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Infrared spectroscopy of the $Ar_{1-x}(N_2)_x$ quadrupolar glass

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The regions of the N-N and of the C-O stretching vibration of $Ar_{1-x}(N_2)_x$ mixed crystals, $0.5<x<1$, doped with CO have been investigated by infrared spectroscopy. The spectra give insight into the dynamics of the translational and rotational lattice modes. The appearance of infrared activity of the N-N vibron upon freezing into the quadrupolar glass indicates local symmetry breaking.

I. INTRODUCTION

In mixed crystals, in which an aspherical species is partially substituted by spherical molecules, an orientational glass state[1] is observed. Prominent examples are $(\text{para-}H_2)_{1-x}(\text{ortho-}H_2)_x$, $Ar_{1-x}(N_2)_x$, and $(KBr)_{1-x}(KCN)_x$. The relevant multipole moment of the aspherical component (ortho-H_2, N_2, CN) is the quadrupole moment. The concentration x, temperature T phase diagram of these systems shows three principal regimes: the high-T "para" phase with dynamical orientational disorder, the low-T, high-x phase with long-range orientational order, and the low-T glass state with a crystalline center-of-mass lattice and randomly frozen-in quadrupole moments for $x<x_c$. For $Ar_{1-x}(N_2)_x$ and p-o-H_2 the center-of-mass lattice of the disordered and of the glass state is hcp, the ordered phase has an fcc center-of-mass lattice, and the moments are ordered in a four-sublattice configuration ($Pa3$ space group).[2-4] x_c is 0.80 for $Ar_{1-x}(N_2)_x$ and 0.53 for p-o-H_2. For the hydrogen system the hcp phase is stable from x_c down to lowest x. This allows one to study the glassy state for lower and lower ortho concentration until finally the situation of isolated quadrupolar impurities in a matrix of spherical molecules is reached. For $Ar_{1-x}(N_2)_x$ existence region of the hcp quadrupolar glass state is limited by the appearance of the Ar-rich fcc phase.[2] The fcc-hcp crossover concentration is about $x=0.2$, but can be shifted by cold working up to 0.5. This leaves a relatively small concentration range $(0.5<x<x_c)$, where one can safely assume that the low-temperature state is single-phase hcp.

Very much in analogy to the spin glasses,[5] the appearance of a glassy state is thought to result from frustrated interactions between the quadrupole moments which occupy the lattice sites randomly. In theoretical treatments this situation is described by a lattice of quadrupoles coupled through random anisotropic interactions, such as the electrostatic quadrupole-quadrupole interaction for $Ar_{1-x}(N_2)_x$ and p-o-H_2. It has been realized[4] that quadrupoles obey symmetries different from those of (magnetic) dipoles, the main consequence being that the quadrupolar random interaction model automatically introduces random quadrupole fields, which in turn give rise to finite values of the quadrupolar glass order parameter[6,4,7] q at any finite T. In a nonrigid center-of-mass lattice the size differences of the substituents are a second source of random (stress) fields, which in turn, act on the quadrupole moments via the translation-rotation coupling.[7]

The experimental information on the quadrupolar glass state of $Ar_{1-x}(N_2)_x$ comes from NMR,[8,9] inelastic neutron scattering,[10] x-ray[11,3] and neutron diffraction,[10] and calorimetry,[12] complemented by dielectric relaxation measurements[13] and ^{13}C NMR (Ref. 14) on the related ternary system Ar:N_2:CO. Here it is assumed that the CO molecule follows the orientational dynamics of the N_2 system. It is agreed upon that there is no phase-transition-line onset of the glass state, but that the system freezes-in gradually. The widths of the NMR lines[8,14] and of the Bragg peaks in the diffraction experiment[11,3] have been regarded as a measure of the glass order parameter q.

This paper deals with the infrared spectroscopy on the N-N and C-O stretching band region of $Ar_{1-x}(N_2)_x$, $0.5<x<1$, doped with 0.1% CO. The experiment will give information on the density of states of the lattice modes and on low-frequency diffusive modes. The unexpected appearance of the N-N vibron in the ir response will be related to the glass order parameter.

II. EXPERIMENTAL

Appropriate proportions of the gases Ar, N_2, and CO have been prepared in an all-metal gas handling system equipped with a pressure gauge (1000 mbar full scale) and have been liquified sequentially in the cold sample cell. The nominal purity of the Ar and N_2 gases is better than 99.9997%. The composition of resulting liquid mixtures is $Ar_{1-x}(N_2)_x$ doped with $(0.1\pm0.02)\%$CO, $x=0.5, 0.55, \ldots, 1$. The absolute error of the gauge translates into an accuracy of 0.01 in x. In order to avoid demixing in the liquidus-solidus region, the liquid mixtures have been solidified rapidly. The solid has been annealed at 57 K, slightly below the solidus line, for homogenization by diffusion. The presumably coarsely polycrystalline hcp solid shows very good light extinction between crossed polarizers indicating that the birefringence is negligible, as one expects for an unstressed hcp solid with an ideal c/a ratio.

Infrared spectra have been taken every Kelvin on cooling and heating. The sample cell is made out of Cu and is equipped with two CaF_2 windows. The absorbing path length between the windows is 0.6 mm. The cell is

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mounted to the cold plate of a closed cycle refrigerator. The temperature of the cell is measured with a Si diode with an accuracy of 0.2 K. The temperature is stabilized by electrical heating in combination with a temperature controller. The minimum temperature of the cell is about 8.5 K, a good stabilization of the temperature (± 0.05 K) is achieved down to 10 K. The comparison of infrared and x-ray-diffraction data on the hcp-$Pa3$ phase boundary $T_c(x)$, $x > 0.80$, shows that the temperature of the cell and of the sample are identical within the accuracy of the thermometers. The infrared transmission data have been taken with an infrared Fourier spectrometer Nicolet DX320. The nominal resolution is 2 cm^{-1}. The Genzel-Happ apodization is used. The resolution of the spectrometer was tested in reference measurements on gaseous CO. The vibrational-rotational lines are well described by Gaussians with a half-width (full width at half maximum) of 1.75 cm^{-1}. Perturbing interference fringes from and between the windows have been eliminated by subtracting background spectra obtained with solid Ar in the cell. The spectra will be given in terms of the absorbance $A = -\log_{10}(I/I_0)$ versus ν. Even for the strongest features in the stretching band regions the ratio I/I_0 is never smaller than 30%. The spectra at a given temperature obtained on cooling and heating are identical, except for x, T states in the hcp-$Pa3$ hysteresis region. The doping with CO has no effect on the N_2 stretching band region as verified in reference measurements on CO free samples with $x = 0.7$ and 1. The absorption line of the ν_3 vibration of CO_2 impurities at 2349 cm^{-1} will be suppressed in the figures of the spectra. No attention will be paid to the vibrations of molecules with isotope combinations other than the most abundant one.

III. N-N STRETCHING BAND

Figure 1 shows a series of spectra on pure N_2, $x = 1$, $T = 10$, 20, 30, 40, and 50 K. These spectra are identical to previous ones of other authors, see, e.g., Ref. 15. The factor group analysis of the α phase requires the N-N vibron to be infrared inactive.[16] In the spectra of the α phase, $x = 1$, a very small signal is nevertheless present at the vibron frequency ($= 2327$ cm^{-1}). The appearance of this signal had led to some discussion[16] whether the space group is $P2_13$ rather than $Pa3$. It is now accepted that the finite intensity is induced by lattice faults such as grain boundaries or domain walls formed by the hcp-$Pa3$ transformation. The other features in the stretching band region are interpreted as infrared activity of the N-N stretching mode induced by lattice modes. Thus they are due to a special type of a two-phonon absorption process,[17] where one of the phonons involved is the vibron and the other one is a lattice mode, which can be either a translational mode of the center-of-mass lattice or an angular mode (libron). Since, furthermore, the bandwidth of the vibron (about 1 cm^{-1}) is small compared to the bandwidth of the lattice modes, the absorbance of the sideband structure mirrors the density of states of the lattice modes:[17,18]

$$A(\nu') \sim g(\nu') \cdot [n(\nu',T)+1]/\nu' \ ,$$

for $\nu' > 0$ and with $n(\nu',T)$ instead of $n(\nu',T)+1$ for $\nu' < 0$, $\nu' = \nu - \nu_{N\text{-}N}$. $n(\nu',T)$ is the Bose thermal population factor and $g(\nu')$ is a weighted density of states of the lattice modes. The weight accounts for the matrix element for a two-phonon infrared-absorption process, in particular $g(\nu')$ does not contain totally symmetric lattice modes. On this basis and guided by inelastic neutron-scattering results,[19] the peaks of the sideband of the α phase at $\nu' = 37$ and 66 cm^{-1} have been assigned to translational modes, while the peaks at 48 and 57 cm^{-1} are assigned to librational modes. At higher T these features broaden and shift.[15] The residual absorbance above the cutoff frequency, about 70 cm^{-1}, of $g(\nu')$ is due to multiphonon processes. The T shift of the individual features and the strong response above the cutoff frequency suggest[15] that the α crystal is strongly anharmonic.

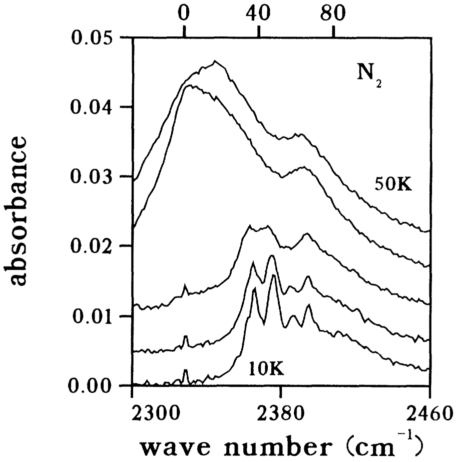

FIG. 1. N-N stretching band region of N_2, for $T = 10$, 20, 30, 40, and 50 K. The absorbance scale is for the 10-K spectrum. The other spectra are offset in steps of 0.05 vertical units.

In the orientationally disordered β phase the sideband structure is rather smooth, without sharp features. Similarly broad spectra have been reported in the lattice mode region of the infrared and Raman spectra.[20–22] There is some controversy concerning the assignment of the residual structures in the spectra to translational and librational modes, including the question whether librations are at all supported by the β phase.[23] Our spectra clearly show a maximum of about $\nu' = 65$ cm^{-1}, for which we favor—in contradiction to Medina and Daniels[20]—an interpretation in terms of center-of-mass phonons, since a translational mode at this frequency has been observed by neutron scattering. In addition it appears plausible that the high-frequency phonons of the hcp phase have frequencies comparable to those of the fcc center-of-mass lattice of the α phase. Just above T_c ($T_c = 35$ K, Ref. 16), the dominant component of the sideband peaks at $\nu' = 0$, i.e., at the origin of the stretching band. The low-frequency part of the spectrum is rather reminiscent of a relaxor spectral response than of the density of states of a harmonic crystal. It is plausible to think of these relaxation processes in terms of the orientational diffusion of the N_2 molecules between the easy axes of the crystal field. Fits of a broad thermally weighted Lorentzian profile centered at $\nu'=0$ to the data are however not satisfactory. Such fits leave the negative curvature of the experimental spectrum for $\nu'<40$ cm^{-1} unexplained and rather suggest that there are additional modes, mainly around $\nu'=15$ cm^{-1} whose weight increases with increasing temperature, eventually giving rise to the maximum at this frequency at highest temperatures. The first excited level of a free N_2 rotator is at a frequency of this order.[23] Thus we favor the idea that the librons of the β phase are always overdamped and that the picture of orientational diffusion is more appropriate. At highest temperature, the N_2 molecules are quasifree rotators.

The mixed crystals are represented by two sets of spectra, see Fig. 2 for $x=0.9$, representing those mixed crystals which still show the hcp-*Pa*3 transformation and Fig. 3 for $x=0.7$, representing the glass forming systems. All mixed crystals show the strongest absorbance around the vibron frequency, i.e., at $\nu'=0$. The response of the hcp phase of the mixed crystals consists of a zero-phonon-vibron spike, whose width is resolution limited, a broad maximum around $\nu'=65$ cm^{-1}, and an additional quasielastic approximately Lorentzian-shaped contribution, which grows and broadens with increasing T in such a way that the high-T spectra of the mixed crystals are—apart from the vibron spike—quite similar to those of β-N_2. Towards low T the quasielastic component sharpens until—at about 20 K—we can no longer separate it from the vibron spike. Although we were unable to decompose the spectrum in an unambiguous way, it is clear that the half-width of the quasielastic component decreases monotonically with decreasing temperature in a way similar to the width of the C-O stretching band (see below, Fig. 10). As for β-N_2 we propose that the quasielastic component is due to orientational relaxation. Because of the narrowing, a structure around 20 cm^{-1} becomes visible in the low-T spectra, which we assign to low-frequency lattice modes, most of them being presumably librational modes.

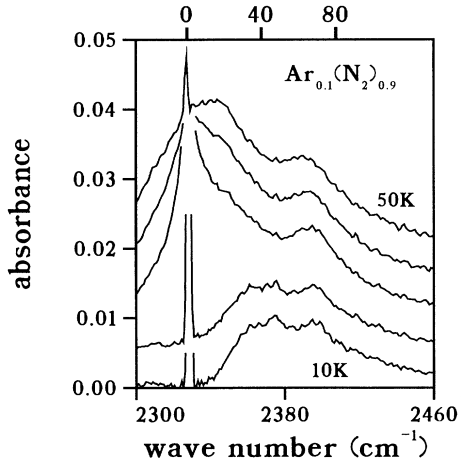

FIG. 2. N-N stretching band region for $x=0.9$.

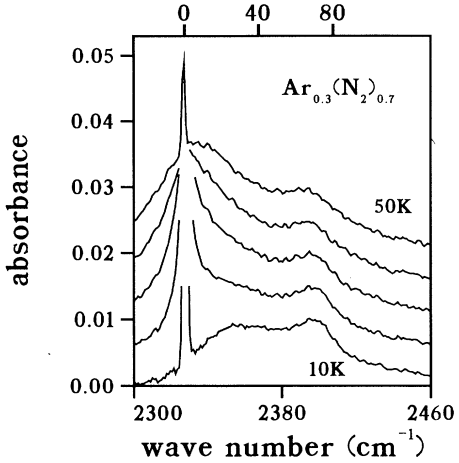

FIG. 3. N-N stretching band region for $x=0.7$.

Note that modes at comparable frequencies in a far-infrared study of the lattice mode region of β-N_2 have been interpreted as strongly damped librons.[22] The maximum at 65 cm^{-1}, representing the high-frequency lattice modes, is not affected by chemical substitution.

The sideband of the mixed crystals in the α phase is a smeared out variety of the α-N_2 sideband. This may be partly due to an enhanced anharmonicity because of increased librational amplitudes, as has been suggested on the basis of Raman measurements,[24] but also to the formation of local modes in different chemical local environments. Roughly speaking the sideband of an α-mixed crystal is similar to that of α-N_2 at a higher temperature.

A Gaussian profile has been fitted to the vibron spike. The Gaussian width has been held at a constant value as given by the instrumental resolution. The x and T dependence of the Gaussian integrated absorbance A and position $\nu_{\text{N-N}}$ is shown in Figs. 4, 5, and 6. There is no hysteresis of $A(T)$ and $\nu_{\text{N-N}}(T)$ except for the hcp-*Pa*3 transformation region (where the data shown are for cooling). For all concentrations, A and $\nu_{\text{N-N}}$ increase with decreasing T. Figure 4 suggests that A, the integrated absorbance of the vibron, disappears in the high-T limit. For $x=0.90$, 0.85 the more abrupt changes of A and $\nu_{\text{N-N}}$ are connected with the phase transition. The transition is of first order, nevertheless jumps of $\nu_{\text{N-N}}(T)$ cannot be expected because of an α-β coexistence region. The width of the coexistence region increases with increasing Ar content.[3] Therefore, the changes of the vibron parameters at the transition are smoother for $x=0.85$ than for 0.90. (For $x=1$ and 0.95 the vibron line is too weak for a precise determination of the parameters.) Raman studies,[25,26] both for $x=1$ and 0.85, show that the vibron line shifts and splits into an A_g and a T_g component when entering into the α phase, in agreement with the factor group analysis. Our $\nu_{\text{N-N}}(T)$ data are consistent with the Raman data if we assume that the vibron line of the infrared spectrum mirrors the A_g component. Furthermore, if the infrared-active vibron would borrow mode strength from both components in about

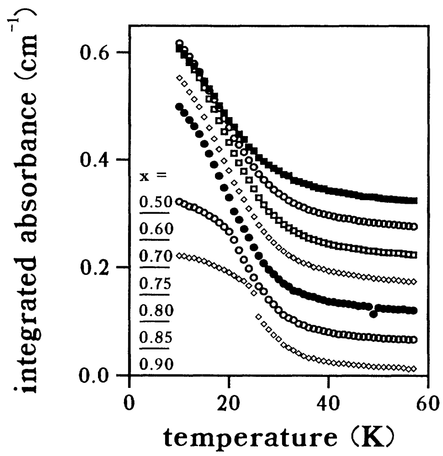

FIG. 4. Integrated absorbance of the vibron spike. The vertical scale refers to $x = 0.9$. The other curves are shifted in the vertical direction. The zero levels are given by the horizontal bars below the specification of the sample composition.

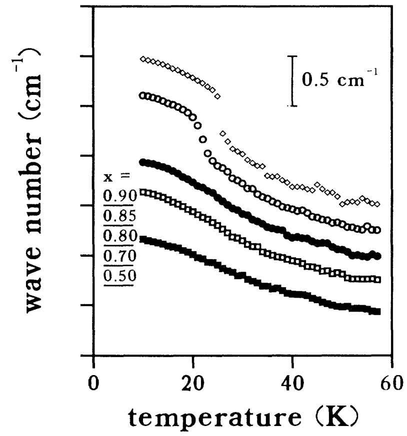

FIG. 5. Frequency of the vibron spike as a function of temperature. The horizontal bar below the specification of the sample composition is the $\nu = 2327$ cm^{-1} reference mark.

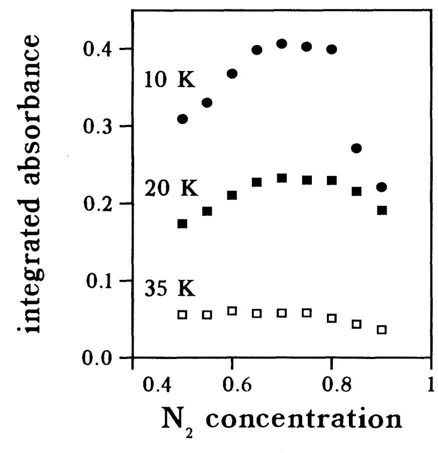

FIG. 6. Integrated absorbance of the vibron spike as a function of composition x for $T = 10$, 20, 35 K.

equal proportions, the factor group splitting should show up through an enhanced width of the vibron which should be detectable even with the limited resolution of the spectrometer. The infrared activity of the vibron and the peculiar x and T dependence of its intensity will be discussed further below.

IV. C-O STRETCHING BAND

The stretching band region of CO impurities in N_2, $x = 1$ (see also Ref. 27) is shown in Fig. 7. Because of the permanent dipole moment of the CO molecule, the stretching vibration is infrared active and gives rise to an absorption line. In the α phase the C-O vibration is well separated from the sideband structure. The sideband covers about the ν' range of the lattice modes of the matrix and contains several maxima, the most prominent at $\nu' = 72$ cm. In the β phase the vibration line is broad, of Lorentzian shape. A residual shoulder superimposed on the high-frequency side of the Lorentzian profile can be identified around 60 cm^{-1}.

As far as the interpretation of the sideband is concerned, two views have been propagated. The first view[28] starts out from the idea of the stretching band region representing the rotovibrational band of an infrared-active defect. Here the sideband peaks are due to the CO librational mode coupled to torsional modes of the N_2 cage surrounding the CO impurity. For the α phase this picture is supported by model calculations.[28] Following these calculations the strongest sideband feature, at 72 cm^{-1}, can be regarded as the local CO libration, well decoupled from the cage modes. The structures remaining would then be various torsional modes of the cage. According to the calculations, their infrared response should be much weaker than that of the CO libration. However, the calculation assumes that the center of interaction and the center of mass of the CO impurity are identical and coincide with an fcc lattice site and that the surrounding N_2 molecules are centered on fcc sites.

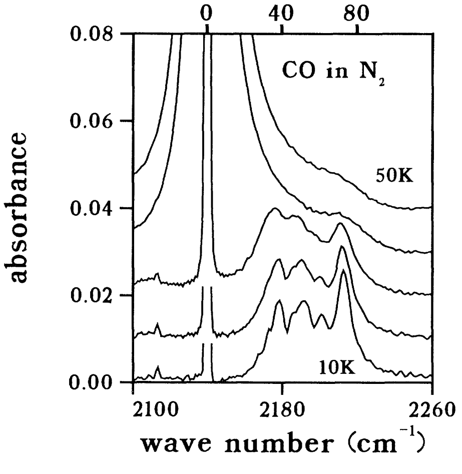

FIG. 7. C-O stretching band region for N_2 (doped with 0.1% CO). The vertical scale refers to the 10-K spectrum. The other spectra are offset in steps of 0.05 vertical units.

Translational modes are expected to mix in if these assumptions are relaxed.

On the other hand a conspicuous similarity of the C-O and the N-N sideband structure in the α phase has been noted and in fact corresponding features can be found in the two sideband structures after a 10% expansion of the ν' scale.[29] This suggests that the sideband represents modes localized at the CO defect, both of translational and rotational character, which in turn should be intimately related with the lattice modes of the N_2 host. In any case it is evident from the absence of multiphonon contributions to the C-O sideband of the α phase that the modes which couple to the C-O stretching vibration cannot be extended lattice modes. According to the first view the sideband intensity is only due to modes of rotational character. Applying this concept to the β phase would suggest that the structure around 60 cm^{-1} represents the CO libration of the β phase. This does not appear likely to us, we rather propose to relate the feature at 60 cm^{-1} to high-frequency translational local modes.

Apart from the feature at 60 cm^{-1} the C-O stretching band of the β phase is highly reminiscent of the ir response of diatomic molecules in a liquid.[30,31] At higher temperatures the overall shape of the C-O stretching band is well described by a thermally weighted Lorentzian. In fact, in the case of a fast relaxation of the vibration due to orientational diffusion the P and R wings of the stretching band are suppressed in favor of Lorentzian profile, centered at $\nu'=0$, Ref. 30. This suggests that the librational motion of the CO molecule is overdamped, at least at higher temperatures.

The C-O stretching band region of a mixed crystal, here for $x=0.7$, is shown in Fig. 8. For higher temperatures, the stretching band is qualitatively identical to that for $x=1$. The Lorentzian width decreases with decreasing T. As the β-α transition is now suppressed, the band profile can be followed down to lower temperatures. At 10 K the vibration line is sharp and superimposed on a smooth and weak sideband spectrum. At 10 K the sideband is similar to that of the N-N stretching band region except for some extra contribution at the low-ν' region, around 15 cm^{-1}, which might be due to CO librations.

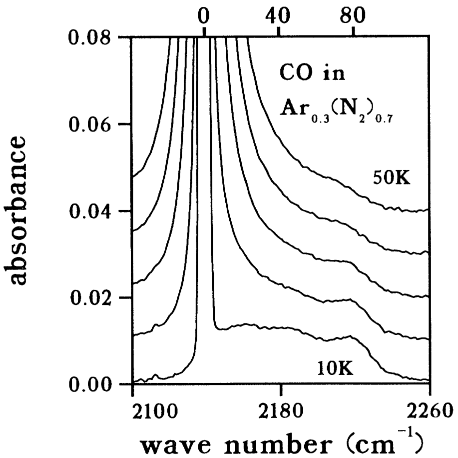

FIG. 8. C-O stretching band region for $x=0.7$.

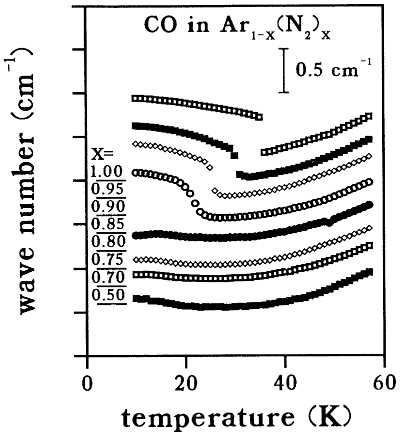

FIG. 9. Frequency of the C-O stretching vibration as a function of T for various sample compositions. The horizontal bar below the specification of the composition is the $\nu=2139\ \mathrm{cm}^{-1}$ reference mark.

The absorption line as a function of x and T has been fitted with a thermally weighted Lorentzian line shape:

$$A(\nu') \sim \exp(\nu'/2k_B T)\Gamma/(\nu'^2+\Gamma^2)$$

folded with a Gaussian-shaped resolution profile. The results on the Lorentzian width Γ and the vibration frequency $\nu_{\text{C-O}}$ are shown in Figs. 9 and 10. A comparison of the absorbance between samples of different x has not been made because of the large relative error of the CO doping level from sample to sample. The hcp-$Pa3$ phase transition is apparent from jumplike changes, steps or kinks of $\Gamma(T)$ and $\nu_{\text{C-O}}(T)$. The change of $\nu_{\text{C-O}}$ at the transition is about equal to that of the N-N vibron frequency. The discontinuity at 13 K for $x=0.80$ is presumably due to an hcp-orthorhombic transition which

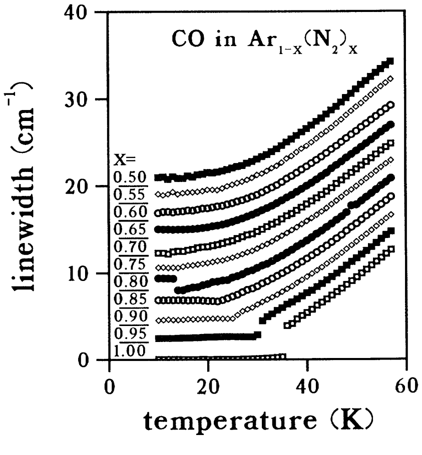

FIG. 10. Intrinsic Lorentzian width Γ of the C-O stretching vibration. The horizontal bar below the specification of the sample composition gives the zero level of the corresponding data.

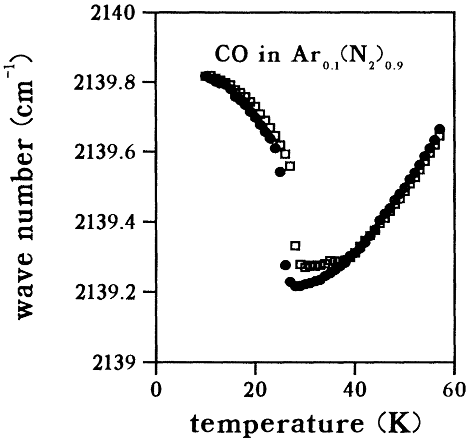

FIG. 11. Frequency of the C-O stretching vibration for $x=0.9$ for cooling (solid circles) and heating (open squares).

has been observed by x-ray diffraction[3] in that region of the phase diagram. Within the $Pa3$ phase the intrinsic width is T independent and small compared to the instrumental resolution. There is a slight increase of the low-T limit of $\Gamma(T)$ with increasing Ar content. Within the hcp phase $\Gamma(T)$ increases strongly with T starting from very low values $\Gamma(T \rightarrow 0)$. Thus the T-induced width is large compared to the T-independent component. As a function of T, the stretching frequency $\nu_{\text{C-O}}$ passes through a shallow minimum around 25 to 30 K. At higher T the T dependence is anomalous and opposite to that of the N-N vibron. One may speculate that thermal population of the translational and rotational degrees of freedom of the host lattice leads to a local contraction of the lattice around the CO impurity.

Recently it has been observed that for concentrations x in the range $0.8 < x < 0.95$, an intermediate orientationally disordered phase with an fcc center-of-mass lattice can be stabilized on heating the sample starting from temperatures within the $Pa3$ phase.[32] Further evidence for this phase has been brought forth by Raman measurements on the splitting, shift, and width of the N-N vibron.[33] Our results on $\nu_{\text{C-O}}(T,x=0.90)$ are qualitatively similar to the Raman results. As can be seen in Fig. 11, $\nu_{\text{C-O}}(T)$ behaves differently on cooling and heating. The plateau of $\nu_{\text{C-O}}(T)$ on heating, $28 \text{ K} < T < 37$ K, is regarded as a fingerprint of the fcc phase.[33] We conclude from this observation that the frequency and width of the C-O stretching vibration and of the N-N vibron are sensitive to the orientational state but are little influenced by the change of the center-of-mass lattice.

V. DISCUSSION

In the α phase of pure N_2 the N-N vibron is ir inactive, in agreement with the factor group analysis. The theoretical situation is less clear for β-N_2. Here the center of the N_2 molecule is not located at an inversion center and the symmetry predictions on the infrared activity of the vibron depend on the model assumed for N_2 orientations. From an experimental point of view however it is evident from the ir spectra that the decoupled vibron of β-N_2 is inactive. The infrared activity of the vibron is a peculiarity of the mixed crystal, only. In a simple view one assumes that the perturbed environment creates a local electric field E at the N_2 site. The induced absorbance A_{ind} is then proportional to $(\partial\alpha/\partial Q)^2E^2$ integrated over the lifetime of the vibration.[34] Here α is the polarizability of the molecule and Q the normal coordinate (which means that the induced ir activity is connected with the Raman cross section). Clearly, a shell of unlike Ar and N_2 neighbors in a mixed crystal gives rise to such a local field E (as e.g., demonstrated by the appearance of the N-N stretching line in ir measurements on 2% N_2 embedded in an Ar matrix[35]). On the other hand, this effect of substitutional disorder should be temperature independent. Furthermore, since the local field enters quadratically into the expression of A_{ind}, a rapid translational or orientational motion at higher temperatures will not average A_{ind} to zero. Thus there is no simple explanation for the peculiar T dependence of the induced vibron intensity.

Forbidden vibrations have been observed in two other mixed crystals with glassy properties at low T: In the dipolar "proton glass," $Rb_{1-x}(NH_4)_xH_2PO_4$, some Raman-active internal vibrations, such as the ν_2 mode of the PO_4 tetrahedron, leak into scattering geometries in which they are forbidden on the basis of the average high-T crystal structure.[36] This effect is already present at high temperatures and is presumably due to a canting of these units induced by the chemical disorder. In the "dipole glass," $K_{1-x}Li_xTaO_3$, two optic modes have been observed which should be Raman forbidden in the cubic Perovskite average lattice.[37] The appearance of one of them at low T has been interpreted by a symmetry reduction at a conventional phase transition, since its T dependence is that of a Landau-type order parameter. The Raman intensity of the other one could be traced up to almost room temperature. Dipolar microregions have been cited for the interpretation. This view is of no help for the present problem of the appearance of a dipolar intensity in a quadrupolar system. In KBr:KCN the quadrupolar freezing has no effect on the dipolar susceptibility.[1]

The *ad hoc* explanation for the low-T infrared activity of the vibron is simply that some of the lattice modes of the mixed crystals, which give rise to the ir activity of the sideband, are transferred from finite to zero frequency $\nu'=0$, in the freezing process. Hence these lattice modes can be understood as static translational ("off-center") and angular displacement patterns, which break the symmetry of the high-T average lattice. The transfer of formerly propagating or at least viscous modes to $\nu' \approx 0$ is characteristic of glass formation, and solidification in general. Such an appearance of a static or quasistatic component in the spectral density has been proposed in a NMR study[38] of the quadrupolar glass state of p-o-H_2. In the orientational glass KBr:KCN the static component has been observed in inelastic neutron scattering.[39] Here the relevant modes are transverse-acoustic phonons coupled to orientational modes. At the freezing temperature some oscillator strength of these modes is transferred to

$\nu'=0$ giving rise to the so-called central peak. The central peak intensity is a measure of the glass order parameter q (Refs. 40 and 7). We suggest that the same picture holds for the $Ar_{1-x}(N_2)_x$ quadrupolar glass and read the vibron intensity as a measure of q. Thus an understanding of the ir activity of the vibron is no longer so much the problem of the understanding of selection rules but requires an understanding of the freezing process of the quadrupolar glass, which admittedly is in a poor state.[6] Reliable models for the temperature dependence of q may exist for spin glasses,[5] but are missing for quadrupolar glasses.[6] Nevertheless, as mentioned in the introduction, one expects that for quadrupolar glasses $q(T)$ is finite at any finite T because of random-field effects. This is confirmed by the present results.

As far as the x dependence of the intensity of the vibron spike is concerned, the simplest way is that the intensity is proportional to the N_2 concentration x, multiplied by the chance that a given molecule has unlike neighbors, i.e., $A \sim x^2(1-x)$. This expression is maximum at $x=\frac{2}{3}$, in rough agreement with the experiment, Fig. 6.

In Fig. 12 the T dependence of the integrated vibron absorbance A, $x=0.6$ is compared with two other quantities which have been regarded as measures of $q(T)$, namely the ^{13}C NMR width[14] of Ar:N_2:CO and the width of an x-ray-diffraction line[3] of $Ar_{1-x}(N_2)_x$. In Fig. 12 all quantities have been normalized on a common low-T limit. The figure suggests that $q(T)$ grows rather gradually with decreasing T, in qualitative agreement with results on $q(T)$ of p-o-H_2 and KBr:KCN (Refs. 4 and 39). The results of the two local probes, NMR and infrared spectroscopy, coincide, in spite of the fact that they represent the response of different symmetry and have different inherent time scales. The broadening of the diffraction line which reflects the condensation of long-wavelength lattice distortions sets in at considerably higher temperatures. This is also apparent by visual inspection of the samples between crossed polarizers. Already around 40 K strain birefringence gives the sample a fine grained spotty appearance. We conclude that long-wavelength distortions condense first and that eventually the N_2 orientations freeze in this distorted environment. Similar views have been propagated for the mixed cyanides:[7,1] Random stresses are introduced by substitutional disorder because of the size difference of the substituents. The induced inhomogeneous strain grows with increasing T and eventually blocks the CN reorientations.

A finite vibron intensity not only exists in the hcp quadrupolar glass but also in the α phase of the mixed crystals. Finite values of a glass order parameter in a long-range-ordered phase might be surprising at first sight, but it is expected that in the vicinity of an Ar impurity the local N_2 orientations will deviate from the $Pa3$ pattern and rather approach a "T" configuration, which is known to minimize the quadrupole-quadrupole pair interaction.[41] Hence some glassy frozen-in disorder will be present at low temperatures for any Ar concentration, even within the α phase. Analogous observations have been made in NMR studies on the α phase of p-o-H_2 (Ref. 4).

In KBr:KCN the question whether the central peak represents truly static displacement patterns has not been answered in a satisfactory way, because of limited experimental resolution of the neutron experiment.[42] For the present system we are confronted with the same problem. We do not know whether the vibron line is infinitesimally sharp. Guided by Raman measurements[43] on the vibron in $Ar_{1-x}(N_2)_x$, $0.85<x<1$, one would think that the vibron ir line width should be much smaller than our instrumental resolution. On the other hand we do observe that a quasielastic Lorentzian-shaped component grows underneath the vibron spike. Such extra low-frequency modes have been also found in Raman measurements[44] of the C-N stretching band of KBr:KCN and have been deduced from measurements[38] of the spin-lattice relaxation time of p-o-H_2.

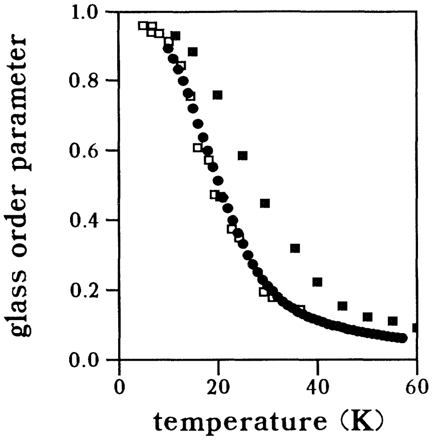

FIG. 12. Compilation of quantities which have been regarded as measures of the glass order parameter: ir vibron intensity of $Ar_{0.4}(N_2)_{0.6}$, this work (solid circles); width of Bragg lines in x-ray diffractometry on $Ar_{0.4}(N_2)_{0.6}$, Ref. 3 (solid squares); width of NMR line of $Ar_{0.4}(N_2)_{0.4}(CO)_{0.2}$, Ref. 14 (open squares). The data are normalized to a common $T \rightarrow 0$ limit.

A reliable determination of the T dependence of the Lorentzian width Γ has not been possible for the N_2 stretching band but is available from the C-O stretching band (Fig. 10). Within the concept of orientational diffusion, Γ is identical to the diffusion rate. $\Gamma(T)$ grows approximately exponentially with T: $\Gamma(T)=\Gamma_0+c\exp(E_0/k_BT)$. E_0 is the energy barrier for CO reorientations. Fits yield values between 102 and 110 K for $0.5<x<0.8$ with a trend to the higher values for higher x. Hence the barrier is of the order of the average lattice mode frequency.

VI. SUMMARY

The ir N-N and C-O stretching band regions of $Ar_{1-x}(N_2)_x$ mixed crystals doped with CO have been investigated systematically as a function of the sample composition and temperature. The most surprising individual feature of the ir spectra is the appearance of the N-N zero-phonon vibron line in the mixed crystals. Its intensity reflects frozen-in lattice modes and is therefore interpreted as a measure of the quadrupolar glass order parameter. The glass order parameter is finite at any finite temperature and grows monotonously towards lower temperatures. Analogous observations have been made on the quadrupolar glass order parameter of p-o-H_2 and mixed cyanides. Furthermore the ir spectra give an insight into the dynamics of the N_2 (and CO) orientations and of the phonons of the center-of-mass lattice. It is suggested that—except at lowest temperature—the hcp phase does not support librational excitations but that the orientational dynamics is rather of the diffusive type, the diffusion rate slowing down with decreasing temperature.

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