

Peculiar spin echo in thick ^3He films on boron nitride

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Results are reported for pulsed NMR studies of thick films (25 layers) of ^3He physisorbed on carefully prepared hexagonal boron nitride substrates. Peculiar doublet structures in the NMR spin-echo shapes have been observed for temperatures $0.9 \leq T \leq 1.2$ K. These echo shapes are interpreted in terms of a two-component system: (a) a solid phase (up to 4.6 layers) near the substrate, and (b) a liquid phase near the free surface of the film. [S0163-1829(99)50406-2]

In this paper we present preliminary results from pulsed nuclear magnetic resonance (NMR) studies of thick ^3He films (25 layers) adsorbed on boron nitride (BN). The aim of the experiments was to determine the fraction of the films that behave as solid layers compared to those that are liquid. Studies of the nuclear spin-lattice relaxation time T_1 and the nuclear spin-spin relaxation time T_2 provide information about the dynamics of the ^3He atoms and thus distinguish between the bulk liquid and the adsorbed solid or solidlike ^3He near the substrate.

Studies of helium films in the presence of a variety of substrates (graphite,¹⁻⁵ fluorocarbon microspheres,⁶ boron nitride,⁷ aerogel,⁸ silver powder,⁹ and mylar¹⁰) have attracted attention for more than 20 years because these systems provide a unique testing ground for two-dimensional (2D) nuclear magnets and 2D phase transitions. The underlying mechanism of these systems, however, is still far from being completely understood.

A layer model¹¹ has been proposed for helium films in which the first layer is assumed to have the density of high-pressure solid ^3He , the second layer that of low-density solid ^3He , and the rest is bulk liquid. This model has been confirmed qualitatively by experimental results in multilayer studies, but there is considerable uncertainty concerning the number of solidlike layers which seem substrate dependent, and varies from one to a few atomic layers. Helium films on graphite are the most extensively studied. Measurements of the heat capacity³ and neutron-scattering studies⁴ have shown that helium films on graphite form a stratified Fermi system; the first two monolayers at sufficiently low temperatures¹² are solid and subsequent layers are 2D liquid. Magnetization measurements¹³ of ^3He films on graphite show that while the completed first atomic layer is a paramagnetic solid with a triangular lattice structure and a vanishingly small exchange frequency $J \leq 1$ kHz, the second layer upon solidification displays both antiferromagnetic and ferromagnetic tendencies depending on layer density. Although BN has some important advantages for studies of magnetic properties, the characterization of helium layers adsorbed on BN is not as advanced as for graphite. Recent pioneering studies⁷ of ^3He on BN have clearly identified solid layers, but these studies did not identify at what film thickness the liquid phase would start to form. We wanted to

answer this question by performing NMR experiments of layer-by-layer coverages of helium films on BN.

The dynamics and nuclear spin ordering in ^3He is governed by the existence of spin exchanges that results from the quantum zero point motions. It has been shown that these exchanges can involve cyclic permutations of several atoms (up to fifth order) resulting in the existence of several exchange interactions of competing strengths: ferromagnetic for permutations of odd numbers of fermions, and antiferromagnetic for even numbers of fermions. The effective Hamiltonian $H = -\sum_n (-1)^n \mathcal{J}_n \mathcal{P}_n$ where \mathcal{P}_n is the permutation operator for cyclic permutation of n fermions (e.g., $\mathcal{P}_2 = \sigma_i \sigma_j$).

It is well known that several layers of solid ^3He adsorbed on surfaces exhibit Curie-Weiss magnetization $M_s = C / (T - \theta_\omega)$, where the Curie constant C is proportional to the real coverage of the surface solid and the Weiss constant θ_ω is typically 0.5 mK. The total magnetization M is the sum of M_s and the liquid magnetization M_l . A universal feature observed for all substrates studied is the existence of a Curie-Weiss-type contribution to the magnetization where at least part of this effect is generated by the surface-adsorbed atoms.

Ahonen *et al.*¹⁰ measured the magnetization of ^3He adsorbed on mylar sheets and identified the two typical contributions; one was temperature independent and is attributed to the bulk liquid and the other is well described by a Curie-Weiss law. The relative weight of the Curie-Weiss contribution varied weakly with magnetic field and was ascribed to five times the estimated quantity of ^3He contained in the first adsorbed layer. It was difficult to attribute this contribution to five or more layers of solid arising from the influence of the van der Waals potential since this potential is negligible at such large distances. Later, Spanjaard *et al.*¹⁴ proposed that the Curie-Weiss contribution could arise from the liquid in the second or third atomic layers. In this ferromagnetic liquid model, the van der Waals potential V_b that the boundary exerts on the liquid causes an increase in the density of states at the Fermi surface. Consequently, the liquid susceptibility is increased, and the liquid closest to the substrate may be ferromagnetic if the potential V_b is sufficiently large. This description seemed to be confirmed in studies of ^3He adsorbed on Carbolac by Ahonen *et al.*¹⁵ Godfrin *et al.*¹⁶ using continuous wave NMR to study various substrates (such as alumina powder, Grafoil, and platinum powder) indicated

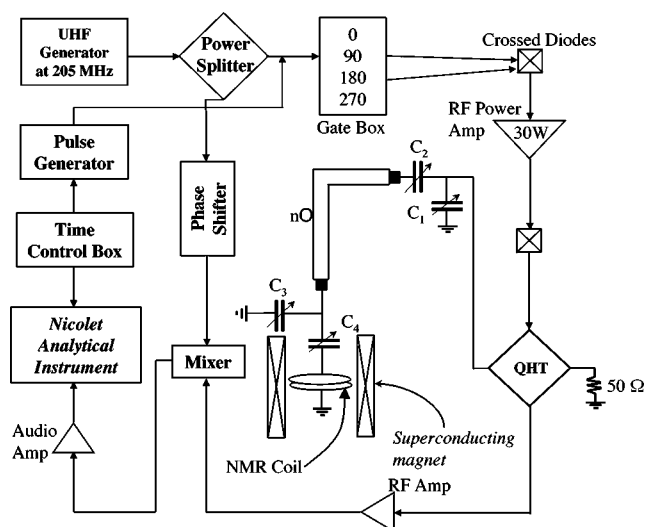


FIG. 1. The pulsed NMR spectrometer at 205 MHz consisted of a coherent UHF quadrature hybrid-tee (QHT) bridge circuit using two sets of tuning capacitors for impedance matching.

that the relative weight of the Curie-Weiss-type contribution corresponded to only the ^3He contained in the first layer. Bozler *et al.*² using pulsed NMR studies of ^3He /Grafoil reported similar behavior to that observed by Godfrin *et al.* Okuda *et al.*⁹ have observed the existence of a ^3He magnetization contribution of Curie-Weiss type which is equivalent to five atomic layers adsorbed on silver powder. More recently, Halperin *et al.*¹⁷ have observed a Curie-Weiss contribution from the magnetization of the surface solid ^3He films adsorbed on aerogel strand, and found that there are two layers of solid ^3He on the aerogel surface and that the magnetization of the liquid remains temperature independent in the superfluid. Bäuerle *et al.*¹⁸ have measured the nuclear magnetic susceptibility of second-layer ^3He films adsorbed on graphite and showed that the measured temperature dependence of the second-layer magnetization is described well by the Curie-Weiss temperature θ_w .

A pulsed NMR spectrometer (Fig. 1) operating at 205 MHz was employed for these studies. We used a quadrature hybrid tee (QHT) to form a high-frequency bridge configuration for the spectrometer. The ultrahigh sensitivity ($\sim 10^{14}$ spins detectable) required for the very low filling factor of these NMR studies was achieved by employing two sets of capacitors;¹⁹ one set permits the impedance matching between the NMR coil ($\frac{1}{4}$ -inch diameter, 2 turns) and the transmission line in the low-temperature region, and the second set provides further fine tuning at room temperature between a QHT and the transmission line. The spin echo shown in Fig. 2 was formed by applying a single sweep of the pulse sequence. In addition, a sealed NMR sample cell suitable for studies at reduced geometries was developed successfully using easily machinable Kel-F²⁰ with an indium seal between the Kel-F and the metal end plates.

Hexagonal BN as a substrate has recently gained considerable interest in experimental studies of physisorbed films because of its similarity in crystal structure to graphite. BN is superior to graphite for NMR measurements because it has a much lower electrical conductivity and a lower diamagnetism, thereby permitting for NMR studies at ultrahigh fre-

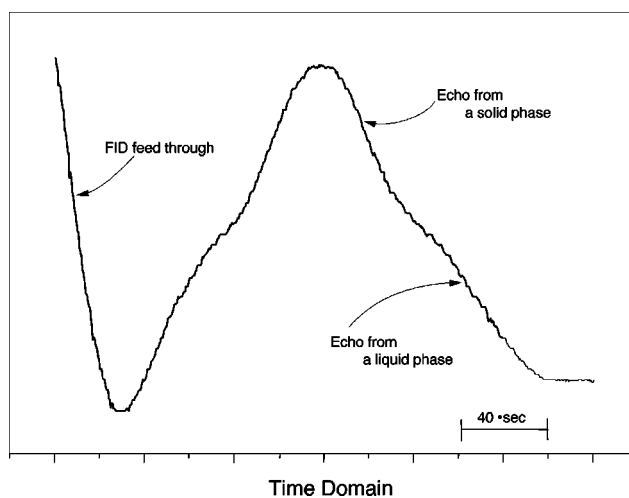


FIG. 2. Double structures of the spin-echo shape in thick ^3He films adsorbed on BN. The echo consists of a broad Gaussian base line attributed to a liquid phase at free surface and a narrow Lorentzian central line attributed to the solid phase near the BN substrate.

quencies, which is not possible for graphite.⁷ The high conductivity and diamagnetism of graphite at low temperatures distort the NMR line shapes and the phase relationship of the applied RF to the NMR signals, so that detailed line shapes are not reliable, particularly in the ultrahigh frequency region. The characterization of the lattice structures of adsorbed systems on BN, however, is not as advanced as for graphite. It is well known that monolayer helium film forms $\sqrt{3} \times \sqrt{3}$ registered solid structure commensurate with the graphite substrate, with each physisorbed molecule occupying every third carbon ring.^{4,21} It is also well established that $^3\text{He}/^4\text{He}$ films on graphite are atomically layered; clear periodic structure has been seen in the compressibility of the films, as determined from studies of adsorption isotherms,²² heat capacities,^{12,22} and third sound velocities.²² NMR studies of ^3He on BN have clearly identified the coverage for the commensurate $\sqrt{3} \times \sqrt{3}$ (75% of a full monolayer) with an incommensurate structure appearing at high coverages.⁷ The precise monolayer coverage is known from careful adsorption isotherm studies of HD on BN in our laboratory.²³

The BN samples were rinsed with deionized water and then washed in methanol in a clean ventilation facility, and outgassed for 4 h at 200 °C. The samples were then annealed for 24 h at 900 °C under a vacuum of 10^{-6} Torr.

The purity of the adsorbed ^3He was specified by the manufacturer to be 99.999%. The ^3He sample was introduced into the NMR sample cell for 24 h to make sure that adsorbed layers form uniform films on BN.

$90_x^\circ - \tau - 180_x^\circ$ NMR spin-echo techniques were used in order to determine the liquid-solid transition in thick films of ^3He adsorbed on BN. This pulse sequence has the advantage that extremely long relaxation times may be measured from easily reproducible starting conditions, namely, saturation, and also that the measurements need not be carried past one or two time constants, thus obtaining the maximum amount of information in a given time. Different values of T_1 and T_2 were observed for the two components of the NMR echoes (or line shapes) showing that these components correspond to independent systems. The T_1 and T_2 values of the solid component of the echoes were observed to be, respectively,

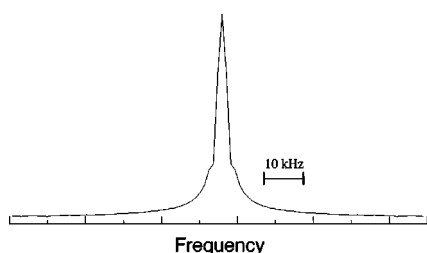


FIG. 3. A typical NMR line shape of thick ^3He films adsorbed on BN.

short ($T_1 = 88 \mu\text{s}$) and long ($T_2 = 285 \mu\text{s}$) at $T \approx 1.2 \text{ K}$. These values of T_1 and T_2 are consistent with a relaxation determined by spin diffusion through a five-layer solid with $J \sim 10 \text{ MHz}$. This value is in agreement with the values of the exchange frequency observed in the bulk solid and is strong evidence that the Lorentzian component of the echo originates from solid layers. The liquid (Gaussian) component of the NMR line shape had distinctly different values for the relaxation times; with $T_1 \sim 100 \mu\text{s}$ and $T_2 \sim 33 \mu\text{s}$.

The presence of the liquid helium plays a key role in determining the overall shape of the NMR spectra because it perturbs contributions from the adsorbed solid layers. Only narrow Lorentzian liquidlike NMR line shapes were observed in the previous studies^{6,8} for systems in which less than two adsorbed ^3He layers are solid. The solid atoms in the second layer are expected to exchange more rapidly with the atoms of the liquid,⁶ and for monolayers one cannot distinguish the solid phase component in the overall NMR line shapes with a conventional NMR tank circuit. If the number of adsorbed solid atoms is large enough to suppress the increased mobility of localized atoms by the presence of the liquid, we would expect to see a distinctive NMR line spectrum due to a solid phase near substrates plus a liquid phase near the free surface.

We have observed a peculiar double structure in the NMR spin-echo shapes for thick ^3He films adsorbed on BN. A typical spin echo seen for this system is shown in Fig. 2. This spin echo is not symmetric because at small times a residual of the free induction decay signal adds to the baseline for the echo. We therefore used the second half of the spin echo to obtain the NMR line shape by the Fourier transformation. The NMR line shape obtained from the Fourier transformation of the echo is shown in Fig. 3. This ‘‘rocket’’-shaped NMR line shape was observed and interpreted in terms of a two-component system; (i) a broad Gaussian line [full width at half maximum (FWHM) $\sim 8 \text{ kHz}$] which forms the base of the NMR spectrum and is attributed to adsorbed solid ^3He films near the BN substrate, and (ii) a narrow Lorentzian line (FWHM $\sim 3 \text{ kHz}$) which is attributed to liquid ^3He films near the free surface. (The contribution of the field inhomogeneity is $\sim 250 \text{ Hz}$.) The two-component system interpretation is based on the observation of the ratio of the integrated areas of the narrow component of the NMR line to the broad component. The narrowing that leads to the Lorentzian line is believed to result from the relatively high mobility of the helium adatoms along the free surface. In order to estimate the areas of the two components, we used cutoffs out in the wings of the line at $\pm 50 \text{ kHz}$. Any error

this cutoff would make would be to underestimate the solid layer component. Subtracting the integrated areas of the broad spectrum from the overall spectrum observed in these preliminary measurements indicates that a solidification occurs predominantly in about five layers closest to the substrate. This two-component model is consistent with measurements of T_1 and T_2 and spin-echo amplitudes. The solid layer component for the system studied is twice as large as those reported for ^3He films adsorbed on graphite. This result may be due to the fact that BN has a stronger attractive potential for helium than that of graphite as evidenced by continuous-wave NMR studies of thick films (12-layer) of molecular hydrogen adsorbed on BN.²⁴

In conclusion, we have observed a distinct two-component structure in the NMR line shapes of ^3He films adsorbed on BN, a broad Gaussian-like base NMR line associated with the first four or five solid layers near the substrate, and a narrow Lorentzian-like central line attributed to the liquid phase at the free surface. Further confirmation of our results can be obtained from a number of different experiments including neutron scattering, heat capacity measurements, and rotational Raman scattering to determine the precise number of solid layers in thick ^3He films. Due to the enhanced mobility of the last two solid layers adjacent to the outer liquid layers, there can be an uncertainty of one or two layers in the previous studies which did not see a solid layer component in NMR studies of ^3He films on graphite. This may also be due to the fact that because of its relatively high conductivity and strong diamagnetism, graphite does not produce reliable NMR spectra for adsorption studies. The field inhomogeneities induced by graphite substrates add uncertainties to the line shapes, and also in pulsed NMR the loss of well-defined rf phase relationships because of the conductivity of graphite can interfere with the formation of echos and make the analysis uncertain. The calculated line width for the liquid NMR line shape is remarkable, and this is believed to be due to the combined effects of the solid layers and the substrate playing a dominant role in determining the dynamics of the atoms and thus the overall shape of the NMR echoes. At the same time, the line width for the solid phase is smaller than the expected value (10–20 kHz) (Ref. 25) for bulk solid helium, and this can be understood in terms of the increased mobility of helium adatoms which apparently overcomes the crystal field interactions from the solid films and with the BN substrates. This motion leads to the narrowed solid NMR line shape. However, the observed line width is larger than that (3–6 kHz) observed by Rollefson¹ for monolayer ^3He film on graphite. It is, therefore, believed that thick films of ^3He adsorbed on BN are two-dimensional characteristics as well as three-dimensional ones. Further experimental studies at various film coverages increased layer-by-layer are needed to establish more reliable experimental data for the dynamical NMR studies of ^3He films adsorbed on BN in order to fully understand the behavior of these 2D systems.

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