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Specific heat of solid nitrogen-argon mixtures: 50 to 100 mol % N_2

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We have measured the specific heat, C_p, of solid N_2-argon alloys of 49.75, 62.83, 70.43, 79.85, and 100 mol % N_2 concentration between 4.5 and 40 K. The measurements were made to investigate the possible formation of a rotational glass phase similar to that of solid H_2. The three lower-concentration samples showed no evidence of a sharp transition to a glass phase nor any thermal remanence indicative of a glass, although the rotational contribution to the specific heat was qualitatively similar to that of the solid H_2 glass. The 49.75-mol % sample did not exhibit the martensitic hcp-to-fcc crystalline transition expected at 23 K, indicating that cold working is important to forcing this transition. The α-β phase transition in pure N_2 was very sharp upon cooling to the transition point, without any pretransitional effects, whereas the α-β transition in the 79.85-mol % sample had a λ-like appearance.

I. INTRODUCTION

We have measured the specific heat of various solid alloys of nitrogen and argon to search for properties indicative of the formation of a molecular rotational glass phase. The N_2 molecule is a good example of a classical rotator having an intermolecular orientational interaction which is (1) primarily electric quadrupole-quadrupole (EQQ) in character, and (2) primarily nearest neighbor. Argon and N_2 form solid alloys across the entire range of N_2 concentrations, therefore allowing an arbitrary dilution of the N_2 quadrupoles. The N_2-argon system is similar in principle to the solid orthohydrogen-parahydrogen alloys which show some properties of a molecular rotational glass, the so-called quadrupolar glass. The N_2-argon solid offers some experimental simplifications over the H_2 solids but the N_2 molecules are classical rotators as opposed to the quantum nature of the orthohydrogen molecules. Although there have been previous studies of the thermal properties of solid N_2-argon alloys, the present work concentrates on the temperature-concentration range most analogous to the solid H_2 glass. This work is the first set of specific-heat measurements for $4 < T < 40$ K presented on a set of N_2-argon alloys grown in a consistent manner for N_2 concentrations greater than 50 mol %. In the process we also report results concerning the long-range molecular ordering transition in solid N_2.

The remainder of the paper is divided as follows. In Sec. II we describe the phases of solid N_2 and argon and their similarity to solid H_2, and refer to previous experimental results. The details of the present experiment and its data analysis are given in Sec. III. The remaining sections describe the specific-heat results in the three phases of solid N_2-argon which we measured.

II. SOLID N_2-ARGON ALLOYS

Pure N_2 exists in two phases under its own vapor pressure. In the high-temperature β phase the molecules precess about a local c axis in an hcp crystal lattice. Below $T = 35.6$ K the solid goes into the fcc α phase, in which the molecular rotation is quenched and the molecular moments are aligned along body diagonals of cubic sublattices, a $Pa3$ structure. The electric quadrupole-quadrupole interaction between the molecules is primarily responsible for the phase change and the alignment of the molecules. Dilution of the N_2 lattice with argon atoms depresses the α-β transition until it disappears at 77.5 mol % of N_2, as shown in the phase diagram of Barrett and Meyer[1] [Fig. 1(a)]. Further dilution with argon leads to the formation of another low-temperature fcc phase, presumably without molecular rotational ordering, for N_2 concentrations of less than 55 mol %. The properties of solid nitrogen and its alloys have been thoroughly reviewed in an article by Scott.[2]

Solid H_2 has a similar phase diagram as a function of orthohydrogen concentration [Fig. 1(b)], the exception being that there is no fcc phase at low orthohydrogen concentrations.[3] In solid H_2 samples of less than 55 mol % ortho-H_2 concentrations, mea-

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surements of NMR absorption and relaxation indicate a gradual freezing of the molecular moments without any long-range molecular order.[4] The so-called quadrupolar glass region is indicated by the dotted line on the H_2 phase diagram. The similarities of the N_2-argon and H_2 phase diagrams suggest that a quadrupolar glass phase would exist in solid N_2 for N_2 concentrations 55 mol% $<X(N_2)<78$ mol% in the hcp phase for $T<20$ K. Owing to orthohydrogen-to-parahydrogen conversion the quadrupole concentration of solid H_2 is never at equilibrium, unlike the situation in N_2-argon. Also the heat released in orthohydrogen conversion leads to thermal gradients in the H_2 sample which may be of importance at the low temperatures at which the glass is formed. Therefore, the N_2-argon alloys are more amenable to experimental investigation.

We have measured the specific heat C_p for samples of N_2 concentrations of 49.75, 62.83, and 70.43 mol% to find evidence of the quadrupolar glass. In addition, we measured samples of 79.85 and 100 mol% N_2 composition to examine the α-β phase transition and to diagnose the problems of sample growth. The location of the concentrations measured are indicated by arrows on the phase diagram Fig. 1(a).

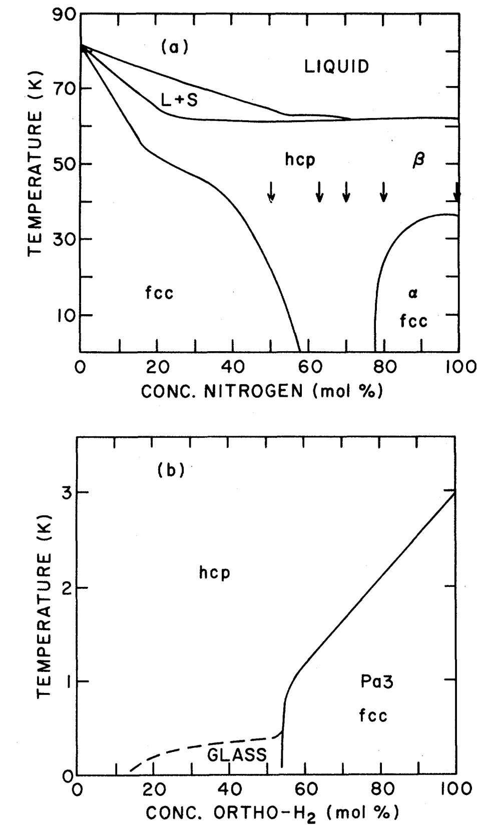

FIG. 1. (a) Phase diagram of solid N_2-argon alloys under vapor pressure as a function of N_2 molecular concentration. After Ref. 2. Arrows indicate concentrations measured in the present work. (b) Phase diagram of solid orthohydrogen-parahydrogen alloys under vapor pressure as a function of orthohydrogen molecular concentration. After Ref. 3 with additions from Ref. 19.

III. EXPERIMENT

The specific heat of the samples were measured by the Joule method in a copper cell of 25.1-cm^3 volume. The cell and an isothermal shield were enclosed in a vacuum can immersed in liquid helium. The cell was packed with a brush of thin copper wires to reduce the thermal impedance between the cell and the N_2-argon sample. The solid samples were grown by first condensing and freezing the necessary amount of the argon gas into the cell and then adding a measured amount of the N_2 component at a pressure of about 2 atm. Both sample gases were Matheson Ultra-High-Purity (99.999%) grade. The sample cell was then closed off to the filling volumes and heated to allow mixing of the N_2 and argon. Sample annealing consisted of holding the cell for 10–50 h slightly below the melting curve. A major concern of this work was the ability to produce homogeneous solid mixtures. To assure that proper mixing of the species had occurred, several of the samples were grown, annealed, measured for C_p, and then melted, reannealed, and remeasured. In these cases it was found that the C_p results were reproducible within the instrumental error of the apparatus.

The samples were heated with current pulses of 10–60 sec to a heater mounted on the copper cell. The temperature change of about 0.1 K produced by the heat was measured with a commercially calibrated germanium resistor monitored by a self-balancing conductance bridge. To compensate for the background temperature drift, typically less than 0.5 K/h, and for the thermal relaxation between the cell and sample, the temperature-drift curve was extrapolated from times before and after the heat pulse to measure ΔT. In general, the C_p results were reproducible to $\pm 3\%$ and the accuracy of the apparatus was checked by the measurement of the specific heat of the copper cell as well as by measurements of C_p of pure N_2 samples. The scatter of the experimental data increased for $T>40$ K, a result of a change in the sensitivity of the commercial conductance bridge and the decreasing sensitivity of the germanium thermometer at those temperatures.

Since the samples were grown at low pressures the solids were presumably under their own vapor pressure for those measurements. For the purpose of analyzing rotational contributions to the specific heat, C_p was corrected to C_v using the semiempirical relation

$$C_v = C_p - ATC_p^2 .$$

The constant A was chosen to be 3.1×10^{-4} (mole/cal) as calculated from data on pure N_2 below 10 K. This constant is relatively temperature independent and the factor ATC_p^2 is no more than 12% of C_v at the highest temperatures reported here. The lattice specific heat was approximated as a Debye contribution with characteristic temperature $\Theta_D = 82.5$ K as for pure N_2.[5] While it is true that Θ_D and A would vary for the different N_2 mixtures the variation should be small and was ignored in favor of overall consistency. The excess C_v left after subtraction of the Debye contribution is assumed to be mainly due to the rotation of the N_2 molecules, and it is thus referred to as C_{rot}.

IV. THE α-β PHASE TRANSITION

In the course of the experiments we measured the α-β phase transition in samples of 80 and 100 mol % N_2 concentration. Comparison of this data to the measurements of Pace *et al.*[6] allowed us to confirm the proper mixing of the N_2-argon samples and the basic accuracy of the measurements.

In our 100 mol % N_2 sample we carefully and repeatedly measured the specific heat at temperatures slightly above the α-β phase transition at 35.6 K. As pointed out by Scott,[2] although the specific heat of pure N_2 has been measured many times,[7–9] there are few data points for C_p for $35.6 < T < 40$ K. Measurements of the thermal expansion in the β phase disagree as to the behavior for T slightly above $T_{\alpha\text{-}\beta}$.[10–12] In particular, one set of x-ray-diffraction measurements shows a minimum in the thermal expansion at about 38 K.[12] Additionally, experiments by Koloskova *et al.*[13] showed that the thermal resistivity of pure solid N_2 decreases with increasing temperature slightly above $T_{\alpha\text{-}\beta}$ leading to a weak minimum at $T = 42$ K.

The behavior of C_p in the range $T_{\alpha\text{-}\beta} < T < 45$ K was measured under varying conditions, i.e., cooling from the β phase after warming through $T_{\alpha\text{-}\beta}$, and also after annealing at T slightly greater than $T_{\alpha\text{-}\beta}$ for several hours. It was found that the experimental results were reproducible except in the instances when C_p was measured soon after warming from the α phase. The anomalously high values of C_p recorded in these cases we attribute to remanent α-phase crystallites located in the β phase. The results for well-annealed β samples are shown in Fig. 2, with C_p data from the measurements of Clusius *et al.*,[9] and Giauque and Clayton.[7] The present results are uniformly about 5% above the previous data and show C_p to be increasing roughly linearly with temperature above $T_{\alpha\text{-}\beta}$ with no sign of a local minimum. The lowest temperature of these points was 35.8 K.

The 80 mol % N_2 sample showed an α-β phase transition at 22. 5 K, in qualitative agreement with the phase diagram of Pace *et al.*, and Barrett and Meyer. The specific-heat anomaly is rounded above $T_{\alpha\text{-}\beta}$ since $dT_{\alpha\text{-}\beta}/dX(N_2)$, unlike the case of pure N_2, as shown in Fig. 3. The latent heat of the transition was calculated following the method of Pace *et al.* The specific heat was smoothly extrapolated from below to above the transition. The remaining anomalous contribution at the transition was then integrated to produce a latent heat of 9.5 cal/mole. This value differs significantly from the value of 21.18 cal/mole given for the 83.072-mol % sample of Pace *et al.*, and may arise from differences in extrapolation of the specific-heat anomaly, since the

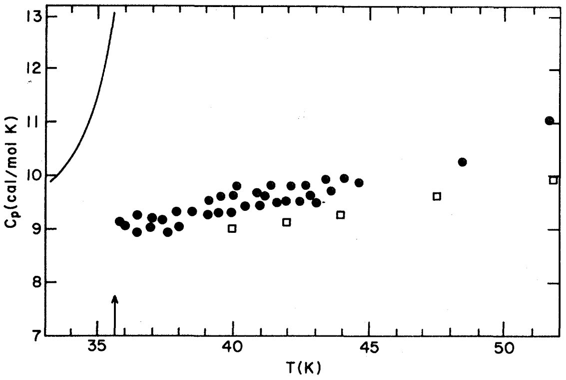

FIG. 2. Specific heat C_p for solid 100-mol % N_2 at temperatures above the α-β phase transition. ●, present work. □, Clusius *et al.* (Ref. 9).

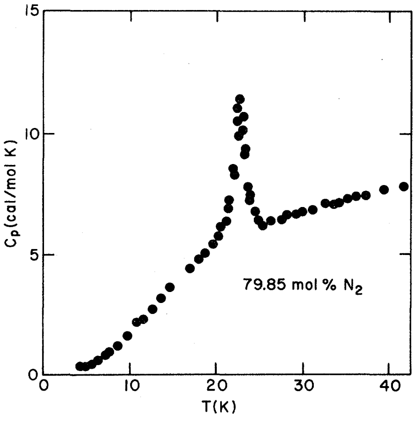

FIG. 3. Specific heat C_p of 80-mol % N_2-argon.

C_p values agree well in the two experiments. The agreement of our 80-mol % measurements with previous work indicates that our samples were reproducibly mixed by our growth and annealing process.

V. 49.75, 62.83, AND 70.43 mol % N_2 SAMPLES

We measured the specific heat of three samples having N_2 concentrations in the regime analogous to the solid hydrogen rotational glass: 49.75, 62.83, and 70.43 mol %. The specific heat C_p of these samples is shown in Fig. 4 and Table I, and the excess specific heat C_{rot}, calculated from the smoothed values of C_p, is shown in Fig. 5.

First we discuss the 49.75 mol % N_2 sample, in which the hcp to fcc transition is expected at about 25 K from the measurements of Barrett and Meyer. In the present specific-heat data there is no sign of the transition although the sample was repeatedly cycled in temperature and remeasured in the range of the expected transition. Barrett and Meyer noted that the phase change to the low-temperature fcc phase could be produced only by cold working of the samples, a facility not available in our apparatus. It is thus possible that our 49.75 mol % N_2 sample remained in the hcp phase down to the lowest measured temperatures. The similarity of the 49.75-mol % specific heat to the 62.83- and 70.43-mol % samples supports this possibility. Another alternative is that the energy difference between the fcc and hcp phases is too small to be discerned in the present experiment; however, we consider this less likely because of the martensitic nature of the transition and the arguments noted above.

The excess specific heats of all of these lower-concentration samples show a similar behavior. The specific heat C_{rot} has a rounded peak in the range of 17 K and drops off quickly at lower temperatures. There is no evidence of a first- or second-order phase transition which might be associated with the formation of a glass phase in the sample below 20 K. The specific-heat data was reproducible upon temperature cycling or upon reannealing of the samples, and there were no other signs of thermal remanence in the samples. We examined the thermal relaxation between the cell and sample after individual heat pulses to the cell. Although this relaxation is a function of the specific heat and the thermal conductance, formation of a rotational glass might lead to anomalously long relaxations at low temperatures. The measured relaxations for our samples were a smoothly varying function of temperature, without any such anomalously long relaxations.

Our data does not show the peak in C_{rot} below 10 K predicted by the mean-field calculation of Dunmore[14] although there is similarity above 15 K. The rapid drop in C_{rot} at lower temperatures in our results would indicate that the energy difference between the ortho and para species of the N_2 mole-

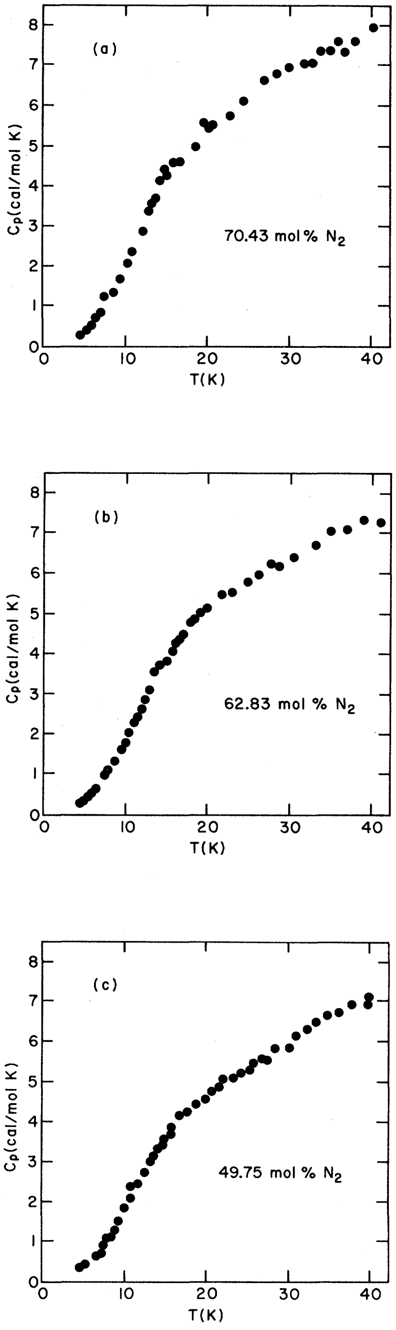

FIG. 4. Specific heat C_p of the lower N_2 concentration samples: (a) 70-mol % N_2, (b) 63-mol % N_2, and (c) 50-mol % N_2.

TABLE I. Smoothed values of C_p (cal/mole K) for various N_2 concentrations.

Temperature (K)	49.75 mol %	62.83 mol %	70.43 mol %	79.85 mol %
5.0	0.35	0.30	0.35	0.35
6.0	0.55	0.50	0.55	0.55
7.0	0.70	0.80	0.80	0.80
8.0	1.00	1.10	1.10	1.10
9.0	1.4	1.4	1.5	1.45
10.0	1.8	1.8	1.95	1.8
11.0	2.1	2.2	2.4	2.25
12.0	2.5	2.6	2.9	2.6
13.0	2.9	3.05	3.35	3.05
14.0	3.2	3.4	3.8	3.5
15.0	3.5	3.8	4.2	3.85
16.0	3.8	4.2	4.5	4.2
17.0	4.05	4.5	4.75	4.55
18.0	4.25	4.75	5.0	5.0
19.0	4.4	4.95	5.2	5.2
20.0	4.5	5.15	5.4	5.7
21.0	4.8	5.3	5.55	6.6
22.0	4.95	5.5	5.75	8.4
23.0	5.1	5.6	5.95	10.35
24.0	5.2	5.7	6.1	7.4
25.0	5.3	5.85	6.25	6.25
26.0	5.45	5.95	6.4	6.35
27.0	5.5	6.1	6.55	6.45
28.0	5.7	6.2	6.7	6.6
29.0	5.8	6.35	6.8	6.7
30.0	5.95	6.45	6.9	6.9
31.0	6.1	6.55	7.0	7.0
32.0	6.25	6.65	7.1	7.05
33.0	6.35	6.75	7.2	7.15
34.0	6.5	6.85	7.3	7.3
35.0	6.6	6.95	7.4	7.4
36.0	6.7	7.05	7.5	7.5
37.0	6.9	7.2	7.7	7.7
38.0	6.9	7.2	7.7	7.7
39.0	7.0	7.3	7.8	7.8
40.0	7.1	7.4	7.9	7.85

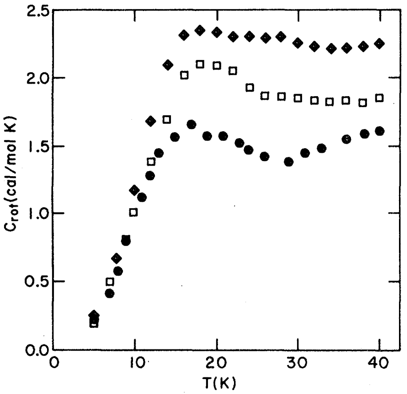

FIG. 5. Rotational contributions to the specific heat in the lower N_2 concentration samples: ◇, 70-mol % N_2; □, 63-mol % N_2; ●, 50-mol % N_2.

cules is much less than the 5 K calculated in that theory.

In Fig. 6 we compare the specific heat below 12 K of our 70.43-mol % sample with the data reported by Chausov *et al.*[15] for a 68-mol % N_2-argon sample. Their sample was grown by rapid freezing of a gas jet aimed at a cold surface, and therefore likely had many crystalline defects. The present work using crystals well annealed at the melting curve shows a specific heat almost twice as large as the data of Ref. 15 at 7 K although the difference decreases at lower temperatures. We consider this difference to be a result of the differing sample-growth techniques rather than of any intrinsic rotational motion in the N_2.

The excess specific heats were integrated to calcu-

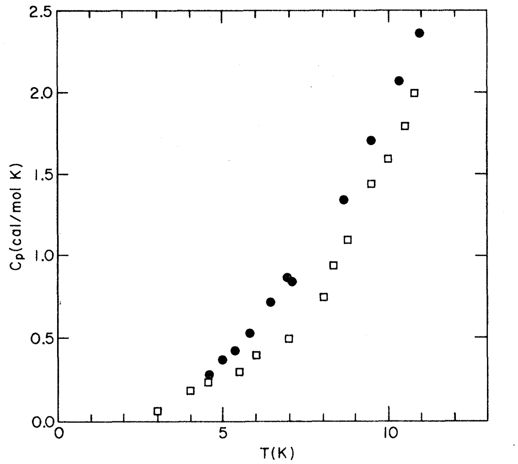

FIG. 6. Comparison of the specific heat C_p for samples of about 70-mol % N_2 concentration. ●, 70-mol % N_2, the present work; □, 68-mol % N_2, Chausov, Manzhelii, and Freiman (Ref. 15).

late the nominal rotational entropy of the N_2 molecules, where

$$S=\int_{T=0}^{T} C_v/T\,dT\ .$$

The function C_v/T had a peak for each sample in the region of 14 K and at low temperatures decreased smoothly toward zero at $T=0$. The calculated entropy at $T=40$ K was 3.48, 2.95, and 2.38 cal/mole for the 70.43-, 62.83-, and 49.75-mol % samples, respectively. Division of these values by the N_2 molar concentration X gave $S(T=40\ \text{K})/X=4.88\pm0.1$ cal/mole for all three samples. This agreement would indicate that the excess specific heat calculated here is primarily due to the N_2 molecular rotation.

VI. DISCUSSION

The major result of this work is that we have found no indication of the formation of a molecular rotational glass in solid N_2-argon alloys. The samples in the N_2 concentration range of 50–70 mol % show no evidence of a discrete phase transition or of any thermal remanence or long-term thermal relaxation. The specific heat of the samples, however, does show several similarities to the specific heat of solid H_2 in the orthohydrogen concentration range associated with the so-called quadrupolar glass.[16] The data is consistent with a gradual freezing of the rotational orientations but in our experimental time scale no "glassy" properties appeared.

Our data is consistent with recent studies of N_2-argon alloys by other techniques. Recent NMR absorption and stimulated echo measurements of a 67.5-mol % $^{15}N_2$-argon sample[17] show a continuous orientational freezing starting at about 20 K and stabilizing at 7 K. Alloys of 72 mol % N_2 concentration have been measured at Julich[18] by neutron scattering. Inelastic scattering showed no evidence of a sharp rotational phase transition but the results were consistent with a gradual progression to frozen-in rotational disorder at about 5 K.

The specific heat of the 50-mol % N_2 sample does not exhibit evidence of the martensitic transition to the fcc phase at 25 K expected from x-ray diffraction measurements. We consider this to mean that in the absence of cold working the sample remained in the hcp phase down to 4 K despite thermal cycling.

In measurements of the α-β phase transition in pure N_2 we found the specific heat to show a sharp transition upon cooling without any rounding above $T_{\alpha\text{-}\beta}$. By contrast, the α-β phase transition for our 80-mol % sample showed a λ-like appearance of the specific heat.

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