrogen[21] show that the position of the atoms depends on the diameter ratio α. Smaller atoms ($\alpha < 1$) show a preference for the a sites, while larger atoms ($\alpha > 1$) prefer the c sites. For $\alpha = 1$ no preference was found. Concluding, although only one new mode appears at pressures up from 12 GPa, it is very likely that this signal marks the transition from β^* to δ^*. Considering the slow change in the intensity ratio both boundaries of the two-phase region must run quite steeply towards one another.

For the mixtures with $x < 0.75$ the spectra contained no δ^* modes, up to the highest pressures investigated (15 GPa). Therefore the right β^* boundary must be situated between $x = 0.50$ and 0.75 at 15 GPa.

Concerning the boundary of the region where the krypton-fcc structure, indicated as $S_{\mathrm{Kr}*}$, is stable, several difficulties arise. First of all, no discontinuity in the frequency was found in the entire pressure range for all samples with $x < 0.75$. In addition, in contrast to fluid-solid transitions in this system, solid-solid transitions do not show visually. However, based on the difference in behavior of the FWHM for the various mixtures, some suggestions can be made. Looking at the spectral linewidth in Fig. 2(b), for $x = 0.50$ and 0.25, a change in the slope can be observed above 12 and 10 GPa, respectively, likely to be associated with a phase separation.

For $x = 0.06$ the evolution of the FWHM with pressure looks different; the change in the slope of the linewidth, which occurs at 9 GPa, is more abrupt. It is reasonable to assume that for the first two mixtures the change in the slope marks the boundary of the β^* phase. This means that there must be a rather sharp change in the phase boundary; within a pressure interval of about 2 GPa the maximum solubility of krypton in β-nitrogen decreases from 50% to 25%. On the other hand, there is no sign of the existence of a stoichiometric compound for high krypton concentration. Since there is also no known phase transition in solid krypton, the coexisting phase is probably the Kr–N_2 mixed solid (fcc), indicated as $S_{\mathrm{Kr}*}$ in Fig. 6. The behavior of the linewidth for $x = 0.06$ can be explained as follows. The increase in linewidth is due both to the appearance of the fcc solid and to the rapid change in the composition of the β^* phase, which has a much broader Raman line [Fig. 5(a)]. At higher pressures the relative amount of β^* in the sample decreases and therefore, the linewidth does not show a second change (increase) in the slope.

V. DISCUSSION AND CONCLUSIONS

A remarkable phenomenon is the fact that, in the solid phases, the mixed N_2–Kr system shows very broad vibrational lines. While in the pure system the FWHM reduces considerably at the fluid-solid transition pressure and remains well below 0.5 cm^{-1} in the β phase, as can be seen in Fig. 2, in the 25-, 50-, and 75-mole % mixtures, the widths are barely or not at all reduced at the transition. As a result, in the mixed solid the line is much broader than in pure nitrogen. Even in the diluted solution with $x = 0.93$, the widths are more than twice those in the pure component. Moreover, the FWHM in the homogeneous mixed β^* phase increases strongly with pressure, from about 1 up to 2, 2.5, and even 3 cm^{-1} for $x = 0.25$, 0.50, and 0.75, respectively, while there is only a weak pressure dependence in neat β-nitrogen. Also the δ^* modes in the homogeneous phase [$x = 0.93$, Fig. 2(a), solid triangles] are much broader compared to the pure system. Note that for pure nitrogen no data on the linewidth is available for pressures above 8 GPa. To our knowledge, such an extreme broadening in a crystalline solid has not yet been reported.

The phenomenon of the occurrence of a maximum in the FWHM at equal volume fractions for noncritical concentration fluctuations in binary fluids has been predicted.[22] Previous experimental results on the systems CH_3I–$CDCl_3$,[23,24] N_2–He,[25] N_2–Ne, and N_2–Ar confirm this hypothesis. The solid phase regions ($S_{\mathrm{Kr}*}$ and β^*) in the systems N_2–Ne and N_2–Xe, due to very low solubility, are too small to make an appropriate comparison. Since the solubility of Ar in β-nitrogen is large, the results on the linewidth can best be compared to those of the N_2–Ar system. In this system all values remain well below 1 cm^{-1} in the homogeneous β^* phase.

For convenience, the FWHM-x data of N_2–Ar are pictured in Fig. 5(b). For both systems the squares represent the widths in the homogeneous fluid at 0.7 GPa and the circles those in the homogeneous low-pressure solid phase at 5.0 GPa. It must be noticed that in the given pressure and temperature interval both systems are far from critical conditions. It is clear that the effect of the concentration on the linewidth is considerable enhanced in the fluid krypton mixture compared to the fluid argon mixture. In the solid phase, the differences are even much larger.

In the following, we will try to explain this behavior for the N_2–Kr system. It has been shown previously that differences in intermolecular forces of the components of a mixture lead to a variation of both the frequency and the linewidth with composition. The effect on the linewidth is mainly due to the long-range forces. Since the attractive well depth of the krypton potential is larger than that of nitrogen, we expect lower frequencies for N_2 in N_2–Kr compared to the pure system. The difference in the well depth between argon and nitrogen is much smaller.

There seems to be a contradiction for the solid phase; in order to obtain a good mutual solubility in the solid phase, the intermolecular interaction should be more or less the same for both components. On the other hand, for a substantial effect of the composition on the linewidth, the interactions should be different. One should realize, however, that the repulsive forces play a major role in the solubility, and the long-range forces in the linewidth. The size of the krypton atoms is nearly that of nitrogen molecules but the attractive forces are much larger for Kr. The contribution of concentration variations to the linewidth will be small for krypton- and nitrogen-rich mixtures, since the environment of the nitrogen molecules will mainly consist of Kr, respectively, and N_2, and will not change much in time and space. On the other hand, for equal mole fractions, the variation in the environment is maximum. For that reason, in the solid phase, the widths will show a maximum at equal mole fractions. Note that, in the fluid, it will be at equal volume fractions but this is nearly the same, since $\alpha \approx 1$.

Why is the concentration effect on the width so much higher in the solid than in the fluid phase? To answer this question we first define a few important parameters. The vibrational linewidth is determined by the standard deviation of the distribution of the momentary vibrational frequency (the amplitude of modulation Δ),

$$\Delta = \sqrt{\langle \omega_{\mathrm{vib}}^2 \rangle - \langle \omega_{\mathrm{vib}} \rangle^2} \tag{1}$$

and by the correlation time τ_c,

$$\tau_c = \lim_{t\to\infty} \int_0^t \Omega(s)ds \tag{2}$$

with the autocorrelation function of the frequency

$$\Omega(t) = \frac{\langle \omega_{\rm vib}(0)\omega_{\rm vib}(t)\rangle - \langle \omega_{\rm vib}(0)\rangle^2}{\Delta^2}. \tag{3}$$

The total change in the vibrational frequency $\omega_{\rm vib}$, due to surrounding molecules, consists of several contributions: the first- and second-order effects of the external forces, the vibration-rotation coupling and the dispersion correction. Therefore, the total correlation function contains self-correlations and cross terms. Hence, the correlation time consists of a sum of terms for each of the effects.[26]

According to the Kubo theory, for two limiting situations the line shape and the linewidth are given by simple expressions. In the fast modulation regime ($\Delta\tau_c \ll 1$) the line shape is Lorentzian and the linewidth can be calculated with $\mathrm{FWHM} = 2\Delta^2\tau_c$. In the slow modulation regime ($\Delta\tau_c \gg 1$) the line shape reflects the momentary frequency distribution and the width is given by $\mathrm{FWHM} = 2\Delta$.

Molecular-dynamics (MD) simulations on N_2 in N_2–Ne in the homogeneous fluid phase showed that Δ merely decreases as a function of the nitrogen volume fraction. In addition, a strong maximum in τ_c at equal volume fractions was found. Therefore, it was concluded that the increase in the linewidth for the intermediate compositions is caused by the increase of the correlation time rather than an increase of the amplitude of modulation. Moreover, this increase was mainly due to the dispersion correction. It is not to be expected that, in the solid, the change in Δ, due to concentration variations, is much different from that in the fluid. Since the diffusion is slower in a solid, a change in the local composition will most probably take more time in the solid than in the fluid phase. Therefore, the correlation time of the dispersion correction, and thus the linewidth, will also be larger. Moreover, the largely Gaussian line shapes also point into the direction of a large correlation time.[24] Although MD calculations on the system N_2–Kr in the solid region are necessary to answer the question, it seems more obvious to assume that, in this system, not only in the fluid but also in the solid phase, the line broadening for the intermediate compositions is caused by an increase of the correlation time rather than by an increase of the amplitude of modulation.

The fact that the frequencies in the fcc-Kr lattice coincide within experimental accuracy with those in the hcp-β^* lattice is consistent with results on the N_2–Ar system. MD simulations on pure nitrogen[27] in the disordered hcp and the disordered fcc lattice, at 3.3 GPa and ambient temperature, showed that the difference in frequency for both structures is less than 0.1 cm^{-1}. Finally, a few remarks will be made about the phase diagram. To calculate values for α we used the data of Ref. 28 for all systems discussed. In conformity with calculations mentioned earlier on hard-sphere systems with nearly equal diameter, the experimental findings show a monotonic increase of the fluid-solid transition line as a function of the nitrogen concentration and the fluid-solid region is small. The maximum amount of krypton dissolving in β-nitrogen is about 85%, which is slightly more than the solubility of argon in β-N_2. The maximum solubility of nitrogen in krypton, however, is likely not more than 10%.

In the low-pressure region, the system deviates only slightly from that of N_2–Ar in the sense that the two-phase region where the fcc and hcp structures coexist, is narrower. Evidently this is due to a value of α that is closer to 1 in the case of krypton. Hence, the mutual solubility is higher. Since the results are analogous to those for N_2–Ar up to about 5 GPa the reader is referred to Ref. 13 for discussion of this part of the phase diagram.

A remarkable difference with N_2–Ar is the fact that the β^* structure is stable up to very high pressures. Apparently this structure is more suitable for rotating molecules, i.e., the rotational entropy is higher compared to that of the fcc or δ^* structure. Further, the communal entropy in the homogeneous phase is higher than in coexisting phases with low mutual solubility. Evidently, these arguments also hold for N_2–Ar but, since krypton is slightly larger than argon, krypton fits better in the β structure. Especially at high pressures when the structure is more compressed, this detail plays a more important role. Finally, as a consequence of the large β^* region up to very high pressures, the δ^* region is small compared to that of N_2–Ar. The splitting of both δ^* modes into peaks with equal intensity, in the mixture with $x = 0.93$, is not understood and has never been reported before, to the best of our knowledge, for binary systems with nitrogen.

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