^{3}He Binding Energy in Thin Helium-Mixture Films

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We report measurements of the binding energy of dilute coverages of ^{3}He to ^{4}He adsorbed films. These energies, when combined with measurements of the energy gap between the ground state and the first excited state of ^{3}He in the ^{4}He film, provide the binding of the excited state to the film surface. We find that for 0.1 monolayer of ^{3}He and for ^{4}He areal densities, $0.21 \leq n_4 \leq 0.53$ Å^{-2}, the ^{3}He binding energies obtained are in reasonable agreement with values calculated using a density functional description of the film for the ^{4}He coverage dependence of the binding energy.

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The study of ^{3}He impurity states in ^{4}He films is a field of current interest. In thin adsorbed films of ^{3}He-^{4}He mixtures, the ^{3}He is appropriately described as a two dimensional (2D) weakly interacting Fermi gas [1]. These bound states of ^{3}He, localized near the film surface, are analogous to the bound state of ^{3}He at the surface of bulk ^{4}He that was first proposed by Andreev [2] to explain the maximum in temperature of the surface tension shift of helium mixtures [3]. The existence of the surface state on bulk ^{4}He has been verified experimentally using various thermodynamic measurements such as the surface tension [4,5] and the surface sound velocity [6], and found to have a binding energy of 5.02 ± 0.03 K relative to the vapor [6,7], whereas the binding of ^{3}He in the interior of bulk ^{4}He is 2.8 K relative to the vapor [5]. The surface binding energy is sensitive to the density profile of the ^{4}He liquid-vapor interface [7]. Recent density functional theories of helium bulk mixtures by Dupont-Roc *et al.* [8] and Pavloff and Treiner [9] suggest that the ^{4}He surface will in fact support two 2D bound states of ^{3}He.

In the case of films van der Waals forces provide additional binding to the films, and there is a hierarchy of impurity states with a broad range of energies, $\epsilon_0, \epsilon_1, \ldots, \epsilon_n$. Both the ^{4}He density and the surface structure of ^{4}He films evolve as a function of the areal coverage [10], due in part to the short ranged van der Waals forces which bind the films to the substrate, and in part due to the density-density correlations of the helium atoms in the vicinity of the substrate. At least two of these translational states are bound, with energies which depend upon this structure [9,11,12]. Bhattacharyya *et al.* [11] first measured the binding energies and effective masses of the two lowest states at several ^{3}He and ^{4}He coverages using heat capacity techniques. The detailed ^{4}He coverage dependence of the relative energy separation of the lowest lying of these bound 2D states, $\Delta = \epsilon_1 - \epsilon_0$, has recently been measured [12,13] for a dilute ^{3}He coverage ($D_3 = 0.1$ layer) by NMR techniques and agrees quantitatively with energies measured in Ref. [11] and reproduces qualitatively some of the features expected from the structural calculations of the film [9,14]. At low ^{3}He coverages, the ^{3}He constitutes a weakly interacting 2D Fermi liquid [1]. As the ^{3}He coverage increases, the bound states are progressively filled [13] until phase separation occurs, and the ^{3}He density becomes extensive.

It was previously shown [12] that the ^{3}He longitudinal relaxation time, T_1, can be used to measure the energy gap, Δ, since thermal promotion from the ground state Fermi level into higher energy film states results in rapid spin relaxation. This results in Arrhenius type behavior; $1/T_1 \sim \exp(-\delta\epsilon/k_B T)$, where $\delta\epsilon$ is presumed to be the energy gap between the Fermi surface in the ground state and the available momentum states in the first excited state. The Fermi energy ϵ_F at each coverage is accessible through fits to the temperature dependence of the total magnetization, and can be combined with measurements of $\delta\epsilon$ to yield the energy gap between the lowest two states in the film, Δ. These measurements corroborated certain qualitative features in two disparate calculations of the relative energy spectrum [9,14], but quantitative comparisons were complicated by ambiguities in the theoretical coverage scales. The subsequent success of the density functional description of the film in describing wetting phenomena on alkali substrates in the pure ^{4}He film system [15] suggests that the assignment of the coverage scale in these theories is reasonable at least in the limit of weak binding substrates.

In this paper, we show that the magnetization can be used to sensitively monitor the evaporation of ^{3}He from the film, hence revealing the ^{3}He binding energy. In addition, we provide concurrent measurements of Δ, which are shown to be consistent with earlier work [12]. We measure the ground state binding energy of ^{3}He for a submonolayer coverage of ^{3}He adsorbed to a ^{4}He film using measurements of the high temperature ($T > T_F^*$) spin susceptibility made simultaneously with measurements of Δ derived from T_1 as in Ref. [12]. The mixture films are adsorbed to a stack of Nuclepore filters which are fit inside a NMR coil. Nuclepore is a nonconducting substrate which is well suited for use with pulsed NMR. Pulsed NMR techniques at 62.9 MHz are used to measure the magnetization and relaxation time, T_1, at temperatures, $24 \leq T \leq 600$ mK, of a submonolayer cover-

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age of ^{3}He, $n_3=1.08$ μmole/m^2 (≈ 0.1 monolayer). At this coverage ^{3}He-^{3}He interactions are small [10,13] and the energetics remain largely unaffected by the ~ 100 mK variations in the substrate potential [13], thus ensuring uniform coverage of the substrate. The coverage of the adsorbed ^{4}He superfluid film was varied, $7 \geq D_4 \geq 2.6$ layers, where D_4 is the thickness in terms of bulk-density layers and where $n_4 \equiv 12.82$ (μmole m^{-2})/layer $\times D_4$. Further details of the spectrometer and experimental techniques used can be found in Refs. [1] and [12].

The temperature dependence of the magnetization is well approximated [1] by an ideal 2D Fermi gas scaled by the so-called degeneracy temperature, T_F^{**}, and Curie constant, $C = N\mu^2 H/k_B$,

$$MT_F^{**} = [1 - \exp(-T_F^{**}/T)] \,. \tag{1}$$

The quality of fits of this expression to the data where only T_F^{**} is allowed to vary with coverage can be seen in Fig. 1, where the magnetization curves for 79 ^{4}He coverages with $2.6 < D_4 < 7$ layers can be seen to collapse on a universal curve with $90 < T_F^{**}(D_4) < 300$ mK. This is constrasted with helium films adsorbed to Grafoil, where the Fermi liquid interactions are stronger [16] and universal behavior does not follow Eq. (1).

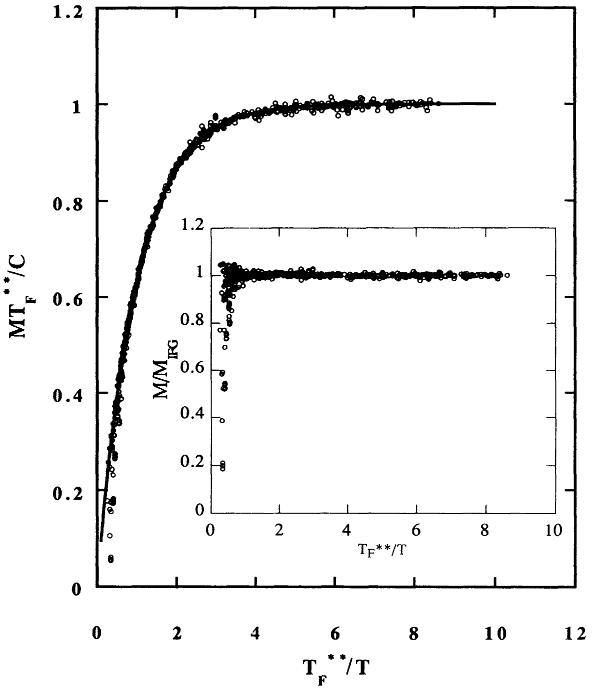

FIG. 1. ^{3}He magnetization at 79 separate ^{4}He coverages, $2.5 \leq D_4 \leq 7.5$ layers, scaled by the Curie constant, $C = N_3\mu^2 H/k_B$, and the degeneracy temperature, T_F^{**}, plotted against the reduced temperature, T_F^{**}/T, follows a universal curve. The solid curve is $(C/T_F^{**})\exp(-T_F^{**}/T)$. Inset: Fractional deviation of the magnetization from the Fermi gas fit. Large deviations at high temperatures are due to ^{3}He evaporation from the film into the vapor phase.

For temperatures $T \gtrsim 300$ mK evaporation of the ^{3}He from the ^{4}He film surface occurs, and as ^{3}He leaves the NMR coil as vapor, a dramatic reduction in the magnetization signal is seen (see Fig. 1 inset). Use of the magnetization to measure the binding energy is possible because at least 99% of the dead volume, $V = 52$ cm^3, in the experiment cell is outside of the NMR coil, while nearly 98% of the surface area, $A = 1.77$ m^2, is inside the NMR coil. Thus, only ^{3}He which remains in the film contributes to the measured ^{3}He magnetization as the temperature is raised. Fitting the magnetization at all coverages requires four fitting parameters at each coverage: ϵ_B, A/V, m^*/m, and ϵ_F, the surface binding energy, surface to volume ratio, effective mass, and Fermi energy, respectively. Of these, A/V and m^*/m are fixed experimental parameters. The Fermi energy is determined at each coverage from the low temperature dependence of the magnetization, which leaves the binding energy as the sole adjustable parameter to fit the magnetization in the temperature range where evaporation occurs.

The binding energy of the ^{3}He to the film surface is obtained by equating the chemical potentials of the film and the vapor phase, in analogy with Andreev's treatment of the evaporation of ^{3}He from the surface state into the ^{4}He bulk [2]. For the ^{3}He in the vapor phase we can assume that Boltzmann statistics can be applied and use a concise form for the chemical potential of an ideal gas,

$$\mu_v = k_B T \ln(\rho_3 \lambda_T^3) \,, \tag{2}$$

where ρ_3 is the ^{3}He number density of the vapor, and $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the thermal de Broglie wavelength. For the ^{3}He in the film, we adopt a simple dispersion relation

$$\varepsilon(p) = \epsilon_B + p^2/2m^* \,,$$

where p is the 2D momentum in the film. At temperatures [17] $T \geq T_F^*$ occupation of the 2D planar momentum states in the film assumes approximately a Boltzmann distribution. In this limit the chemical potential is to a good approximation

$$\mu = \epsilon_B + k_B T \ln(n_3 \lambda_T^{*2}) \,. \tag{3}$$

Here, λ_T^* is the thermal de Broglie wavelength where the ^{3}He effective mass in the film has been substituted for the bare mass. As evaporation proceeds, n_3 and ϵ_F both rapidly approach zero and the accuracy of this approximation improves.

Edwards *et al.* [6] included in their calculations for the evaporation of ^{3}He from the surface state into the bulk a quartic momentum term in the ^{3}He 2D dispersion, resulting in a chemical potential $\mu = \epsilon_B + \frac{1}{2} n_3 V_0^s + \mu_{\mathrm{IFG}}$, where μ_{IFG} is the ideal Fermi gas chemical potential and V_0^s is a simple quasiparticle interaction potential. Here, we restrict ourselves to the dilute, high temperature limit where Eq. (3) can be used. Using the value of V_0^s for the bulk (~ 11 K Å^{-2} [7]) results in a shift of the chemical potential of only ~ 35 mK for the ^{3}He coverage considered here. Furthermore, Anderson and Miller show [18] that the ^{3}He chemical potential calculated from a ripplon-exchange effective interaction deviates from $\mu_{\rm IFG}$ by no more than 50 mK for the temperatures and coverages considered here.

Equating these chemical potentials in Eqs. (2) and (3), with the constraint that the total $N_3 = An_3 + V\rho_3$ in the sealed sample cell be fixed, the fraction of spins which remain in the film during evaporation is

$$\frac{n_3(T)}{n_3(0)} = \left[1 + \frac{V}{\lambda_T A}\frac{m}{m^*}e^{\epsilon_B/k_B T}\right]^{-1}, \qquad (4)$$

where A is the total surface area and V is the total volume of the experimental cell. We need not modify Eq. (4) to include the effects of evaporation into the second bound state because its energy is very near to the energy of the vacuum state, and has a phase space that is less by another factor of $V/\lambda_T A$. Thus, at temperatures where evaporation occurs, the total ^{3}He in the film is dominated by the occupation of the vapor phase.

If the magnetization were purely Curie-like in its temperature dependence, then we would be in a position to apply Eq. (4) directly. However, as can be seen in Fig. 2, deviations from Curie behavior of $\sim 10\%$ exist at the evaporation temperatures. It is necessary then to make the approximation that the effective mass will not be significantly changed as n_3 decreases. It might reasonably be expected that $m^*/m \to m_H/m$, the hydrodynamic mass, as $n_3 \to 0$. We chose to use the measurements of m^*/m by Bhattacharyya, DiPirro, and Gaspirini [11], who observed that $m^*/m \simeq 1.5$ for coverages $0.1 \le D_3 \le 0.3$ and $4 \lesssim D_4 \lesssim 16$. We make the approximation that $m^*/m \simeq 1.5$ at all coverages, and that the effective mass changes little during the evaporation process [19]. This allows us to ascribe the additional temperature dependence seen in the magnetization to the Curie constant prefactor through the loss of ^{3}He from the film,

$$C(T) = \frac{n_3(T)}{n_3(0)}C(0). \qquad (5)$$

Fits of this type prove to be very effective in describing the high temperature regime of the magnetization curves. Figure 2 shows two such curves for coverages of $D_4 = 3.513$ and 4.358 layers. As can be seen, evaporation is a very abrupt function of temperature, with the onset determined both by the binding energy and by the relative phase space available to the film and vapor phases. It can readily be seen from Eq. (4), for instance, that one-

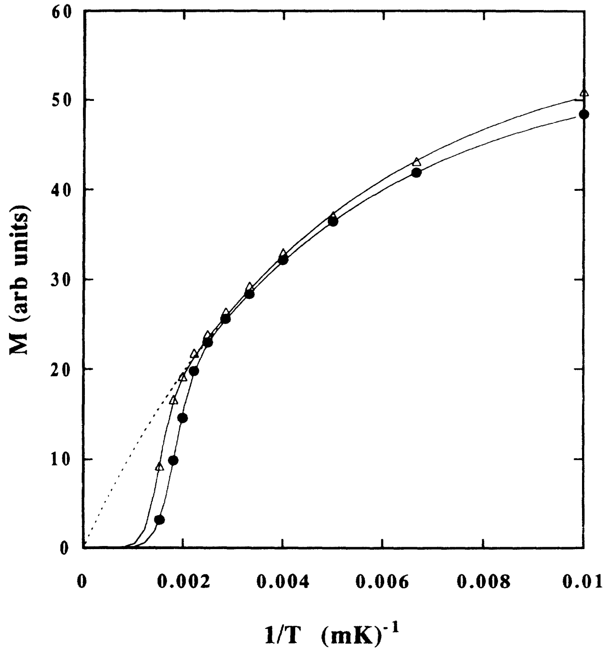

FIG. 2. Magnetization at high temperatures for two ^{4}He coverages, 3.513 layers (triangles) and 4.358 layers (circles), compared with the fit Fermi gas magnetizations (dashed curve). The thin solid curves are the theoretical fits to the evaporation.

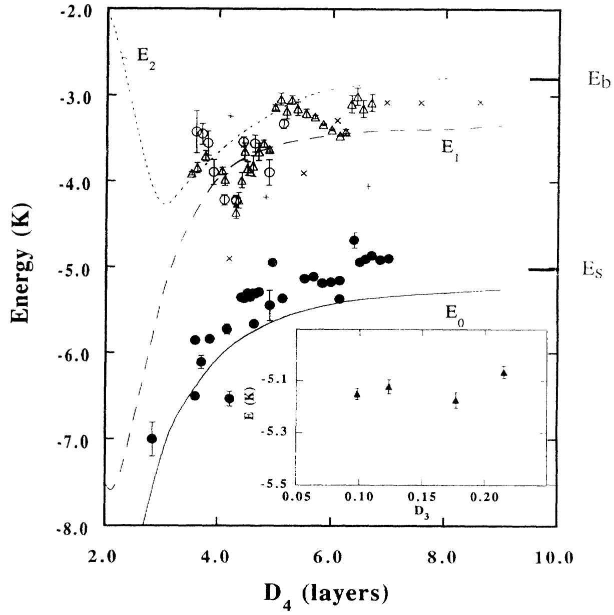

FIG. 3. Binding energies of the ground state ϵ_0 (solid circles) and the first excited state ϵ_1 (open circles and open triangles) of ^{3}He bound to the ^{4}He film surface. ϵ_0 and ϵ_1 values do not both exist for every coverage. Open triangles are deduced from previously reported [12] work. Theoretical curves (labeled E_i) from Ref. [9] for the ground state (solid curve), first excited state (dashed curve), and second excited state (dotted curve) at zero temperature, pressure, and ^{3}He coverage are shown. The energy gaps between the ground and first excited states determined from heat capacity measurement from Ref. [11] have been combined with the theoretical ground state energies at $D_3 = 0.1$ (+'s) and $D_3 = 0.285$ layer (×'s) and are shown for comparison.

half of the atoms evaporate at a temperature $k_BT=\epsilon_B \times\ln(\lambda_T A m^*/Vm)$. Since uncertainties in A and V are both 10%, there is a 3% systematic uncertainty in the values of ϵ_B presented here. Second order dependencies of the chemical potential on the ^{3}He areal density are neglected.

Figure 3 shows the ground state binding energies, $\epsilon_0(\epsilon_0\equiv\epsilon_B)$, of the ^{3}He to the film as a function of the ^{4}He coverage combined with measurements of the energy gap to give ϵ_1. ϵ_1 values derived from the gaps, Δ, from Ref. [12] are also shown in Fig. 3, combined with interpolations of the binding energies reported here. No significant differences between the results from the two sets of energy gap data are seen.

We have investigated the effect on the binding energy of increasing the ^{3}He coverage up to 0.26 layer and find ϵ_0 to be constant to within experimental uncertainty (see Fig. 3 inset). This suggests that the binding energies reported for 0.1 layer of ^{3}He can be taken to be in the zero coverage limit. The solid and dashed curves, denoted E_0 and E_1, in Fig. 3 are the theoretical predictions of Pavloff and Treiner [9] (with no adjustments made to the coverage scale) for the energies of the three lowest lying bound states. We point out that at $D_4=7$ layers, ϵ_1 is well below the binding energy E_b of ^{3}He dissolved in bulk ^{4}He; ϵ_0 is within 2% of the value of the known bulk surface state, E_s. This is in seeming agreement with theory; ϵ_1 is predicted [9] to remain below E_b as n_4 increases, consistent with a prediction by Dupont-Roc *et al.* [8] that there exist two bound surface states of ^{3}He on bulk ^{4}He. The authors of Ref. [8] point out that two surface states have not been observed in surface tension measurements or in surface sound measurements in bulk helium mixtures.

To summarize, we have made measurements of the evaporative loss of ^{3}He from a ^{3}He-^{4}He mixture film as a function of ^{4}He coverage and temperature. This, when combined with measurements of the energy gap between the ground and first excited states in the film, provide values for the binding energy of ^{3}He to a ^{4}He film and for the energy of the first excited state. The selectivity of the NMR technique to the ^{3}He nuclei means that it is more sensitive to evaporation from the film than heat capacity or surface tension measurements since no background subtractions are needed.

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