Structure and thermal expansion in solid deuterium

P. E. Sokol[*] and R. O. Simmons

*Department of Physics and Materials Research Laboratory, University of Illinois
at Urbana-Champaign, Urbana, Illinois 61801*

J. D. Jorgensen and J. E. Jørgensen

Argonne National Laboratory, Argonne, Illinois 60439

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Neutron-diffraction measurements are reported on a strain-free polycrystalline deuterium sample with a $J = 1$ concentration $x = 0.46$ between 0.20 and 14.0 K. The lattice remains simple hcp down to the lowest temperature studied. No new reflections or changes in diffuse scattering are observed as the sample is cooled. The molar volume has been determined from the lattice constants. Our results are consistent with measurements of C_V and $(\partial P/\partial T)_V$. Our diffraction data showed no evidence for a transition to a glassy phase at $T = 0.5$ K as suggested by the NMR experiments.

The existence of a "quadrupolar glass" phase in solid hydrogen (H_2) and deuterium (D_2) has been the subject of much debate.[1] This phase is proposed to exist for $J = 1$ concentrations, x, below $x = 0.55$, and temperatures below 0.5 K. H_2 has a simple hexagonal-close-packed (hcp) structure in this range;[2] diffraction work to date on D_2 has been only at higher temperatures.[3,4] The hcp structure is unfavorable to orientational ordering of the $J = 1$ molecules,[5] through their electric quadrupole quadrupole (EQQ) interaction, and frustrates the formation of a long-range high-symmetry ordered phase. It has been proposed that the $J = 1$ molecules, unable to order and reduce their orientational interaction energy, form a "quadrupolar glass" phase, similar to the Edwards-Anderson spin-glass phase[5] for dipoles.

The evidence for the existence of a quadrupolar glass phase comes almost exclusively from NMR.[6] A peak in the relaxation rate and a broadening of the absorption line are observed at temperatures below 0.5 K for $0.3 < x < 0.5$. These are taken as indicators of the formation of a glass phase and used to define the transition temperature. Heat-capacity measurements on solid H_2 (Refs. 7 and 8) below 1 K show anomalous behavior while similar measurements on D_2 (Refs. 7, 9, and 10) show only smooth behavior. Measurements of the pressure, which yields $(\partial P/\partial T)_V$, show only smooth behavior below 1 K for both H_2 (Refs. 11 and 12) and D_2 (Ref. 13). Heat capacity and $(\partial P/\partial T)_V$ measurements, in both H_2 and D_2, show a broad anomaly at 2–3 K for intermediate $J = 1$ concentrations.

To gain further insight into the possible existence of the quadrupolar glass phase we have carried out a neutron-diffraction study of solid deuterium. Neutron diffraction is sensitive to the orientational ordering of the $J = 1$ molecule, and long- and short-range order may be observed through superlattice peaks or diffuse scattering, respectively. Deuterium (rather than H_2) was chosen for its small incoherent cross section, which minimizes the background scattering, and for its much slower conversion rate. The slower conversion, and resultant smaller self-heating, make it possible to perform experiments at nearly constant $J = 1$ concentration that last days, instead of hours as for H_2; it also simplifies the problem of heat removal from the sample.

We report here the first detailed measurement of the temperature dependence of the molar volume for D_2 at intermediate $J = 1$ concentrations. This work was carried out using the special environment powder diffractometer (SEPD) at the intense pulsed neutron source at Argonne National Laboratory. This is a time-of-flight powder-diffraction instrument with a resolution of $\Delta d/d = 0.005$ for a fixed 90° scattering angle. Knowledge of the Bragg line shape from calibration samples allows the peak center to be determined accurately and gives an overall accuracy of 50 ppm for lattice constants. The D_2 sample was contained in a vanadium can (5.4 cm long × 0.83 cm diameter), with copper wires at the top and a copper plug at the bottom, both thermally anchored to the mixing chamber of a dilution refrigerator. Only the time-focused 90° detector banks of the SEPD were used, so that the aluminum radiation shields could be masked with cadmium and a diffraction pattern from only the D_2 sample could be obtained.

The solid sample was grown from the liquid, at vapor pressure, and formed a polycrystalline sample judged from the Bragg line shape to be strain free. The initial $J = 1$ concentration of the gas used to form the sample was $x = 0.49$ and the final concentration was $x = 0.43$, giving a mean concentration $\bar{x} = 0.46$ and a conversion rate $\bar{k} = 0.01/h$, in good agreement with the accepted rate in the solid.[14] Fourteen Bragg peaks were observed, each of which was separately fit to the line-shape function[15] to obtain d spacings. Lattice constants a and c at each temperature were then obtained by weighted least-squares fit to the d spacings. The c/a ratio was found to be constant, within experimental uncertainties, and equal to 1.6322 ± 0.0002. The molar volume, obtained from a and c, is shown in Fig. 1. The data points were taken in random order as a function of temperature, and found to be repeatable, indicating that there is little hysteresis, at least above 2 K. Our values for this molar volume are in good agreement with those of Yarnell, Mills, and Schuch[3] and comparable to the values of Schuch and Mills[4] and Mucher, Harris, White, and Erickson.[16]

We do not observe any deviations from the simple hcp lattice structure; thus the possibility that the sample undergoes an hcp-fcc transition at this concentration can be ruled out for $T > 0.2$ K. No new reflections, indicating long-range order, or increase in diffuse scattering, indicating short-range order, are observed at any temperature. We conclude that (a) a low-symmetry ordered state does not oc-
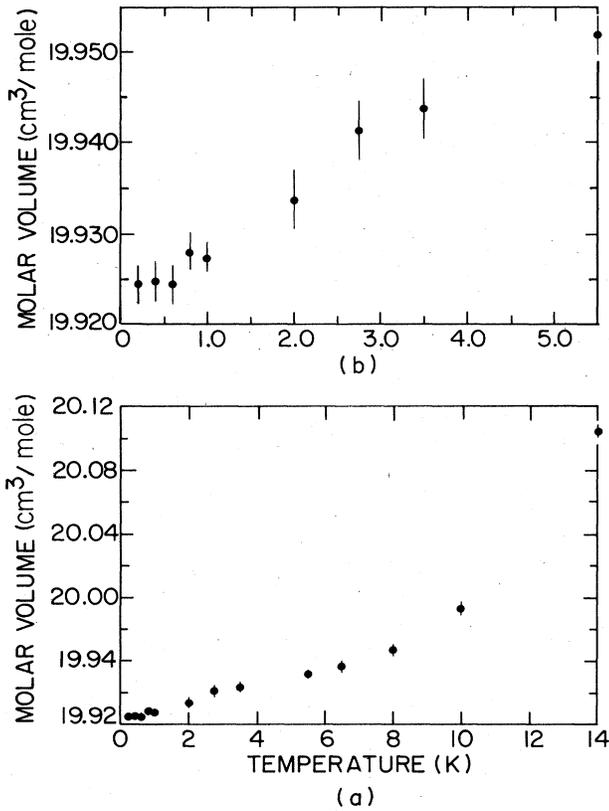
FIG. 1. Molar volume vs temperature: (a) 0.2–14 K; (b) 0.2–5.5 K.

FIG. 2. $\square$—this work, $\triangle$—Eq. (1), $\bigcirc$—Eq. (3). Error bars are not shown. Below 6 K all measurements are in agreement within the respective errors.

cur on the hexagonal lattice (calculations of the diffraction pattern for any of the proposed ordered hexagonal ground states[17] indicate they would be easily visible with SEPD under our conditions), and (b) that no significant amount of short-range order exists.

The volume thermal expansion β may be related to the $(\partial P/\partial T)_V$ measurements of Ramm, Meyer, and Mills[13] through the compressibility. Rather than numerically differentiating our results, which would lead to unacceptably large errors, we numerically integrate the $(\partial P/\partial T)_V$ data, which are more precise. We then obtain

$$V(T) = \frac{K_T}{V} \int_{T'}^{T} (\partial P/\partial T)_V dT'' + V(T') \ , \qquad (1)$$

where the isothermal compressibility K_T has been assumed temperature independent over the range of the $(\partial P/\partial T)_V$ data (0.3–4.2 K), which is a good approximation. Using the compressibility from the equation of state of Driessen, deWall, and Silvera[18] we can directly compare our results to the $(\partial P/\partial T)_V$ measurements of Ramm et al.[13] A comparison of the molar volume and integrated $(\partial P/\partial T)_V$ is shown in Fig. 2. Within experimental uncertainties we find that Eq. (1) is satisfied from 0.3–4.2 K. Thus, our results are thermodynamically consistent with those of Ramm et al.[13]

The heat capacity may also be related to the volume thermal expansion using a Gruneisen picture. In this case
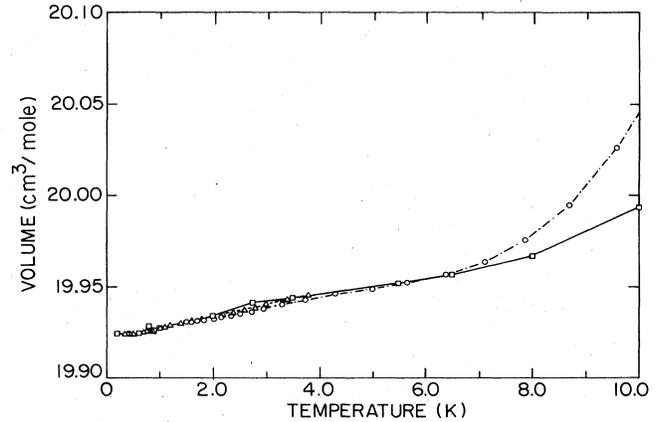
$$\beta = \frac{\gamma K_T}{V} C_V \ , \qquad (2)$$

where γ is the Gruneisen constant and C_V is the constant volume heat capacity. Over a temperature range in which temperature dependence of γ and K_T may be ignored, integration of Eq. (2) yields

$$V(T) = \gamma K_T \int_{T'}^{T} C_V(T') dT'' - V(T') \ . \qquad (3)$$

The integral in Eq. (3) may be calculated using the constant volume heat capacity of Grenier and White[10] in the temperature range 1.5–10 K. The integrated heat capacity multiplied by γK_T, where $\gamma = 3.5$, is compared to the molar volume in Fig. 2.

At temperatures below 5 K we find a temperature-independent Gruneisen constant from Eq. (3). We find $\gamma = 3.5 \pm 0.5$, in good agreement with the accepted value of 3.66 (Ref. 13). The total Gruneisen constant measured here is the sum of a lattice contribution (2.0 ± 0.1) (Ref. 13) and a quadrupolar contribution $(\frac{5}{3})$. From our measurements, we find no indication of a temperature-dependent γ below 6 K.

At temperatures above 6 K a significant difference develops between our direct volume measurements and the integrated heat capacity, which is larger (Fig. 2). At least part of this can be attributed to temperature variation of K_T, which decreases with increasing temperature. In addition, variation of the lattice contribution to γ is to be expected as modes other than the long wavelength modes responsible for the low-temperature specific heat become important. From a preliminary assessment of these effects, we conclude that our measurements are consistent with the heat-capacity measurements.

In conclusion, we find that the D_2 lattice is hcp at all temperatures and that there is no evidence of any rotational ordering of the quadrupolar moments at low temperatures. Our results are consistent with both C_V and $(\partial P/\partial T)_V$ measurements indicating the system is always in thermodynamic equilibrium over a time scale of 12 h, the duration of the shortest of these experiments. The anomalous behavior at 2–3 K observed by $(\partial P/\partial T)_V$ and C_V is also seen in our results. This is presumably due to depopulation of the rotational sublevels.[10] No evidence is found, either in our diffraction measurements, or in the heat capacity and

$(\partial P/\partial T)_V$ measurements, of the transition at 0.5 K as observed by NMR.

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*Permanent address: Department of Physics, Harvard University, Cambridge, MA 02138.

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