Measurement of the magnetic susceptibility of solid hydrogen and deuterium at 4.2 K

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(Submitted 24 November 1988)
Zh. Eksp. Teor. Fiz. **95**, 2090–2096 (June 1989)

The present study describes a measurement of the static magnetic susceptibility of solid hydrogen and deuterium at 4.2 K by means of a SQUID-magnetometer. By using absolute calibration, thereby excluding the need for materials of known susceptibility, a value of $-(3.5\pm0.2)\cdot10^{-6}$ cm^3/mol has been obtained for the diamagnetic susceptibility of solid hydrogen, which is relatively close to the susceptibility of a free hydrogen molecule. A value of $-(3.7\pm0.2)\cdot10^{-6}$ cm^3/mol has been obtained for deuterium. The change in the magnetic susceptibility of solid hydrogen at 4.2 K due to ortho-para conversion was also measured and the rate constant of this process was determined to be $(1.9\pm0.1)\cdot10^{-2}$ hr. The analysis reveals that the forces responsible for ordering in solid hydrogen are weak at 4.2 K.

In spite of the fact that the condensed phases of hydrogen and deuterium have been studied for over 60 years, no magnetic susceptibility data on them have been available. This can be attributed to its small value as well as the fact that direct magnetic measurements are difficult to implement at low temperatures.[1] Moreover the data obtained by dynamical techniques (NMR, neutron radiography) of investigating a number of phenomena in solid hydrogen, particularly quantum diffusion, contradict results of statistical equilibrium experiments where specific heat measurements are largely used. We therefore thought it would be interesting to employ a superconducting quantum magnetometer[2] to carry out a direct measurement of the static magnetic susceptibility of solid hydrogen at 4.2 K.

Preliminary experiments revealed that fused quartz is the best material for fabrication of the test ampule. It produces a stable, low-level diamagnetic response on the magnetometer which is weakly temperature-dependent, allows simple and reliable surface cleaning to eliminate all possible ferromagnetic impurities, very nearly eliminates the possibility of reverse conversion and guarantees hydrogen purity in the ampule after sealing. The test ampule (Fig. 1), the idea of which was borrowed from Lazarev and Shubnikov,[1] consisted of a quartz tube with partition 1. The ampule stem 2 was evacuated to $\sim10^{-3}$ torr and sealed. The reservoir 3 with a volume of ~0.4 *l* was located at the top of the ampule. Such a test ampule design allows the diamagnetic contribution of the ampule to the total response to be minimized (the ampule partition 1 was the only ampule element to produce a magnetometer response). The pure hydrogen used to wash and fill the ampule was obtained by first passing hydrogen from a containment vessel through liquid nitrogen-cooled SKT-4 activated carbon for dehydration, and then through a Pd–Ag filter heated to 300–350 °C. The ampule was evacuated to $\sim10^{-4}$ torr upon heating to 250–300 °C, was then washed 6–8 times and filled with pure hydrogen to 0.9 atm and sealed. The solid hydrogen column 4 condensed above the partition as the ampule was slowly submerged in a helium cryostat; this solid hydrogen also served as the specimen. The inner diameter of the ampule in the specimen area was 5.4 ± 0.05 mm. Chromatographic analysis of the hydrogen in the ampule revealed that the concentration of the impurity posing the greatest danger for magnetic measurements—oxygen—was less than 10^{-5} vol.%, which yields a magnetometer reading below the sensitivity of the instrument in any oxygen condensation conditions. This same technique was used to prepare the solid deuterium specimen.

The error bars were reduced and the magnetic moment sensitivity of the unit[2] was substantially improved by optimizing the number of turns and the dimensions of the collection coils of the flux transformer in order to perform measurements of the magnetic susceptibility of solid hydrogen; the sensitivity of our experiments was 10^{-11} J/T. The SQUID recording electronics operated in a feedback mode and recorded the magnetic flux in the flux transformer of the magnetometer as a function of the specimen position (the magnetometer response).

In order to determine the absolute magnetic susceptibility from these initial measurements we will find the magnetic flux Φ induced in the collection coils with a winding radius of R_2 uniformly magnetized by a cylindrical specimen of radius R_1 and height $2H$ (Fig. 2):

$$\Phi=\oint_1 \mathbf{A}_1\,d\mathbf{l}_1-\oint_2 \mathbf{A}_2\,d\mathbf{l}_2, \tag{1}$$

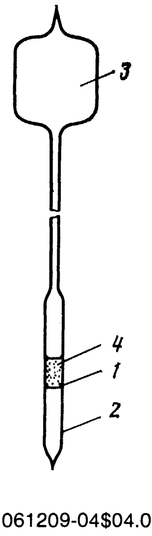

FIG. 1. Test ampule: 1—Partition; 2—ampule stem; 3—0.4 *l* reservoir; 4—solid hydrogen column.

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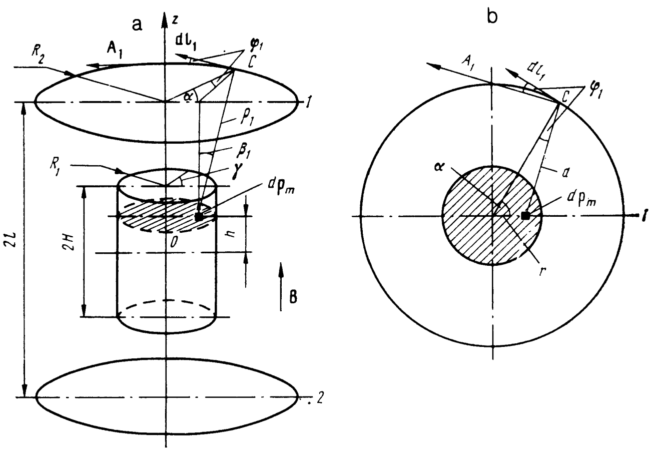

FIG. 2. a—Uniformly magnetized cylinder between collection loops 1 and 2 of the flux transformer; b—determination of the vector potential of the point magnetic dipole $d\mathbf{p}_m$ in upper collection loop 1.

where the contour integrals are taken over the circles (collection loops) 1 and 2 approximating the collection coils, while the minus sign appears because they are pointing backward in the magnetic gradiometer circuit of the flux transformer.

We will represent the specimen as a set of point dipoles with a magnetic moment $d\mathbf{p}_m$. We have the following expression for a specimen with magnetic susceptibility χ in a uniform vertical magnetic field **B** on the cylinder axis:

$$d\mathbf{p}_m = \frac{\chi B}{\mu_0} dV, \tag{2}$$

where $dV = r d\gamma dr dh$ is the elementary volume corresponding to the point magnetic dipole in cylindrical coordinates. The vector potential of the point dipole at a random point C of the upper collection loop 1 has the following absolute value:

$$dA_1 = \frac{\mu_0}{4\pi} \frac{dp_m \sin\beta_1}{\rho_1^2}. \tag{3}$$

The vector potential of the entire specimen is

$$A_1 = \int_V dA_1 = \frac{\mu_0}{4\pi} \int_V \frac{dp_m \sin\beta_1}{\rho_1^2} = \frac{\chi B}{4\pi} \int_V \frac{\sin\beta_1}{\rho_1^2} dV. \tag{4}$$

The magnetic flux in the upper collection loop is written as

$$\Phi_1 = \oint_1 A_1 \, dl_1 \cos\varphi_1 = \frac{\chi B}{4\pi} \oint_1 \int_V \frac{\sin\beta_1}{\rho_1^2} \cos\varphi_1 \, dV \, dl. \tag{5}$$

Since $\sin\beta_1 = a/\rho_1$, $\cos\varphi_1 = (a^2 + R_2^2 - r^2)/2aR_2$, $dl = R_2 d\alpha$, we have

$$\Phi_1 = \frac{\chi B}{4\pi} \int_0^{2\pi} \int_V \frac{a^2+R_2^2-r^2}{2\rho_1^3} dV \, d\alpha. \tag{6}$$

The expression for Φ_2 is written analogously. Taking into account

$$a^2+R_2^2-r^2=2R_2(R_2-r\cos\alpha), \quad \rho_1=[a^2+(L-h-z)^2]^{1/2},$$

we finally obtain the following expression for the magnetic flux in the collection coils of the flux transformer:

$$\begin{aligned}\Phi = {} & \frac{\chi B}{4\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{R_1} \int_{-H}^{+H} R_2 r (R_2 - r\cos\alpha) \\ & \times \left\{ \frac{1}{[a^2+(L-h-z)^2]^{3/2}} - \frac{1}{[a^2+(L+h+z)^2]^{3/2}} \right\} d\gamma \, d\alpha \, dr \, dh \\ = {} & \chi B \int_0^{\pi} \int_0^{R_1} \int_{-H}^{+H} R_2 r (R_2 - r\cos\alpha) \{ [R_2^2+r^2-2R_2 r\cos\alpha \\ & + (L-h-z)^2]^{-3/2} \\ & - [R_2^2+r^2-2R_2 r\cos\alpha + (L+h+z)^2]^{-3/2} \} d\alpha \, dr \, dh \\ = {} & \chi B R_2^2 f_1 (R_1/R_2, L/R_2, H/R_2, z/R_2).\end{aligned} \tag{7}$$

The z coordinate specifies the position of the center of the specimen relative to the center of a segment connecting the centers of the collection loops.

After the simplifications numerical integration was carried out for different values of R_1, R_2, L, H. The complete representation of the function $\Phi(z)$, which gives the dependence of the collection loop flux on specimen position, is shown in Fig. 3.

Then for our setup ($R_2 = 5$ mm and $L = 5$ mm) we determined the flux amplitude

$$\Phi_{\text{amp}} = \chi B R_2^2 f_2 (R_1/R_2, \ L/R_2, \ H/R_2) \tag{8}$$

for different specimen dimensions (R_1 and H) (Fig. 3). The corresponding number of magnetic flux quanta N_{amp} registered by the SQUID is proportional to Φ_{amp}:

$$N_{\text{amp}} = K\Phi_{\text{amp}}. \tag{9}$$

The coefficient k was determined from calibrating the apparatus by two independent techniques: with a superconducting lead sphere of diameter 0.73 mm and a small current-

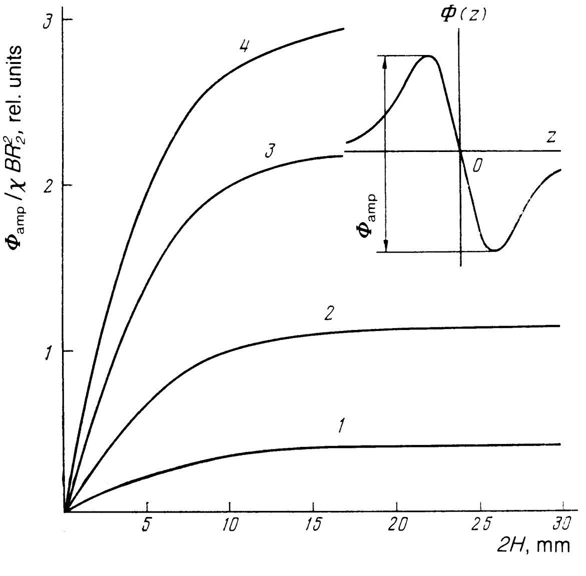

FIG. 3. The magnetic flux amplitude Φ_{amp} in the collection coils plotted as a function of specimen dimensions for our flux transformer configuration ($R_2 = L = 5$ mm); R_1 is equal to 0.5 (1), 2.5 (2), 3.5 (3) and 4 mm (4). The insert shows the total magnetic flux in the flux transformer plotted as a function of z.

carrying coil of diameter 0.9 mm. The similarity of the results obtained ($6.59\cdot10^{12}$ quantum/T·m^2 for the superconducting sphere and $6.56\cdot10^{12}$ quantum T·m^2 for the current-carrying loop) suggests that the calibration is reliable, and eliminates the need for standards with a known susceptibility. It is therefore possible to determine the magnetic susceptibility from (8) and (9) by measuring the magnetometer response as the cylindrical specimen is displaced between collection coils 1 and 2 of the flux transformer:

$$\chi=\frac{N_{\rm amp}}{kBR_2^2 f_2(R_1/R_2, L/R_2, H/R_2)}. \qquad (10)$$

A representative magnetometer response in measuring the solid hydrogen specimen in the quartz ampule is shown in Fig. 4. Curve 1 represents the response from a hydrogen-containing ampule and curve 2 represents the response from an empty ampule washed by pure hydrogen and evacuated to $\sim10^{-5}$ Torr, while curve 3 was obtained by subtracting curve 2 from curve 1 and represents the response from the solid hydrogen specimen alone.

We investigated the changing response of the setup in different condensation conditions of the solid hydrogen specimen. The condensation conditions were selected visually using a glass cryostat with a temperature field similar to the field in the magnetometer measurement volume. We established that a transparent cylindrical column of solid hydrogen $\sim$10–11 mm in height (depending on the initial hydrogen pressure in the test ampule) condenses in the ampule above the liquid helium level upon moderately rapid (20–30 minutes) cooling of the test ampule. By measuring the magnetometer response at different hydrogen condensation rates we found the discrepancy to be less than 3%. This is evidently due to smearing of the upper boundary of the polycrystalline specimens formed in the process, which results in some ambiguity in the height of the specimen and the coefficient f_2 in Eq. (10) dependent on specimen height.

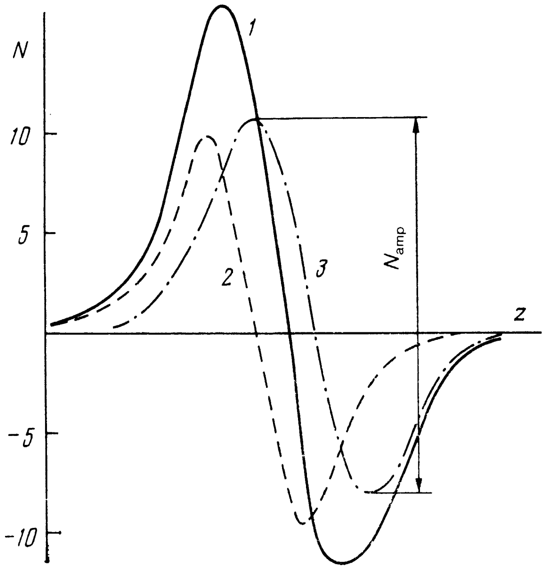

FIG. 4. Process for obtaining the magnetometer response from the solid hydrogen specimen (magnetization field: 62 mT): 1—Total response of the test ampule and the solid hydrogen specimen; 2—response of the test ampule; 3—response of the solid hydrogen specimen; N—change in the number of magnetic flux quanta recorded by the instrument from displacement of the test ampule between the collection loops of the flux transformer.

An equilibrium ortho-para composition of the hydrogen and deuterium in the test ampule at room temperature was guaranteed by feeding the hydrogen from the containment vessel through a heated Pd–Ag filter immediately prior to filling of the ampule. The susceptibility measurements were carried out 20–30 minutes after condensation of the solid hydrogen specimen. Five to six such measurement cycles were performed. We estimate the increase in the diamagnetic susceptibility attributable to the ortho-para conversion resulting from this process to be of the order of $5\cdot10^{-8}$ cm^3/mol, which is much less than the absolute measurement error. For subsequent measurements the ampule was scrubbed and refilled with hydrogen or deuterium with an equilibrium ortho-para composition at 20 °C.

A value of $-(3.1\pm0.2)\cdot10^{-6}$ cm/mol was obtained for the magnetic susceptibility of solid hydrogen of normal ortho-para composition. Subtracting the nuclear paramagnetism contribution

$$\chi_{\rm nuc}=\frac{3}{4}\frac{N_A}{3}\frac{8\mu_p^2}{k_{\rm B}T}=0.41\cdot10^{-6}\ {\rm cm^3/mol}$$

we obtain for the diamagnetic susceptibility of solid hydrogen at 4.2 K

$$\chi_{\rm diam}=-(3.5\pm0.2)\cdot10^{-6}\ {\rm cm^3/mol},$$

which is less than the diamagnetic susceptibility of gaseous hydrogen $-(3.9\text{–}4.0)\cdot10^{-6}$ cm^3/mol (Ref. 3). Theoretical calculations for a free hydrogen molecule yield $-(3.8\text{–}4.0)\cdot10^{-6}$ cm^3/mol (Ref. 4, 5).

Similar measurements for deuterium (containing less than 1% protium), whose nuclear paramagnetism can be ignored, yielded

$$\chi_{\rm diam}=-(3.7\pm0.2)\cdot10^{-6}\ {\rm cm^3/mol};$$

with the calculated value for a free deuterium molecule equal to $-4.03\cdot10^{-6}$ (Ref. 5). In converting the volume susceptibility χ to the molar susceptibility

$$\chi_M=\frac{\chi}{4\pi}V_M$$

we employed the recommended values of the molar volumes V_M (Ref. 6): 22.9 cm^3/mol for hydrogen and 19.9 cm^3/mol for deuterium.

We also carried out an experimental investigation of the effect of ortho-para conversion in solid hydrogen at 4.2 K on the magnetic susceptibility. It is important to point out that in spite of the fact that the conversion rate in solid hydrogen has long been a subject of investigation, the data obtained by different authors often vary quite substantially. This is due to the catalytic action of the most insignificant paramagnetic impurities present in both the solid hydrogen specimen itself and the material used to fabricate the test vessels. We therefore believe that the ortho-para conversion data represent an important indicator of experimental purity.

In order to perform this analysis the setup was converted into a flow-type SQUID-magnetometer allowing susceptibility measurements in a setup where liquid helium is continuously fed through a capillary in a quantity sufficient to compensate its natural evaporation from the cryostat. The total "ampule + solid hydrogen specimen" diamagnetic response was partially magnetically compensated by four turns of 0.05 mm paramagnetic platinum wire around the ampule near the partition. This yielded a fourfold improvement in measurement sensitivity. The ampule containing the hydrogen with a normal ortho-para composition was held in the magnetometer for approximately 25 hours at 4.2 K. The resulting change in magnetic susceptibility is shown in Fig. 5. Assuming that this increase in diamagnetism can be attributed solely to the diminishing nuclear paramagnetism due to ortho-para conversion, we obtained from least-squares processing of these data (the solid curve in Fig. 5) the result $(1.9 \pm 0.1)\cdot 10^{-2}$ hr^{-1} for the conversion constant, which is in agreement with published data.[7]

The proximity of the diamagnetic susceptibility values for hydrogen and deuterium in the condensed phase to both the experimental and calculated values for free H_2 and D_2 molecules suggests that no substantial rearrangement of the electron density occurred from crystallization. At this temperature the forces responsible for ordering in solid hydrogen are evidently still too weak to have a substantial effect on the paramagnetism of the ortho-molecules. This confirms the conclusions from other experiments suggesting free rotation of the hydrogen molecules in the solid at helium temperatures. It would be interesting to carry out more rigorous calculations of the magnetic susceptibility, accounting for the interactions in solid H_2 and D_2, in view of the slight discrepancy of the diamagnetic susceptibility of hydrogen and deuterium in the condensed phase and in the free state.

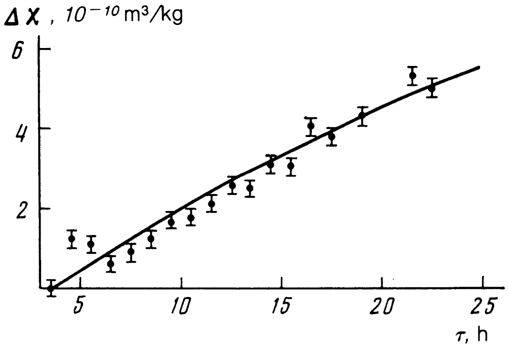

FIG. 5. Increase in the diamagnetic susceptibility $\Delta\chi$ of a solid hydrogen specimen of normal ortho-para composition due to ortho-para conversion at 4.2 K; τ is time from the onset of conversion.

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Translated by Kevin S. Hendzel