

## NMR Evidence for Solid-Fluid Transition near 250 K of $^3\text{He}$ Bubbles in Palladium Tritide

G. C. Abell and A. Attalla

*Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio 45342*

(Received 8 June 1987)

Nuclear-magnetic-resonance relaxation times for  $^3\text{He}$  in microscopic bubbles in 1-yr-old  $\text{Pd}^3\text{H}_{0.62}$  have been measured in the range 100–320 K. The results provide evidence for the melting of He in the range 200–280 K and for He diffusion in solid He below 200 K. The observed melting temperatures give a mean He-atom density, from which the ratio of He atoms to host-atom vacancies is found to be 2.0. An activation energy for He diffusion has been obtained and its relationship to the observed mean melting temperature is compared with that found in bulk  $^3\text{He}$  at much lower densities.

PACS numbers: 64.70.Dv, 62.50.+p, 67.80.Jd, 67.80.Mg

Inert gases are virtually insoluble in metals; upon introduction into a metal (e.g., by ion implantation) they precipitate and form microvoids or “bubbles.” At ambient temperature, these inert-gas bubbles grow by athermal processes rather than by absorption of thermal vacancies. Hence the growth process is driven by gas pressure, which is thus considerably greater than the equilibrium pressure ( $\approx 1$  GPa) required to balance the surface tension of the bubble. Transmission-electron-microscopy (TEM) studies showing bubbles of solid Xe and Ar in Al at room temperature,<sup>1</sup> and solid-to-gas transitions of Kr in Ni and in Cu above 600 K<sup>2</sup> provide dramatic evidence for the existence of highly overpressurized bubbles. The greatest technological interest, though, is with He in metals, which has a fairly extensive literature.<sup>3</sup> Unfortunately, because of the low-scattering power of He, TEM has not provided information on the physical state of He within bubbles. uv-absorption-spectroscopy studies<sup>4</sup> suggest that He bubbles in Al solidify upon cooling to about 150 K, but the current overall picture for the density and physical state of He in metals—based on a variety of experimental techniques—is confused, with a wide range of reported densities and no clear evidence for a solid-to-gas transition.<sup>3</sup>

Nuclear-magnetic-resonance (NMR) studies of *bulk*  $^3\text{He}$  show that while atomic exchange is important for relaxation in the bcc structure, it is inconsequential for pressures above about 10 MPa (where the solid is hcp).<sup>5</sup> In the latter case, modulation of the dipolar interaction by vacancy motion dominates  $^3\text{He}$  spin relaxation.<sup>6</sup> The temperature dependence of the spin-lattice relaxation time ( $T_1$ ) is here well described by the classical Bloembergen, Purcell, and Pound (BPP) formulation,<sup>7</sup> exhibiting the characteristic (frequency dependent) minimum. When melting occurs,  $T_1$  increases by 2 to 3 orders of magnitude, thus providing a clear indication of the phase change.<sup>8</sup> The observed bulk relaxation behavior suggests that  $^3\text{He}$  relaxation-time measurements might yield valuable information relating to the physical state and dynamics of He within bubbles, provided that NMR sensitivity limitations can be overcome and that the bulk mechanisms are not obscured by wall effects.<sup>9</sup> Ion im-

plantation of  $^3\text{He}$  can be used to prepare samples for NMR investigation,<sup>10</sup> but it is difficult to attain an adequate total spin count. An alternate approach is to synthesize a metal hydride with use of tritium ( $^3\text{H}$ , which decays with a half-life of about twelve years, giving  $^3\text{He}$  as a stable product). This latter method provides homogeneous  $^3\text{He}$  deposition and avoids the direct displacement damage caused by ion implantation.<sup>11</sup> However, it requires handling hazardous radioactive material and waiting for a sufficient number of  $^3\text{He}$  spins to form. Previous NMR studies of  $^3\text{He}$  in metal tritides<sup>9,12</sup> provide very little information about the physical state of He, but these studies were limited to older samples where appreciable release of He from the lattice had occurred, presumably a consequence of extensive lattice damage. Ideally, one would like to study a metal tritide old enough to give a  $^3\text{He}$ -spin count sufficient for practical NMR signal-averaging methods, yet not so old that He release is occurring. Depending on the tritium density of the NMR sample, 5–15 months of aging should satisfy these criteria.

This article presents NMR evidence, relating to  $^3\text{He}$  produced by tritium decay in 1-yr-old palladium tritide, for a BPP minimum below 200 K and for a solid-fluid phase transition in the range 200–280 K. Palladium is an ideal system for the present study because (i) the physical properties of palladium hydride have been thoroughly investigated,<sup>13</sup> (ii) the magnetic properties of Pd nuclei (small gyromagnetic ratios) and of bulk palladium hydride (small magnetic susceptibility) should simplify interpretation of  $^3\text{He}$  NMR measurements, (iii) pressure-composition-temperature characterization of the Pd- $^3\text{H}$  system is fairly extensive,<sup>11</sup> and (iv) TEM imaging of He bubbles in 66-day-old  $\text{Pd}^3\text{H}_{0.6}$  provides information about bubble size and density.<sup>14</sup>

The Pd material used in the present study consists of spherical particles in the size range 75–150  $\mu\text{m}$ . Chemical analysis reveals insignificant concentrations ( $< 10$  at. ppm) of possible paramagnetic impurities (O, Fe, Mn). Preliminary proton  $T_1$  measurements on a protide of this Pd show that dilution with an insulator ( $\text{Al}_2\text{O}_3$ ) has little effect on signal intensity per gram of Pd. Thus, 2.42 g of

undiluted Pd was placed in an NMR sample tube (this gave near-optimum filling within the coil region), loaded with about 0.1-MPa tritium gas, and stored at room temperature. The initial composition was determined from  $P$ - $V$ - $T$  measurements to be  $[^3\text{H}]/[\text{Pd}] = 0.62$ . NMR spin-counting techniques show only about 30% of the expected total number of  $^3\text{H}$  spins in the sample. This shortfall is due to skin effect<sup>15</sup> (the particle diameters are 2–3 times the skin depth at 25 MHz). Significantly, though, the  $^3\text{He}$ - to  $^3\text{H}$ -spin ratio after one year of aging agrees closely with the predicted ratio, implying that the  $^3\text{He}$  NMR results described below are representative of all the He born in the lattice. (The NMR system used in the present study has been described elsewhere.<sup>9a</sup>)

Figure 1 shows the temperature dependence of  $T_1$  and  $T_2$  (spin-spin) relaxation times at a Larmor frequency of 25 MHz for  $^3\text{He}$  in 1-yr-old Pd $^3\text{H}_{0.62}$ . The abrupt change in  $T_1$  near 220 K, by almost 1 order of magnitude, is strong evidence for a phase transition. Actually, there is a region of coexistence between 200 and 280 K where the time dependence of the magnetization recovery is well described by a sum of two exponentials corresponding to varying relative amounts of the two phases. (Analogous behavior has been observed<sup>8a</sup> near the melting point for bulk  $^3\text{He}$ .) Outside the coexistence region, the recovery is ostensibly exponential. The observed range of melting temperatures ( $T_m$ ) is considerably larger than what would be expected for isochoric melting of He at a single density<sup>16</sup>; it most likely reflects a distribution of densities for the ensemble of bubbles. From the observed melting curve<sup>16</sup> for bulk  $^4\text{He}$  between

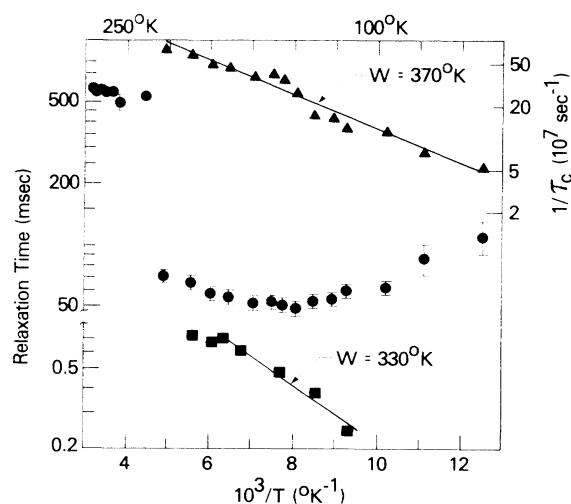


FIG. 1. Temperature dependence in 1-yr-old Pd $^3\text{H}_{0.62}$  of  $^3\text{He}$   $T_1$  (filled circles) and  $T_2$  (filled squares) relaxation times at 25 MHz (left-hand scale); and of  $^3\text{He}$  jump frequency  $\tau_c^{-1}$  (filled triangles) obtained from BPP analysis of  $T_1$  (right-hand scale). The  $T_1$  data set includes 99%-confidence-interval error bars. Note that the left-hand scale is broken.

100 and 350 K, we infer bubble pressures ranging from 6.0 to 11.0 GPa corresponding to  $200 < T_m < 280$  K. Using a high-pressure equation of state developed<sup>17</sup> for  $^4\text{He}$  (the isotope effect is small<sup>18</sup>), we obtain from these bubble pressures a range of densities from 0.18 to 0.22 mole/cm<sup>3</sup>. The ratio of  $^3\text{He}$  atoms to host-atom vacancies (given by the product of  $^3\text{He}$  density with the host-atom volume for Pd $^3\text{H}_{0.62}$ , where the latter quantity is assumed to be the same as that for the corresponding protide<sup>13</sup>) is found to be  $2.0 \pm 0.2$ . This ratio is in good agreement with results for  $^3\text{He}$  in Ta $^3\text{H}_x$  based on dilatometry measurements,<sup>19</sup> and also with a recent theoretical prediction,<sup>20</sup> thereby supporting our interpretation. The low-temperature phase in Fig. 1 shows a distinct minimum for  $T_1$ ; by analogy<sup>6</sup> with bulk hcp  $^3\text{He}$ , we attribute this to He-vacancy diffusion in solid  $^3\text{He}$ .  $T_1$  results at 45.7 MHz (not shown) are qualitatively consistent with the predictions of BPP theory<sup>7</sup> concerning frequency dependence (i.e., the minimum shifts to higher temperature and the magnitude of  $T_1$  near the minimum scales with frequency). BPP analysis of the low-temperature 25-MHz  $T_1$  data yields the  $^3\text{He}$  jump frequency ( $\tau_c^{-1}$ ) results shown in Fig. 1, and an activation energy for He-vacancy motion ( $W$ ) of  $370 \pm 40$  K (0.032 eV). The  $T_2$  data shown in Fig. 1 give a value for  $W$  of  $330 \pm 100$  K. According to BPP theory, the magnitude of  $T_1$  at the minimum is proportional to density squared (with a proportionality constant nearly independent of structure)<sup>7,8b</sup>; this relationship gives a  $^3\text{He}$  density of about 0.13 mole/cm<sup>3</sup>. The discrepancy between the  $^3\text{He}$  density obtained from the BPP analysis and that from  $T_m$  is not surprising, given that the observed distri-

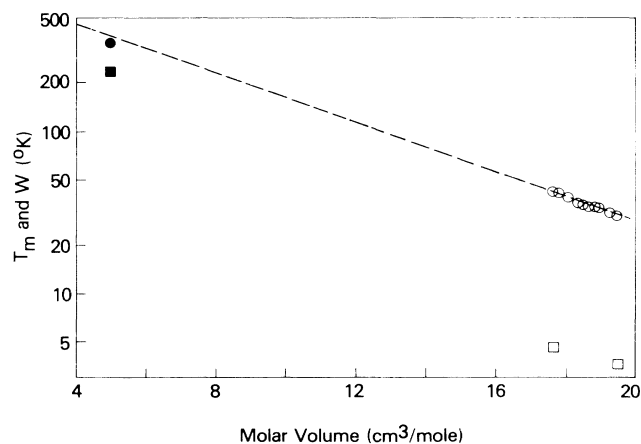


FIG. 2. Melting temperature ( $T_m$ ) and He-vacancy activation energy ( $W$ ) as a function of molar volume in  $^3\text{He}$ . Open circles,  $W$  from NMR data of Ref. 6; open squares,  $T_m$  from  $^3\text{He}$  melting curve (Ref. 18) and pressure vs molar volume [linear interpolation based on two points from Ref. 8(a)]; filled circles and filled squares,  $W$  and  $T_m$  from present study. The dashed line serves as a guide to the eye.

bution of densities implies a distribution of activation energies for vacancy diffusion.<sup>6</sup> It can be easily demonstrated that in such a case, BPP analysis of  $T_1$  and  $T_2$  based on the assumption of a single density will substantially underestimate both mean density and mean activation energy. Moreover, for reasonable distributions, relaxation times will appear exponential over the limited range of experimentally accessible sampling intervals for magnetization recovery. Measurement of the dipolar rigid-lattice second moment<sup>7,8b</sup> would provide a more direct NMR determination of mean density. However, this will require liquid-helium temperatures and improved receiver recovery characteristics. Using the present determination of mean density for He within bubbles, together with the bubble density obtained from a TEM study<sup>14</sup> of 66-day-old Pd  $^3\text{H}_{0.6}$  (there is evidence that in Zr  $^3\text{H}_{1.6}$ , bubble density saturates within one or two months<sup>21</sup>), we obtain for 1-yr-old Pd  $^3\text{H}_{0.62}$ , a mean bubble diameter of 4 nm and a mean bubble occupancy of  $4 \times 10^3$  atoms.

Figure 2 shows  $W$  and  $T_m$  as a function of molar volume and compares the present results with results from an NMR study<sup>6</sup> of bulk hcp  $^3\text{He}$ . There is evidence<sup>22</sup> that for vacancy diffusion  $W$  scales with  $T_m$ ; however, direct proportionality over the range of  $T_m$  shown in Fig. 2 would be surprising. As discussed earlier, though, the magnitude of  $W$  obtained in the present study is probably a lower bound, so that the true scaling is more nearly linear than depicted. At any rate, the important point of Fig. 2 is the correlation of properties of  $^3\text{He}$  in palladium tritide with those of bulk  $^3\text{He}$ , which provides strong support for our interpretation of the NMR data shown in Fig. 1. If the present interpretation is essentially correct, then Fig. 2 represents a remarkable range of molar volumes for which information about  $^3\text{He}$  dynamics in solid He is available.

The authors acknowledge D. West, L. Matson, and W. Tadlock for sample synthesis; and G. J. Thomas, W. G. Wolfer, and R. C. Bowman, Jr. for enlightening discussions. Mound is operated by Monsanto Research Corporation for the U.S. Department of Energy under Contract No. DE-AC04-76DP00053.

<sup>1</sup>A. vom Felde, J. Fink, Th. Müller-Heinzerling, J. Pflüger, B. Scheerer, G. Linker, and D. Kaletta, Phys. Rev. Lett. **53**, 922 (1984).

<sup>2</sup>J. H. Evans and D. J. Mazey, J. Phys. F **15**, L1 (1985).

<sup>3</sup>S. E. Donnelly, Radiat. Eff. **90**, 1 (1985).

<sup>4</sup>S. E. Donnelly, A. A. Lucas, J. P. Vigneron, and J. C. Rife, Radiat. Eff. **78**, 337 (1983).

<sup>5</sup>A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Clarendon, Oxford, 1982), Chap. 3.

<sup>6</sup>N. Sullivan, G. Deville, and A. Landesman, Phys. Rev. B **11**, 1858 (1975).

<sup>7</sup>N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948); for application of BPP to bulk He, see D. S. Miyoshi, R. M. Cotts, A. S. Greenberg, and R. C. Richardson, Phys. Rev. A **2**, 870 (1970).

<sup>8a</sup>H. A. Reich, Phys. Rev. **129**, 630 (1963).

<sup>8b</sup>R. L. Garwin and A. Landesman, Phys. Rev. **133**, A1503 (1964).

<sup>9a</sup>R. C. Bowman, Jr., and A. Attalla, Phys. Rev. B **16**, 1828 (1977).

<sup>9b</sup>R. C. Bowman, Jr., Nature **271**, 531 (1978).

<sup>10</sup>H. T. Weaver and W. Beezhold, J. Nucl. Mater. **53**, 346 (1974).

<sup>11</sup>R. Lässer, J. Less Common Met. **131**, 263 (1987), and references therein.

<sup>12</sup>H. T. Weaver and W. J. Camp, Phys. Rev. B **12**, 3054 (1975).

<sup>13</sup>G. Alefeld and J. Völkl, *Hydrogen in Metals I and II* (Springer-Verlag, Berlin, 1978).

<sup>14</sup>G. J. Thomas and J. M. Mintz, J. Nucl. Mater. **116**, 336 (1983).

<sup>15</sup>D. Kotzur, M. Mehring, and O. Kanert, Z. Naturforsch. A **28**, 1607 (1973).

<sup>16</sup>P. Loubeyre, J. M. Besson, J. P. Pinceaux, and J. P. Hansen, Phys. Rev. Lett. **49**, 1172 (1982).

<sup>17</sup>R. L. Mills, D. H. Liebenberg, and J. C. Bronson, Phys. Rev. B **21**, 5137 (1980).

<sup>18</sup>R. L. Mills and E. R. Grilly, Phys. Rev. **99**, 480 (1955).

<sup>19</sup>T. Schober, R. Lässer, J. Golczewski, C. Dieker, and H. Trinkaus, Phys. Rev. B **31**, 7109 (1985).

<sup>20</sup>W. G. Wolfer, to be published.

<sup>21</sup>T. Schober, in *Hydrogen in Disordered and Amorphous Solids*, edited by G. Bambakidis and R. C. Bowman, Jr. (Plenum, New York, 1986), p. 377.

<sup>22</sup>R. A. Hultsch and R. G. Barnes, Phys. Rev. **125**, 1832 (1962).