# Surface-Induced Ferromagnetism in $^3$He

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Pulsed NMR measurements of the susceptibility and the transverse and longitudinal relaxation times of $^3$He intermixed with 9 nm of carbon particles have been performed down to 0.4 mK. The results indicate that the first atomic layer has an antiferromagnetic exchange interaction. The intermediate solid-liquid region, ~5 atomic layers thick, favors ferromagnetism and approaches a ferromagnetic transition at the lowest temperatures.

Recent measurements on $^3$He at millikelvin temperatures in confined geometries, inside a stack of Mylar plates[1] and intermixed with ultrafine carbon powder,[2] have revealed a pronounced enhancement of the susceptibility of $^3$He as compared to that of the normal bulk Fermi liquid. The excess susceptibility exhibited ferromagnetic behavior.

We have extended the measurements on $^3$He intermixed with the 9 nm of carbon particles to lower temperatures, down to 0.4 mK at zero pressure and to 0.5 mK at 6, 15, and 25 bars. By using an improved detection technique we have been able to distinguish two contributions in the recorded free induction decays, one of them associated with the first tightly bound layer of atoms on the carbon surfaces, corresponding to a monolayer of $^3$He atoms, and the other coming from the rest of the sample. The results show that the solid-liquid system near the surface approaches a ferromagnetic transition, as evidenced by the rapid increase of the transverse relaxation time $\tau_2^*$ below 2 mK. No superfluid transition is observed in $^3$He inside the carbon black because the average distance between the carbon grains, 14 nm, is much smaller than the coherence length of the superfluid pairs.

Monolayer and submonolayer films, as well as multilayer systems, in the presence of a variety of substrates have been studied intensively during the last ten years. The common observation in all the measurements has been an increase in the relaxation rates[3] $1/\tau_1$ and $1/\tau_2$, compared to those of bulk solid or liquid $^3$He, and an enhanced susceptibility in the few layers next to the substrate.[1,2,4] Because of the van der Waals attraction there is a deep potential well near the substrate and therefore a strong local pressure gradient. A layer model[4] where the first layer is assumed to be like high-pressure solid $^3$He, the second layer is like low-density solid $^3$He, and the rest is bulk liquid, has been found to explain satisfactorily the experimental results in multilayer studies.

Our measurements were performed in a nuclear demagnetization refrigerator. The temperature in the experimental cell was determined by measuring the nuclear susceptibility of a powdered platinum sample. The $^3$He specimen contained less than 10 ppm of $^4$He. The carbon powder was packed to 6% of the volume inside a cylindrical NMR coil, 5 mm in diameter and 6 mm long. The coil was glued onto an epoxy tower on top of the sample cell; a copper gauze at the end of the coil shielded the bulk liquid outside the coil from the rf field. The characteristic surface area of the powder was measured with the Brunauer-Emmett-Teller (BET) method to be 350 m$^2$/g, giving a total surface area of 4.9 m$^2$ for the carbon sample. All the measurements were performed in a magnetic field of 28 mT, corresponding to a resonance frequency of 920 kHz.

A pulsed NMR spectrometer was employed for recording the free-induction-decay signals which, extrapolated to time $t=0$, are proportional to the static susceptibility of the sample. The free-induction-decay signal could be followed starting 40 $\mu$s after the transmitter pulse. The recorded signals appeared to have two contributions, the larger decaying much more slowly ($\tau_2^* \simeq 400$ $\mu$s) after the transmitter pulse. The recorded signals appeared to have two contributions, the larger decaying much more slowly ($\tau_2^* \simeq 400$ $\mu$s) than the smaller one ($\tau_2^* \simeq 40$ $\mu$s). In what follows the corresponding susceptibilities are called $\chi_1$ and $\chi_2$, respectively, and their relative magnitudes are such that $\chi_1/\chi_2 \simeq 3.5$ at temperatures above a few millikelvins.

Within the scatter of data, $\chi_2$ was independent of the applied pressure in the cell and had an antiferromagnetic nature, with a Curie-Weiss constant $\Theta_2 = -0.09$ mK. Relating this to the magnitude of the exchange constant $J$ we obtain $J = (4/z)\Theta_2 = -0.06$ mK using $z = 6$ as the number of nearest neighbors. Bulk solid $^3$He ordinarily exhibits antiferromagnetic exchange; the $J$ de-

termined above would correspond to a molar volume of 21 $cm^3$ for bulk solid $^3$He, i.e., high-pressure $^3$He. The apparent spin-spin relaxation time $\tau_2^*$ of the smaller signal was very short, $\simeq 40$ $\mu$s, and independent of applied pressure and temperature. The thickness of the region giving rise to $\chi_2$ was estimated to be ~1.2 atomic layers in a manner described later. On the basis of these observations we believe that the smaller contribution originates from the first, well-localized sheet of $^3$He atoms on the carbon surfaces.

Comparing the properties of the assumed first layer to monolayer results, it is found that our $\tau_2^*$ is roughly the same as that observed in a monolayer on graphitized carbon black[5] but smaller than the $\tau_2$ of a monolayer on Vycor,[6] 2 ms, or on Grafoil,[7] 0.2 ms. The discrepancies result presumably from the different substrates having various amounts of paramagnetic moments due to impurities or dangling bonds. The molar volume of the first layer, deduced from $\Theta_2$, is smaller than that of a monolayer of $^3$He on Grafoil,[8] which calculated from the measured areal density 0.11 atoms/Å is 16.5 $cm^3$/mole. However, it seems plausible that the mobility of atoms, and thus the magnitude of the exchange constant $J$, in the first layer of a multilayer system is higher than in bulk solid $^3$He with the same density because of the less dense layer above the tightly packed one.

The inverse susceptibility of the major contribution $1/\chi_1$ is shown as a function of temperature in Fig. 1 at the different pressures. We assume

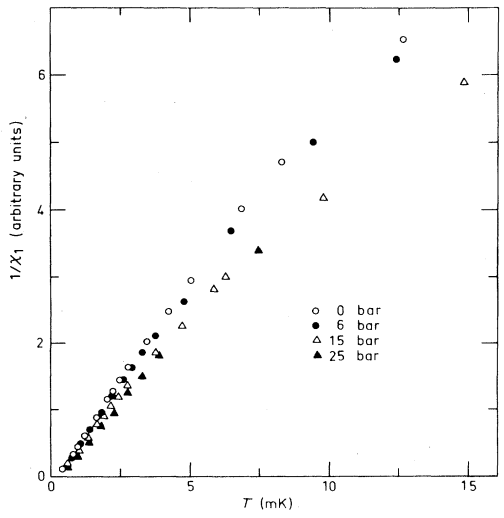


FIG. 1. The inverse susceptibility of the major contribution of the free-induction-decay signal $1/\chi_1$, as a function of temperature at the various pressures.

$\chi_1$ to be associated with the next few atomic layers having a density $\rho > \rho_{bulk}$ and a Curie-Weiss susceptibility, and with the Fermi liquid in the center of the pores having a constant susceptibility in the temperature range of interest. Therefore we may write

$$\chi_1 = c_1/(T - \Theta_1) + c_2 , \quad (1)$$

where $c_1$ and $c_2$ are constants. The bulk liquid contribution can be separated by plotting $\chi_1$ vs $1/T$ and extrapolating $1/T \to 0$. The $c_2$'s obtained at the different pressures scale within $\pm 20\%$ as the susceptibilities of bulk liquid $^3$He. The temperature-dependent first term on the right-hand side of Eq. (1) will be called $\chi_1'$. At 25 bars $c_2$ is 2.5% of the total signal $\chi_1$ at 1 mK and at zero pressure $c_2$ is 1.2% of $\chi_1$ at 1 mK.

The thicknesses of the various regions can be estimated from the ratios $\chi_1'/c_2$ and $\chi_2/c_2$. Fixing the density and susceptibility of the intermediate region, which gives rise to $\chi_1'$, to those of solid $^3$He at the melting pressure yields values from 4.5 to 5.5 atomic layers for its thickness.

The inverse susceptibilities $1/\chi_1'$ at the different pressures are shown in Fig. 2 versus temperature below 3 mK; our results at $p = 0$ in the whole temperature range studied are shown as an inset in the upper left corner of the figure. The

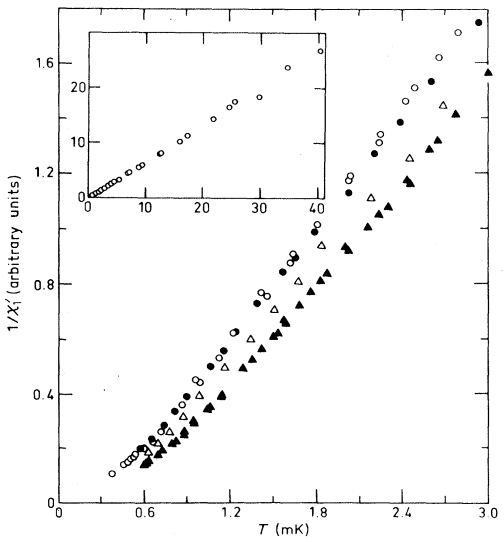


FIG. 2. The inverse susceptibility $1/\chi_1'$ as a function of temperature below 3 mK at different pressures: open circles, 0 bar; solid circles, 6 bars; triangles, 15 bars; solid triangles, 25 bars. The inset shows $1/\chi_1'$ vs $T$ at zero pressure up to 40 mK; the units on the axes are the same as in the main figure.

behavior of $\chi_1'$ is ferromagnetic with a positive, slightly pressure-dependent Curie-Weiss constant $\Theta_1$ which increases from 0.35 to 0.5 mK on going from 0 to 25 bars. A deviation from the Curie-Weiss–type linear temperature dependence of $1/\chi_1'$ is seen to start at the lowest temperatures. This may be due to the quasi–two-dimensional nature of the intermediate layers; in two-dimensional systems a magnetic transition approaches absolute zero because of fluctuations near the critical point.

An alternative way of interpreting the data is suggested by the resemblance of our results shown in Fig. 1 to the solid susceptibility data of Prewitt and Goodkind[9] above the magnetic transition at 1.1 mK. At the high-temperature end $\chi_1$ seems to be antiferromagnetic with a Curie-Weiss $\Theta = -2.6$ to $-2.8$ mK at the different applied pressures but below 10 mK $\chi_1$ appears to become ferromagnetic. The antiferromagnetic $\Theta$ values correspond to solid $^3$He with a molar volume of 24 cm$^3$/mole, i.e., very near to the melting pressure solid density. Within this model we lose the information about the layer structure based on the bulk liquid contribution $c_2$ but if we still assume that $\chi_2$ is associated with the first atomic layer, we can calculate the thickness of the $\chi_1$ system from the measured ratio of the corresponding signals allowing for the pressure dependence of the susceptibilities. We then obtain roughly 4 atomic layers.

The apparent spin-spin relaxation times $\tau_2^*$, the time constants of the free induction decays, at the various pressures are shown in Fig. 3. Down to about 5 mK the relaxation times decrease linearly with temperature, the pressure dependence of $\tau_2^*$ being typical for liquid $^3$He in that $\tau_2^*$ increases at higher pressures. Around 2 mK the relaxation times start to increase rapidly. This is in accordance with the bahavior of a ferromagnet in the neighborhood of its transition temperature.[10]

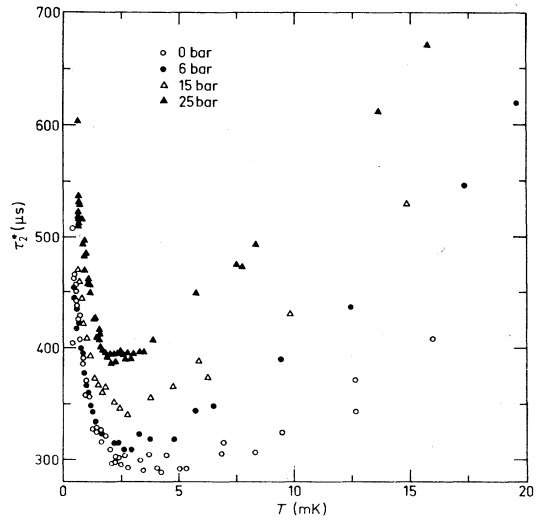


FIG. 3. The apparent spin-spin relaxation time $\tau_2^*$ as a function of temperature at the different pressures.

The spin-lattice relaxation time $\tau_1$ was measured at zero pressure between 0.4 and 70 mK by applying $90°$-$\tau$-$90°$ pulse sequences. Above 5 mK $\tau_1$ was approximately linear in temperature; at 10 mK $\tau_1$ was 30 ms and at 40 mK it was 60 ms. At the lowest temperatures below 5 mK the measurements were complicated by heating effects caused by eddy currents in the copper net acting as an rf shield. The linear temperature dependences of $\tau_1$ and $\tau_2^*$ agree with the observations of Kelly and Richardson[3] at higher temperatures in a similar $^3$He–carbon-black system.

As to the major part of the free-induction-decay signal, the most interesting temperature region in our measurements is below 10 mK where the observed susceptibility is ferromagnetic and the transverse relaxation time $\tau_2^*$ starts to increase. In $^3$He research, attention has lately been focused on this same temperature region for several reasons. Apart from the superfluid phases of liquid $^3$He and the magnetic transition of solid $^3$He, the susceptibility of low-density solid $^3$He has been observed to deviate from the antiferromagnetic behavior seen at higher temperatures,[9] and the temperature dependence of the thermal boundary resistance between liquid $^3$He and a metal surface changes[11] from $R_K \propto 1/T^6$ to $R_K \propto 1/T$. The observed ferromagnetic susceptibility in the surface layers may have the same origin as the ferromagnetic trend in bulk solid $^3$He and these surface layers evidently play a role in the heat transfer mechanism between liquid $^3$He and a solid. The importance of the surface layers in the Kapitza conductance is displayed by the disappearance[11] of the $1/T$ dependence of $R_K$ after adding to the sample a small amount of $^4$He, which displaces the $^3$He layer from the walls because of its larger van der Waals attraction.

It has been suggested that the ferromagnetic interaction in solid $^3$He arises from a temperature-dependent exchange interaction as a consequence of next-nearest-neighbor and three- and four-spin interactions[12] or from vacancy-induced ferromagnetism.[13] The vacancy theory seems appealing in the present case; the quasi–two-dimensionality

of the intermediate region could lead to an increased number of vacancies.[14] This in turn could explain why in the low-density solid layers the ferromagnetic trend dominates over the antiferromagnetic exchange interaction whereas in bulk solid $^3$He near the melting pressure density a magnetic transition to an antiferromagnetic state apparently takes place[9] in low magnetic fields.

The enhanced susceptibility in the Mylar experiment[1] has been interpreted[15] by attributing properties of a two-dimensional itinerant-electron ferromagnet to the high-density liquid layers next to the solid $^3$He layer on the surface.

In order to gain further insight into these surface-induced effects, new experiments in which the properties of the surface layers could be studied in a well-defined geometry, as functions of temperature, magnetic field, and $^4$He impurity level, would be most desirable.

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*Note added.*—After this paper had been submitted, we received a reprint from H. M. Bozler *et al.*[16] describing similar measurements on $^3$He on Grafoil. They observe a reduction in $\tau_2^*$ below ~1.1 mK instead of the sharp increase found in our experiment roughly in the same temperature region. The discrepancy may be due to the presence of superfluid $^3$He in their geometry.

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## Zero-Sound Attenuation from Order-Parameter Fluctuations in Liquid $^3$He

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We calculate the attenuation of zero sound due to fluctuations of the superfluid order parameter above $T_c$. The results appear to account for the excess attenuation recently observed by Paulson and Wheatley.

The attenuation of zero sound in liquid $^3$He increases dramatically just below the superfluid transition temperature. This increased attenuation is now understood to result from coupling between the density oscillations and the collective modes of the order parameter.[1] Recently Paulson and Wheatley[2] have reported an increase in the attenuation of zero sound above $T_c$, relative to the attenuation expected for a normal Fermi liquid. We have calculated the attenuation of zero sound above $T_c$ due to fluctuations of the order parameter. This contribution to the sound attenuation seems able to account for the excess attenuation found by Paulson and Wheatley.

 