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Orientational-ordering transition fcc-*Pa*3 of $Ar_{1-x}(N_2)_x$

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Solid solutions of $Ar_{1-x}(N_2)_x$, $0.83<x<0.937$, have been studied by x-ray diffraction. On heating, the orientational disordering (*Pa*3-fcc) transition precedes the fcc-hcp reconstruction of the center-of-mass lattice. The long-range orientational-order parameter has been determined.

The ordering of diatomic molecules on high-symmetry center-of-mass lattices, such as fcc, bcc, or hcp, is a problem of fundamental interest in the field of structural phase transitions. Solid ortho-H_2, para-D_2, N_2, and CO are obvious candidates.[1-3] In fact, all these systems show an orientationally-disordered hcp high-T ("β") phase and an orientationally-ordered cubic *Pa*3 ("α") low-T phase. In the α phase, the centers of mass are arranged on an fcc lattice and the quadrupole moments of the molecules are along $\langle 111 \rangle$ in such a way that in each of four sublattices all moleucles are parallel to one of the four $\langle 111 \rangle$ directions. The transition involves not only quadrupolar ordering, but also a reconstruction of the center-of-mass lattice. The theoretical description of this latter aspect is a tremendous and yet unsolved problem. This is why theoretical efforts have concentrated on quadrupolar ordering on a rigid fcc or hcp lattice.[1-3]

In the present paper we will show that, by diluting N_2 with some percent of Ar, the situation can be reached where, on warming, the orientational disordering (at T_{or}) precedes the reestablishment of the hcp lattice (at T_{ch}). Thus the quadrupolar ordering could be studied on the fcc lattice. Analogous observations have been made in para-rich ortho-para-D_2 solid solutions.[2,4,5] Here o-D_2 plays the role of Ar as spherical diluent. First indications of this behavior in $Ar_{1-x}(N_2)_x$ have been reported in our recent article on x-ray diffraction,[6] where all information on the experiment can be found.

Samples with $x=0.937$, 0.900, 0.865, and 0.830 have been investigated by recording the hcp and *Pa*3 Bragg reflections on cooling and heating. On cooling, the hcp reflections disappear in favor of the *Pa*3 reflections in a T

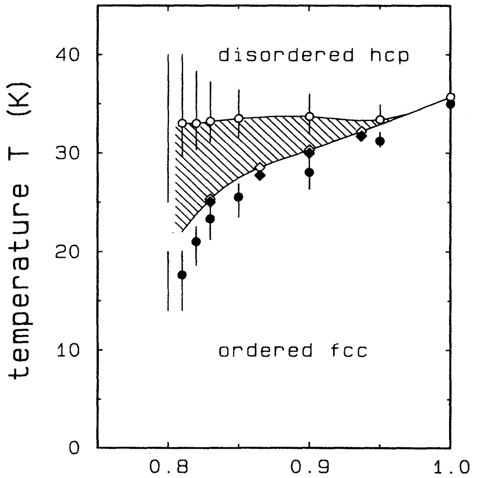

FIG. 1. The x-T phase diagram of $Ar_{1-x}(N_2)_x$ for $x>0.8$. Transition temperatures: (●) $T_{hcp\text{-}Pa3}$, (○) $T_{fcc\text{-}hcp}$, (◇) $T_{Pa3\text{-}fcc}$, (◆) $T_{fcc\text{-}Pa3}$. The cubic (*Pa*3 or fcc)-hcp coexistence regions are indicated by vertical bars. The fcc field, which is only accessible after the sample is first cooled into the *Pa*3 phase, is hatched.

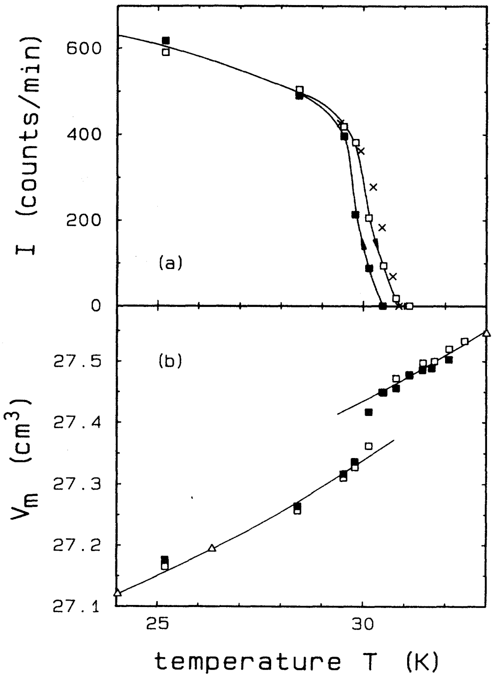

FIG. 2. The temperature dependence of the integrated $(211)_{Pa3}$ Bragg intensity, and of the molar volume above and below the ordering temperature for $x=0.90$, on cooling (■) and heating (□,△). Also shown is the volume fraction (×) of the low-temperature phase as derived by Pace *et al.* from specific-heat data (Ref. 8). The diffraction and the specific-heat data are scaled to coincide at 28 K.

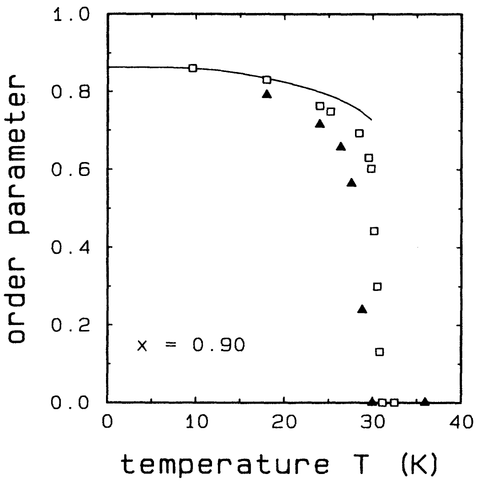

FIG. 3. The long-range orientational-order parameter η_{lr} for $x = 0.90$ as derived from the $(211)_{Pa3}$ intensity on heating from the *Pa*3 into the fcc phase (□) and cooling from the hcp into the *Pa*3 phase (▲). The η_{lr} scale is arbitrary, but it has been normalized to the local order parameter (solid line) of pure N_2 ($x = 1$), Ref. 1, at low temperatures. The temperature scale of the local order parameter is normalized to the $x = 0.90$ ordering temperature.

interval centered around T_{hc}. On heating, the *Pa*3 specific reflections, i.e., those which are absent in an orientationally-disordered fcc lattice, disappear at T_{or}, while the fcc reflections persist to higher temperatures until they disappear and the hcp reflections reappear in a T interval centered at T_{ch}. Thus, on heating, the sequence of phases is *Pa*3-(T_{or})-fcc-(T_{ch})-hcp. T_{hc} and T_{or} decrease, the widths of the cubic-hcp coexistence regions (both on cooling and heating) increase with decreasing N_2 concentration x. T_{ch} is about independent of x. (See the x-T phase diagram of Fig. 1). The ordering process at T_{or} exhibits a small thermal hysteresis of typically 0.5 K (Fig. 2), which indicates that it is a phase transition of first order. The first-order character is also evident from the jump of the molar volume ΔV at T_{or} (Fig. 2). The values of T_{or}, ΔV, and $\Delta V'$, which is the volume change for the hcp-*Pa*3 transition at T_{hc} (on cooling down from the hcp phase), are collected in Table I. The table also includes the transition temperature as obtained from specific-heat measurements[7,8] (which have been obtained on heating). The square root of the intensity of the *Pa*3 specific reflections is a measure of the four-sublattice quadrupolarization; the long-range orientational-order parameter η_{lr}. This quantity is shown in Fig. 3 and compared to the local orientational-order parameter η_{loc} of pure N_2 (Ref. 1)—as obtained, e.g., from NMR.

From the present results we can make a number of definite statements.

(a) On heating samples of $Ar_{1-x}(N_2)_x$, the orientational-ordering transition can be separated from fcc-hcp reconstruction of the center-of-mass lattice.

(b) The quadrupolar ordering on the fcc lattice is a transition of first order. This is in agreement with a Landau-type analysis, which shows the quadrupolar ordering on an fcc lattice invokes third-order invariants, even if the quadrupolar variables are decoupled from volume strains.[9]

(c) The specific-heat anomaly is due to the quadrupolar ordering and not to the lattice reconstruction. In the temperature range of the fcc-hcp reconstruction, there is no anomalous contribution to the specific heat.

(d) For the three higher concentrations, the volume jump is due to the orientational ordering and not to the lattice reconstruction. This is analogous to o-p-D_2 (Ref. 5). The sample with $x = 0.830$ represents those solid solutions which expand upon the hcp-to-*Pa*3 transition.[6] Here the ordering transition evolves without volume change.

(e) η_{lr} and η_{loc} are closely related. At the onset of orientational order, η_{lr} jumps to about 85% of its low-temperature value. This clearly shows that an Ising-type description of the ordering,[10] where the jump is only 50%, is not adequate.

(f) The $T_{or}(x)$ boundary extrapolates to 0 for $x = 0.33$. This is in disagreement with the virtual-crystal approximation which requires $T_{or} \sim x$. For o-p-H_2 it has been argued[11] that a spherical impurity not only dilutes the quadrupolar ensemble, but also leads to local deviations from the *Pa*3 arrangement. The argument refers to the fact that the ground state of two quadrupoles interacting via the electrostatic quadrupole-quadrupole coupling is a "T." The *Pa*3 is frustrated in the sense that it—though being the collective ground state of quadrupoles on an fcc lattice[12]—cannot realize the "T" configuration.

(g) The values of η_{lr} are somewhat smaller when the *Pa*3 phase is entered from the hcp than from the fcc phase (Fig. 3). This is perhaps due to stacking faults[6] which—in the spirit of Ref. 11—might perturb the *Pa*3 orientational pattern locally.

(h) The quadrupolar ordering temperature T_{or} does not coincide exactly with the hcp-*Pa*3 transition temperature

TABLE I. The quadrupolar ordering temperatures T'_{or} (fcc-*Pa*3) and T_{or} (*Pa*3-fcc), the transition temperature T_{sh} of specific-heat experiments (Ref. 8), and the change of the molar volume at the hcp-*Pa*3 ($\Delta V'$) and at the *Pa*3-fcc (ΔV) transition of $Ar_{1-x}(N_2)_x$.

x	T'_{or} (K)	T_{or} (K)	T_{sh} (K)	$\Delta V'$ (cm^3)	ΔV (cm^3)
0.937	31.7±0.15	32.2±0.15	32.25	0.15±0.02	0.148±0.02
0.900	29.95±0.15	30.3±0.15	30.17	0.12±0.02	0.094±0.02
0.865	27.7±0.15	28.5±0.15		0.04±0.02	0.05±0.02
0.830	25.0±0.15	25.3±0.15	25.58	−0.11±0.05	0±0.02

T_{hc}. Recall that we defined T_{hc} as the temperature where, on cooling, the hcp and the cubic intensities are of comparable strength. There is, however, evidence that T_{or} is about identical to that temperature, at which the first traces of cubic reflections appear on cooling. In that sense, one can say that the hcp-*Pa*3 reconstruction is triggered by the quadrupolar ordering process.

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