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The microwave measurements of $(N_2)_xAr_{1-x}$ solid solutions

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A full range of solid solutions $(N_2)_xAr_{1-x}$ $(0 < x < 1)$ have been examined with an x-band microwave dielectrometer. The real part of the permittivity ε' versus temperature T for this non-polar system has been measured with a high accuracy (10^{-6}) at temperatures between 1.5–75 K. A comparative (x, T) phase diagram is constructed with a β-α structural phase transition and the problem of transition to the orientational glass is discussed.

Introduction

There are two different phase diagrams for $(N_2)_xAr_{1-x}$ system. The first was constructed by Barrett and Meyer in 1965 [1] and the second one by Yantsevich and co-workers in 1986 [2]. Both have been determined by x-ray diffraction but differ fundamentally. In contradiction to Yantsevich with co-workers, Barrett and Meyer have treated the N_2 + Ar system as a well miscible one. Their phase diagram is similar to that obtained by Sullivan et al. [3,4] for o-H_2 + p-H_2, the most studied quadrupole glass system [5–8].

The other similar phase diagram that one can observe for $KBr_{1-x}(CN)_x$ orientational glass, was studied experimentally by Moy et al. [9] and is well described theoretically by Michel and co-workers [10–14] and Carmesin and Binder [15]. For all these cases, simple axial molecules (like N_2, ortho-H_2, CN^-) are randomly diluted by spherical atoms (Ar, para-H_2 or Br^- and K^+). These axial molecules, placed randomly in a spherical host lattice, are strongly frustrated [16] and, in general, orientationally disordered with no long range interactions.

There are a few papers reporing orientational freezing for $(N_2)_xAr_{1-x}$ system. This effect has been studied with NMR technique by Esteve et al. [17], in neutron scattering experiments by Press et al. [18] and by x-ray powder diffraction [19]. These authors have found that orientations of N_2 molecules begin to freeze at about 20 K and this process continuously intensifies with cooling. Ward and his co-workers [20] have examined the specific heat of solid nitrogen–argon mixtures and have found rounded peaks in the vicinity of 17 K ascribed to rotational contributions to the specific heat for the concentrations $x = 0.70$, 0.63, and 0.50.

At the beginning of our measurements, we tried to verify the results obtained by Liu and Conradi [21]. These authors have studied a not exactly «pure» quadrupolar system. They have used CO molecules as a dipolar admixture assuming that $CO/N_2/Ar$ solutions should form quadrupolar glass similarly as the N_2/Ar system. Reorientations of CO molecules in this system can be followed dielectrically and these authors have observed cusp maxima characteristic for different types of glasses [22–25]. These maxima allowed them to postulate a glass part of the Ar/N_2 phase diagram [26]. On the basis of this diagram and the Arrhenius expression which has been used by Liu and Conradi to fit the data (for NMR experiments see too [27]), one can find the temperature of the phase transition to the glass state in the microwave x-band. For example, for $x = 0.70$ this temperature should be of about 17 K.

Unfortunately, we have found no traces of any phase transitions near these temperatures and concentrations.

Apparatus

We have examined $(N_2)_xAr_{1-x}$ solid solutions with microwave resonator TM_{010} which has been placed inside a closed vessel. It enabled to observe changes of the real part of the permittivity ε' versus temperature. Gases with a purity of better than 99.99% were used (N_2 — 99. 999% and Ar only 99. 995% but its main contamination was 0.003% of N_2). Samples were mixed in the gas phase inside of a 0.05 m^3 gas cylinder. The gas solution was kept to mix overnight. Composition of the mixtures was controlled chromatographically for the gas phase and dielectrically for the liquid phase (linear changes of $\varepsilon'(x)$ — compare with Fig. 3 for solid). Each sample was enriched first

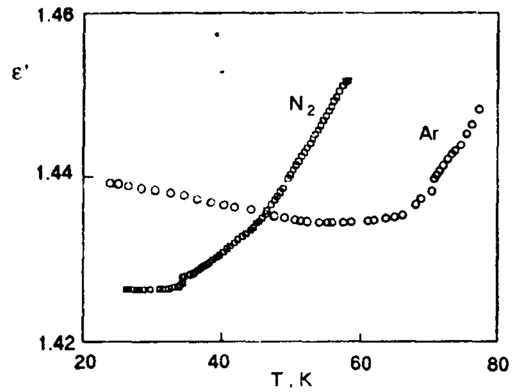

Fig. 1. Real part of permittivity ε' versus temperature for pure N_2 and Ar with structural phase transition β-α for N_2 at 34.5 K.

of about 0.5 MPa. The liquid solution was allowed to mix about three hours — and then the sample was solidified in 2 or 3 h to get the maximum packing of microwave resonator. Some of the samples were annealed after normal or rapid solidification at 60 K for about 6 h but this procedure had no experimentally important consequences. We believe that the samples were still of the polycrystalline rather than of glass structure. For some samples we have made a rapid cooling test. In less than 6 min the gas sample was cooled down to 4 K. But after such a process the packing of the resonator was rather incomplete because the input capillary pipe was blocked.

Experimental

For pure solid nitrogen Fig. 1 shows that the permittivity decreases smoothly with lowering temperature to 34.5 K. At this temperature a small jump to lower values of $\varepsilon'(T)$ has been observed. It is related to a structural phase transition from β to α nitrogen. This transition has been monitored by a few other methods [1,19,28,29] in which 35.6 K is a transition temperature at the ambient pressure. A bit lower temperature for this transition in our experiment could be connected with the low pressure inside the cavity caused by block of input capillary — compare Apparatus and explanation of Fig. 3.

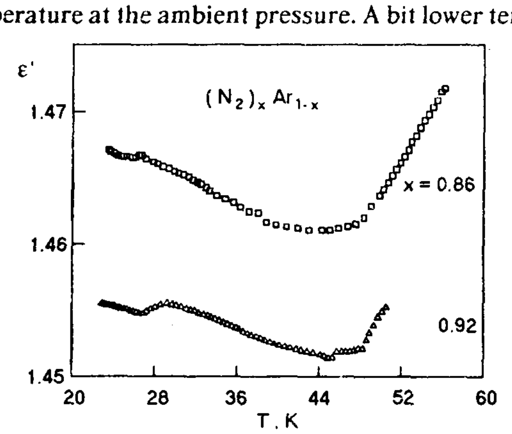

Fig. 2. The $\varepsilon'(T)$ for two concentrations x = 0.86 and 0.92 of the $(N_2)_x Ar_{1-x}$ mixed solid. Minima at about 46 K correspond to the decomposition of the solid solution into N_2-rich and Ar-rich phases.

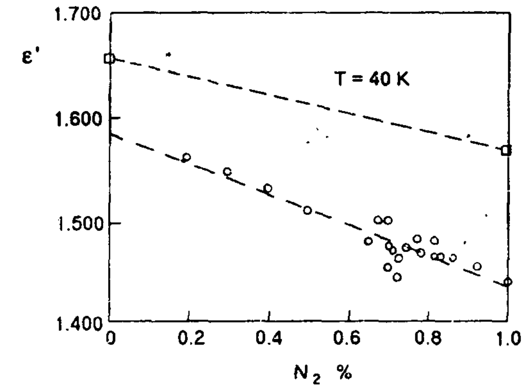

Fig. 3. The $\varepsilon'(x)$ dependence for 40 K. The upper line (- - -) corresponds to a completely filled resonator — side points (□) are calculated from Eq. (1). Dashed bottom line (— — —) is a mean square linearisation of experimental points (O).

Clear traces of structural phase transitions β-α have also been visible for high concentration samples. Figure 2 shows two examples: for x = 0.92 with a structural transition at T = 29.5 K and for x = 0.86 when the transition occurs at 26 K. As follows from the figure for these two cases, upon cooling at the phase transition, the $\varepsilon'(T)$ at first decreases and then increases again. This figure also reveals a new, additional feature of the examined system, that is, a deep minimum in $\varepsilon'(T)$ which can be detected even for the smallest concentrations at temperatures close to 50 K. The minimum in the $\varepsilon'(T)$ curve for pure Ar (Fig. 1) could be attributed to the contamination of N_2 (see Apparatus). Because the generation band of our microwave generator was too narrow we were not able to examine the full concentration range; for pure argon and concentrations x close to it we could observe only with a side-mode of our cavity. This means that for «pure» argon we did not observe corresponding values of $\varepsilon'(T)$, but only the character of $\varepsilon'(T)$ changes.

For pure ingredients (N_2 and Ar) the values of ε' could be found from the Clausius—Mossotti equation (C-M):

$$P = \frac{\varepsilon' - 1}{\varepsilon' + 2} \frac{M}{\rho} \qquad (1)$$

where P is molar polarization ($P = (4\pi/3)N_A\alpha$; N_A is Avogadro's number; α is polarizability — for N_2 mean polarizability of powder samples); ρ is density; M is molecular weight. The Clausius—Mossotti equation is a good approximation for non-polar substances of a general Onsager local field model. All the required values — M, ρ, α — for calculation of ε' for pure N_2 and Ar are given in Table 1:

Table 1

The parameters for N_2 and Ar [30,31] for calculation of side points of the upper line in Fig. 3

Molecule	Parameter		
	M, g	ρ^{40K}, g/cm^3	α, 10^{-24} cm^3
N_2	28.02	0.990	1.767
Ar	39.95	1.7349	1.641

The values of ε' calculated from (1) for pure N_2 and Ar (ε'_{C-M,N_2} and $\varepsilon'_{C-M,Ar}$ accordingly — the side points of the upper line in Fig. 3) allow us to define the packing index λ of a microwave resonator:

$$\lambda = \frac{1}{2}\left[\frac{\varepsilon'_{C-M,N_2}}{\varepsilon'_{expt,N_2}} + \frac{\varepsilon'_{C-M,Ar}}{\varepsilon'_{expt,Ar}}\right].$$

According to our experimental data λ was found to be 0.94.

Note that «expt» means «experimentally», but $\varepsilon'_{expt,Ar}$ can be determined only from the expression $\varepsilon' = -0.00153x + 1.58562$ — a linear regression of experimental values $\varepsilon'(x)$ for 40 K — the bottom line in Fig. 3. It was impossible to measure $\varepsilon'_{expt,Ar}$ directly because of a narrow generation range (8.9–9.4 GHz) of the microwave generator as we mentioned above. The parameters of our resonator were first calculated for the predicted glass state concentration range (ε' near 1.50).

The characteristic shapes of $\varepsilon'(T)$ in a wide concentration range are shown in Fig. 4 for x = 0.20, 0.30, 0.40, 0.50, 0.65, 0.70 and 0.72. This figure has been drawn for the concentrations usually assumed as corresponding to the glass state; however, in our experiment we have not observed the expected cusp maximum characteristic for the glass state and the shapes

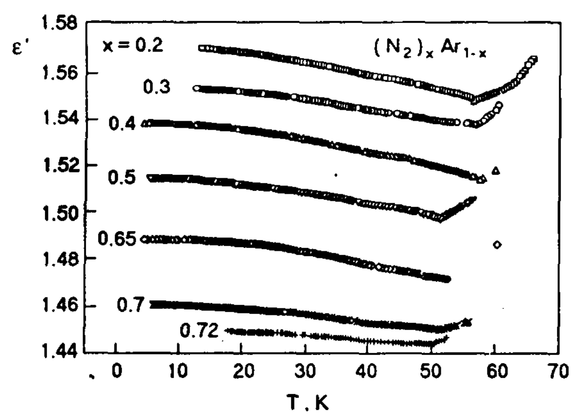

Fig. 4. Variations of $\varepsilon'(T)$ in a wide concentration region — no traces of glassy behavior (lack of cusp maximum) for all concentrations are observed.

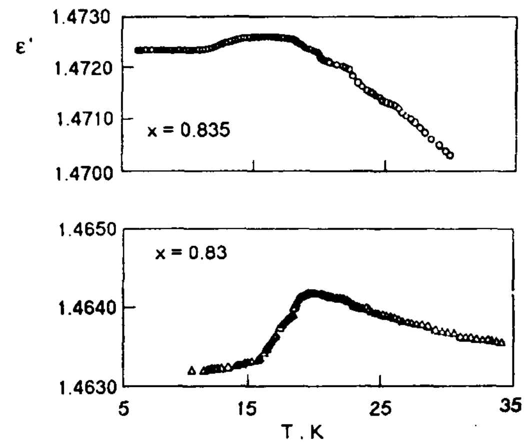

Fig. 5. Cusp maxima from β-α transition region.

of all curves, showing a deep minimum, have been the same down to the lowest concentrations.

Figure 5 shows the results for two concentrations x = 0.83 and 0.835 for which the glassy state could be postulated. But these cusps could only be observed for the concentrations close to the above two. Their transition temperatures were comparable with temperatures of the β-α transition. The cooling rates were the same as for concentrations from Figs. 2 and 4. Therefore we have interpreted these two cusps as indicating β-α phase transition.

Discussion

High accuracy measurements based on the microwave technique have allowed us to investigate dielectric response of even such dielectrically inconvenient systems as pure ^{4}He [32,33]. This fact has caused us to search the other subtle effect — quadrupolar reorientational motion which can lead to variations of inductional polarizability of nonpolar $(N_2)_xAr_{1-x}$ systems.

All available experimental data on N_2 + Ar system are summarized in the comparative phase diagram — Fig. 6. Minima from Figs. 2, 3, and 4 are located close to the line from the Yantsevich diagram [2] which is connected with the decomposition of the (N_2)Ar system. These convergences exist in spite of different ways of obtaining solid species (see Apparatus). An acceptable interpretation of this minimum as a beginning of formation of a glassy state — similar minima occur in KBr: OH [34], in $KBr_{1-x}(CN)_x$ [9] and in some alkali halides containing OH [35] — should be treated skeptically because the lack of a frequency shift of the $\varepsilon'(T)$ minimum for the investigated system — Fig. 7. This shift is characteristic for many types of glasses [8, 16, 22–26, 28, 29, 36–38], which means that by using different frequencies one can observe the glassy state in different stages of

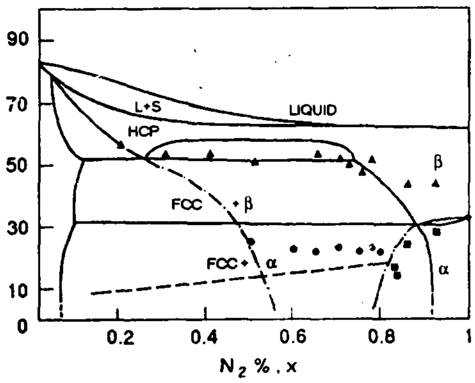

Fig. 6. Nitrogen-argon cumulative (x, T) phase diagram: [1] (– · –); [2] (——); [19] (●); [26] (- - -); and from our experiment: β-α phase transition (■) ; decomposition process (▲).

its formation. In the case of the orientational glass, using lower frequencies, we can detect slower orientational motion (deeper orientational freezing) while measurements at higher frequencies can produce data indicating the real (temperature) point from which the system is in the glass state.

Measurements for 10 and 100 kHz were performed with a tuning capacitor (placed inside the pressure vessel) and an RLC Digibridge 1689M GenRad [34]. Unfortunately, the insufficient accuracy of the RLC bridge did not allow us to verify with this bridge whether the frequency shift existed for the concentrations from Fig. 5 with a glassy cusp. Lack of frequency shift means that the grow of the orientational glass does not start at this high temperature range and confirms the convergence between Yantsevich and our results as far as the decomposition process is concerned. This process can explain the special problem arising from our results, i.e. why $\varepsilon'(T)$ increases for $(N_2)_xAr_{1-x}$ non-polar systems? — spinodal decomposition of N_2 + Ar system can lead to fractal growth of irregular clusters [38] with N_2 — and Ar-rich phases. This can be the reason why $\varepsilon'(T)$ increases in such a wide temperature range — the polarizability of a decomposed system should be higher than that of the system in the state of equilibrium.

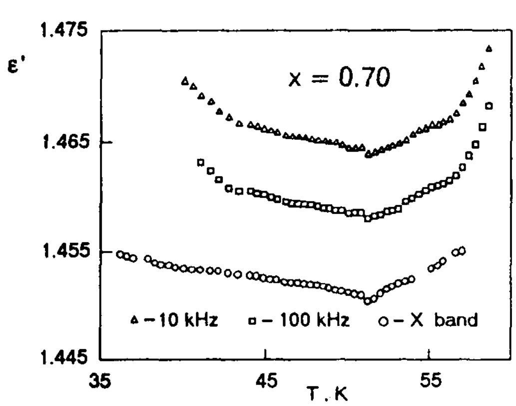

Fig. 7. Illustration of no frequency shift for the observed minimum.

For a separated system of an indefinite composition (due to the process of decomposition) at a maximum value of the electrical field (along the longitudinal axis for TM_{010} resonator) we should accept some small differences in a concentration values of the investigated system. A small shift, in comparison with the Barrett and Meyer data [1] has been visible for all samples with concentrations for which β-α phase transition occurs.

Conclusion

1. The observed dielectric anomalies are related to the β-α phase transition for high x values and with the separation process over a wide range of concentrations x for investigated $(N_2)_xAr_{1-x}$ system.

2. Only close to $x = 0.83$ we were able to observe cusp-like maxima which could correspond to the orientational glass state for the discussed solid solutions.

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