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RAMAN SCATTERING FROM SOLID NITROGEN-ARGON MIXTURES

D. POLANI, R. FEILE, P. LEIDERER*

Institut für Physik, Johannes Gutenberg-Universität Mainz
D-6500 Mainz, FRG

* Fakultät für Physik, Universität Konstanz
D-7750 Konstanz, FRG

For the molecular crystals KCN and NaCN it was shown in many papers that the dilution of the molecular units by spherical ones as e.g. Br- and Cl-ions can suppress the orientational ordering of the molecules and in addition inhibit the structural phase transition observed in the pure compounds [1]. These mixed crystals are considered as to form orientational glasses at low temperatures.

Solid N_2 as another molecular crystal has an ordered low temperature phase (α) of cubic (Pa3) structure which undergoes a phase transition to the high temperature ß-phase at 36 K. In this phase of hexagonal structure (hcp) the nitrogen molecules perform a hindered rotation. Mixed systems of nitrogen and argon can be obtained because of the good miscability of the two components. The dilution of N_2 by Ar leads to a gradual reduction of the α-ß transition temperature and a complete suppression of the transition if the Ar-content exceeds ~20% [2]. Thermodynamic measurements gave an indication that the nontransforming mixtures may be also considered as orientational glasses [3]. The aim of our Raman experiments on N_2-Ar mixtures was to study the dynamics of the N_2 dumbbells from which an information about their orientational freezing was expected.

The samples of pure N_2 and mixtures up to 30% Ar-content were prepared in a closed cycle refrigerator as 'icicles' freely hanging from a cold finger. Visual inspection of the clear samples revealed a few grain boundaries at the surface of the 'icicle' indicating that the samples consisted of several macroscopic crystallites.

For the Raman experiments a laser beam was focussed to the interiour of the transparent samples with powers up to 500 mW without significant heating of the sample. The scattered light was collected under 90 deg from the incident laser beam and analysed by a double grating monochromator. No polarization analysis was performed.

Fig.1 gives the temperature dependence of the Raman spectra from three samples: pure N_2, 10% and 30% Ar admixture, obtained in the region of frequency shifts around the N_2 vibration. Above the α-ß transition the Raman spectra of pure N2 consist of a broad quasielastic distribution of frequencies reflecting the hindered rotation of the N_2-molecules coupled to their vibration. Below the α-ß phase transition the N_2-dumbbells perform a librational motion around fixed directions in which they are locked in. This shows up as a shift of the vibrational sidebands which are now well be separated from the N_2-vibration. The double peak structure exhibits the density of those lattice modes which mainly have librational character [4,5]. The spectra of the 10% Ar sample display similar structures as pure N_2 slightly broadened due to the inhomogenities as a result of the disorder. The transition is obviously shifted to lower temperatures. In the 30% Ar sample the librational band is further smeared out. In addition an enhanced low frequency scattering appears which resembles the 'boson peak' often found in Raman spectra of glasses [6]. This fact may indicate the glassy behaviour of this sample.

The N_2-vibration itself may be used as a probe of the local environment of the molecule. As seen from Fig 2. it displays the phase transition of pure N_2 by the step like increase of the width of the vibration due to an unresolved Davidov splitting in the ordered α-phase. In the 30% Ar sample, however, the linewidth increases gradually towards low temperatures reflecting the suppression of the phase transition and the freezing of the molecules in a distribution of local potentials.

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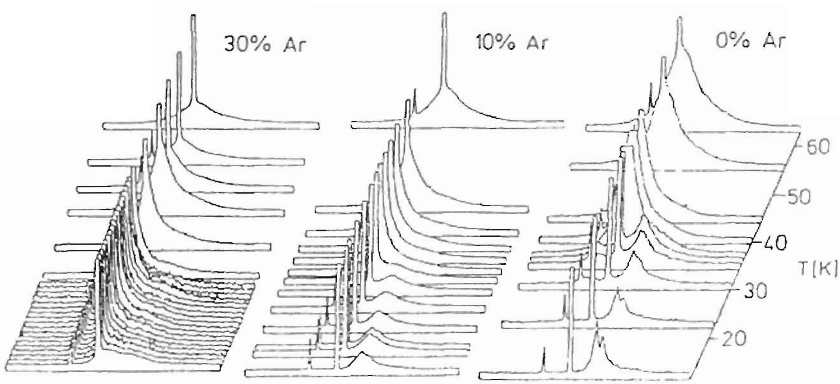

Fig.1 Temperature dependence of the Raman spectra of three N_2-Ar mixtures. The spectra span the range from 2200-2500 cm^{-1}.

Fig.2 The width of the N_2-stretching mode vs. temperature for the transforming pure N_2 and the glassy 30%-Ar sample