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Evidence for the orientationally disordered cubic phase of $Ar_{0.15}(N_2)_{0.85}$ from librational and vibrational Raman scattering

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Vibrational and librational Raman scattering yields spectroscopic evidence for the existence of an orientationally disordered fcc structure of the $Ar_{0.15}(N_2)_{0.85}$ mixed crystal, and directly probes its dynamical properties. At the orientational phase transition, the librational motion suddenly becomes overdamped and the factor group splitting between the A_g and the T_g vibrons disappears, which is accompanied by a jump in vibrational frequency. The purely structural fcc-hcp transition is observed through a different temperature dependence of the stretching frequency for the two phases. The anomalous decrease of the linewidth of the vibrational transition when passing the α-β phase transition in solid N_2 and in $Ar_x(N_2)_{1-x}$ mixed crystals with low Ar content can now be ascribed to the difference in orientational status in the two phases and not to structural changes.

Two phases[1] of solid nitrogen may be discerned at zero pressure. In the high-temperature β phase, the nitrogen molecules are arranged on a hcp lattice. At 35.6 K, a structural and orientational phase transition occurs towards the cubic α phase, where the molecules are oriented along the $\langle 111\rangle$ directions (space group $Pa3$). A molecular dynamics simulation[2] of α-N_2 suggested the possibility of an orientationally disordered region within the low-temperature phase. Since this phase has not yet been experimentally identified, the rotational coupling among the molecules is probably stronger than assumed in these calculations.[2] Nevertheless, large lattice anharmonicities[3,4] and a still unexplained increase[5] in the Raman scattering cross section were observed near the α-β phase transition.

The rotational coupling among the molecules is governed by the quadrupole moment and the anisotropy of the N_2 molecules. By dilution of the crystal with Ar atoms, the potential wells inhibiting free rotation of the molecules are reduced, and as a result their librational amplitude increases. Recently, a new orientationally disordered fcc phase was discovered by x-ray-diffraction measurements.[6,7] This phase is only accessible when warming the sample starting from the low-temperature α phase. The temperature of the orientational phase transition is well separated from the structural phase transition temperature towards the β phase, provided that the Ar concentration is sufficiently high.[7] Cooling from the β phase leaves the crystal in the hcp structure down to the structural and orientational phase transition towards the α phase. In this paper we will provide spectroscopic evidence for the existence of an orientationally disordered fcc phase and present additional information on the dynamical properties of Ar–N_2 mixed crystals. Therefore, we have performed Raman measurements on both the librational and vibrational modes of a single crystal of $Ar_{0.15}(N_2)_{0.85}$, in which the α and β phase are separated by a region of 5 K. Single crystals, or at least transparent crystals with large single-crystal domains, were grown[8,9] using a technique similar to that in Ref. 10. No substantial changes in the Raman spectra were observed over 1-cm height difference in the sample, indicating that no concentration gradients were present.

The low-frequency spectrum[1] of solid N_2 consists of three librational bands and a broad combination band, which extends up to 100 cm^{-1}. In α-$Ar_{0.15}(N_2)_{0.85}$, the E_g and the T_g librons strongly overlap even at low temperature [Fig. 1(a)] and form a broad asymmetric band

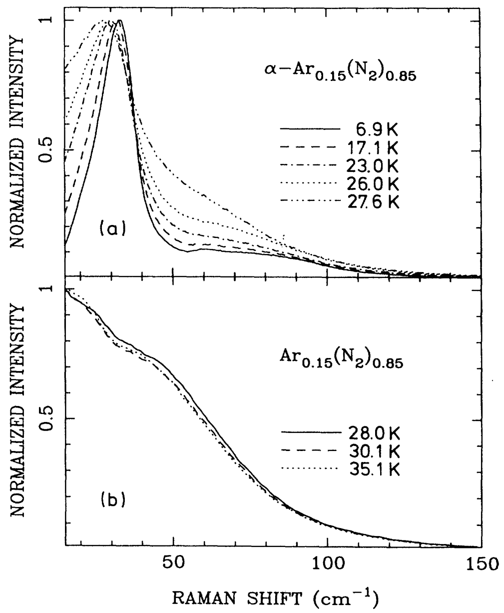

FIG. 1. Raman spectra of the low-frequency region of the three phases of $Ar_{0.15}(N_2)_{0.85}$ crystals without any applied pressure, as a function of temperature. The libron modes, which are prominent in the α phase (a), disappear above the temperature of the orientational phase transition and a broad structure appears (b).

at 33 cm^{-1}. The linewidth is much larger than observed for the pure α-N_2 crystal.[4] The T_g libron at 61 cm^{-1} cannot be clearly discerned in Fig. 1(a) due to its low intensity but is still present. For increasing temperatures, the E_g-T_g band broadens and shifts towards lower wave numbers. Between 27.6 and 28.0 K, the phase transition towards the orientationally disordered fcc phase takes place. The transition temperature is in excellent agreement with the x-ray-diffraction measurements.[7] In the orientationally disordered fcc phase, we observe almost no change in the low-frequency Raman spectrum, and this is apparent from a comparison of the spectra obtained at 28.0 and 30.1 K in Fig. 1(b). Moreover [in Fig. 1(b)], there is no substantial difference between the low-frequency spectra for the fcc structure (at 30.1 K) and hcp structure (at 35.1 K).

In the α phase the stretching vibration of the N_2 molecules is split by the crystal-field symmetry into an A_g and a T_g mode. Delocalized vibron states are formed by the coupling of individual excitations on different sites. This coupling process reduces small local variations in site energy, which is reflected in a reduction of the inhomogeneous linewidth. Also the homogeneous linewidth of the vibron states is much narrower than for isolated molecules.[8] No such collective states have been reported for other phases of either solid N_2 or $Ar_x(N_2)_{1-x}$ mixed crystals. In the α-$Ar_{0.15}(N_2)_{0.85}$ crystal [Fig. 2(a)], we can distinguish both the A_g and the T_g mode. When passing the orientational phase transition temperature [Fig. 2(b)], only one peak is observed, indicating that the crystal no longer has a $Pa3$ space-group symmetry. The line positions are plotted as a function of temperature in Fig. 3. We observe a softening of both the A_g and the T_g mode towards the orientational phase transition temperature, which is very similar compared to the pure N_2 crystal.[4,11] A jump in frequency occurs at about 28 K, corresponding to the transition to the orientationally disordered phase. At the temperature for the fcc-hcp transition (T $\approx$ 33.5 K),[7] no such discontinuity can be resolved. Also, no abrupt change in either volume[6,7] or specific heat[12] was noticed at this temperature. This may be due to the small difference in energy between the hcp and fcc structures.[6] However, when lowering the temperature from the β phase (□ in Fig. 3)—so that the crystal structure is expected to remain hcp down to 28 K (Ref. 7)—we observe a different temperature dependence of the line position of the stretching vibration than for heating the sample (△ in Fig. 3). The linear temperature dependence for the vibrational frequency found upon

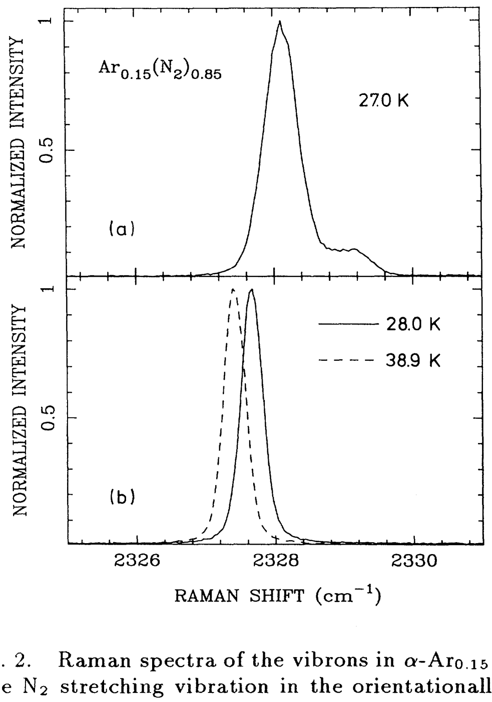

FIG. 2. Raman spectra of the vibrons in α-$Ar_{0.15}(N_2)_{0.85}$ and the N_2 stretching vibration in the orientationally disordered phases as a function of temperature. In the low temperature α phase (a), the T_g mode appears as a shoulder on the high-frequency side of the A_g mode. Above the phase transition (b), only one peak is observed, which shifts towards lower wave numbers for increasing temperature. The peak positions as a function of temperature are given in Fig. 3.

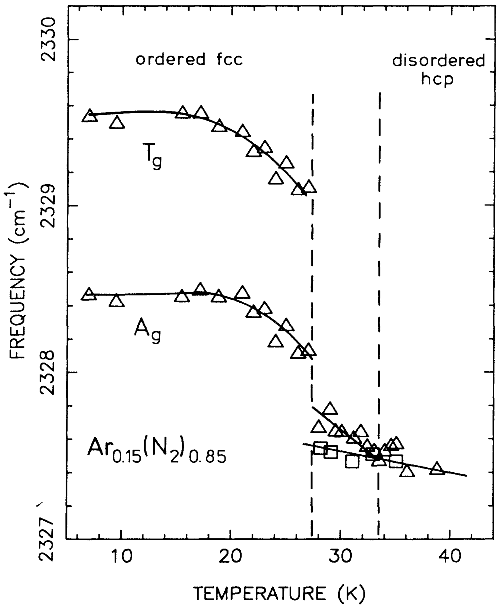

FIG. 3. The frequency of the A_g and T_g mode of the vibrons in α-$Ar_{0.15}(N_2)_{0.85}$ and of the N_2 stretching vibration in $Ar_{0.15}(N_2)_{0.85}$ as a function of temperature. The uncertainty on the frequencies, of the order of 0.05 cm^{-1}, is mainly due to the precision of the monochromator positioning. The triangles correspond to measurements performed when warming the sample starting from the α phase, the squares when cooling the sample from the β phase. Between 27.5 and 33.5 K, the difference between both procedures is clear. The straight line connecting the squares has the same slope as was observed for the β phase of pure N_2 (Ref. 4), but is shifted towards higher wave numbers. The other lines are guides to the eye.

cooling the sample has the same slope as was observed for β-N_2.[4] This difference in temperature dependence of the stretching frequency for different temperature treatments provides evidence for the existence of two structurally different phases with orientational disorder.

The frequencies of the A_g and T_g vibrons in the α phase and of the N_2 stretching vibration in β phase are about 0.9 cm^{-1} higher than in pure N_2 crystals. This is in contrast with the results of Ref. 13, where a decrease of 0.5 cm^{-1} was obtained. We relate this difference to the poor quality of their polycrystalline samples, which were produced by a spray-on technique so that the signal-to-noise ratio and the necessary spectral resolution were reduced. The polycrystalline structure also caused a prominent inhomogeneous broadening of 0.6 cm^{-1} for pure N_2 crystals,[13] to be compared with 0.01 cm^{-1} for single crystals.[8] For Ar concentrations larger than 10%, the A_g and T_g modes could not be resolved in Ref. 13, while they are well separated for single crystals, as is clear from Fig. 2(a), for an even higher Ar concentration of 15%.

Using time-resolved coherent anti-Stokes Raman scattering, we[9] found a remarkable difference in linewidth for the vibrons in α-$Ar_x(N_2)_{1-x}$ and the N_2 stretching vibration in β-$Ar_x(N_2)_{1-x}$. Near the α-β phase transition, the linewidth in pure N_2 crystals is smaller in the β phase ($T_2/2$ = 168 ps, Ref. 14) than in the α phase ($T_2/2$ = 113 ps, Ref. 8). In the α phase, we found scattering from thermal librons to be the main line-broadening process. By substituting N_2 molecules with Ar atoms, the librational amplitude enhances, thereby drastically increasing the linewidth of the vibrons in α-$Ar_x(N_2)_{1-x}$ crystals, while in the β phase only a small increase was found.[9] While inhomogeneous components to line broadening are prominent in the α phase, they could not be resolved in β-$Ar_x(N_2)_{1-x}$ crystals. The dual character of the α-β transition for pure N_2 and $Ar_x(N_2)_{1-x}$ crystals with low Ar content[7] ($x \lesssim 0.05$) does not allow us to distinguish whether this behavior is related to structural or to orientational aspects. However, in the $Ar_{0.15}(N_2)_{0.85}$ crystal both phase transitions are well separated. The spectra measured in the disordered fcc and hcp phases were fitted to the convolution of the transmission function of the monochromator (full width at half maximum of 0.35 cm^{-1}) and a Lorentzian. The full width at half maximum of the Lorentzian in both the fcc and hcp phase turned out to be less than 0.05 cm^{-1}, which corresponds to a dephasing time $T_2/2$ larger than 100 ps. The linewidth is thus much narrower than observed for the vibrons in the α phase, which already follows from visual inspection of Figs. 2(a) and 2(b). We conclude that the sudden decrease in linewidth of the vibrational states depends directly on the orientational ordering and is quite insensitive to the specific structure (fcc-hcp) of the crystal. In accordance with our previous results,[9] we find that in the disordered phases (both fcc and hcp) the linewidth does not depend as strongly on the Ar concentration ($-T_2/2$ = 168 ps and >100 ps for x = 0 and x = 0.15, respectively), as in the α phase. As a result, the anomalous difference in linewidth between the vibrons in the α phase (see Fig. 1 and Ref. 9) and the stretching vibration in the orientationally disordered phases becomes more prominent for higher Ar concentration. The line narrowing and the disappearance of inhomogeneous line broadening does not result from the sudden increase in molar volume, which occurs for pure nitrogen at the α to β phase transition and for low Ar concentrations at the order to disorder orientational transition. Indeed, at the Ar concentration employed in our experiments, x = 0.15, there is hardly any discontinuity in molar volume at the phase transitions.[7]

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