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Ordering Transitions in Helium Monolayers*

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He^3 and He^4 monolayers on graphite at coverages $0.45 \leq x \leq 0.61$ show strong heat-capacity peaks near 3°K. Temperature dependences and densities indicate that both isotopes undergo second-order transitions from the two-dimensional gas state to a regular lattice in registry with the substrate structure.

A current study of helium monolayers adsorbed on graphite discloses several remarkable features not seen in films absorbed on other substrates.[1] The heat capacities of both isotopes at low fractional coverages $0.14 \leq x \leq 0.4$ have been interpreted as indicating quantum degeneracy of two-dimensional (2D) gases in weak lateral fields due to substrate inhomogeneities.[2] In the present Letter we report results at somewhat higher coverages, where the appearance of novel characteristics are suggestive of order-disorder transitions.

The present measurements were made in the same apparatus as those previously reported, on samples having monolayer densities in the range $0.45 \leq x \leq 0.66$. Fractional coverages $x \equiv N/N_m$, where N_m is the He^3 monolayer capacity 90 cm^3 STP obtained from a vapor pressure isotherm at 4.2°K.

Results are presented in Figs. 1 and 2, which compare He^3 and He^4 at three nearly equal coverages. The data show qualitative features indicating a regime distinct from that at lower x. The transition between regimes is evident in Fig. 1(a), which displays peaks for both isotopes at about 3°, while near 1° there are remnants of the isotopically distinct "quantum-degeneracy" characteristics of lower-coverage films. As x is increased, the degeneracy characteristics are further suppressed, while the 3° peaks increase in area.

The appearance of the sharp He^4 peak in Fig. 2 is suggestive of a second-order phase transition, and therefore we examined the data according to the power law[3] $C = a|\epsilon|^{-\alpha} + b$, where $\epsilon = (T - T_c)/T_c$. We found that the data could be described over at least one decade of ϵ by a wide range of exponents, $0.1 \lesssim \alpha \lesssim 0.4$, while $2.92° \lesssim T_c \lesssim 2.94°$. For $\alpha = 0.3$, $T_c = 2.936°$, the agreement extends to $\epsilon \simeq 0.25$, considerably greater than the generally accepted range of critical behavior. However, since the role of low-lying fluctuations is known to be greater in 2D than in 3D systems, the critical region may be as wide as indicated. For the limiting value $\alpha \to 0$ the power law becomes logarithmic, as shown in Fig. 3. The choice $T_c = 2.927°$ gave parallel lines for the low- and high-temperature regions, displaced by about $0.3k$. Kadanoff *et al.*[3] discuss the uncertainties in extracting empirical coefficients from data over limited ranges of ϵ. It is clear that we have not explored the peak in

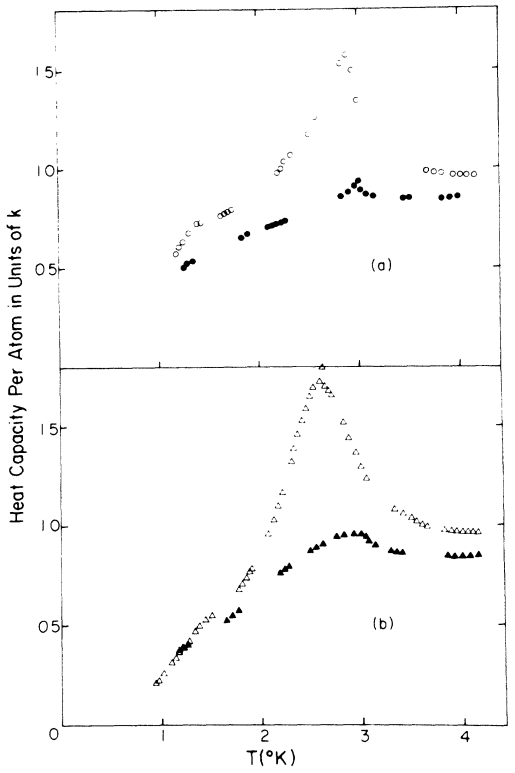

FIG. 1. Specific heat of helium monolayers at fractional coverages x. (a) Open circles, $x=0.452$ He^4, closed circles, $x=0.451$ He^3; (b) Open triangles, $x=0.51$ He^4; closed triangles, $x=0.515$ He^3.

enough detail to obtain more than a semiquantitative estimate of the power-law parameters.

Several pieces of evidence indicate that the peaks are due to ordering transitions of the lattice-gas type. A logarithmic singularity was discovered theoretically by Onsager[4] in his solution of a 2D Ising spin system, and it was later shown by Lee and Yang[5] that the Ising model is isomorphous with a lattice gas. The analogy between physically adsorbed films and 2D lattice-gas models has been pointed out by many authors: Previous failures to observe the expected transitions appear to be due to the heterogeneity of the absorbents. We previously cited evidence[1] for the uniformity of graphite substrates in general and the particular graphite substrate used in our study; and although weak inhomogeneities are adduced[2] to explain the low-coverage results, such variations might be less important in films of higher density.

The differences between the He^3 and He^4 peaks in Fig. 2 appear to be due to variations with coverage rather than to isotopic effects. For comparison with the sharp $x=0.608$ He^4 peak we

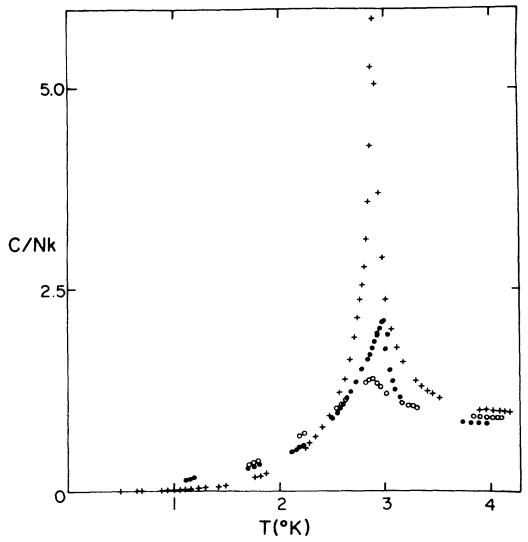

FIG. 2. Specific heat near "critical coverage." Crosses, $x=0.608$ He^4; open circles, $x=0.662$ He^4; closed circles, $x=0.597$ He^3.

also show results for He^4 at $x=0.662$: For this film the peak is asymmetric and lower. Comparable sensitivity to density changes occurs in liquid-vapor transitions near critical density.[3] Very recently, Hickernell, McLean, and Vilches[6] obtained results which confirm and support our observations, for they observed a He^3 peak comparable to our $x=0.608$ He^4 signal under experimental conditions (T, x) virtually identical to ours. Their study was conducted in a different cryostat but used a Grafoil substrate in a cell constructed according to our procedures.[7] Hickernell *et al.* find that the He^3-peak shapes and heights are extremely sensitive to changes in

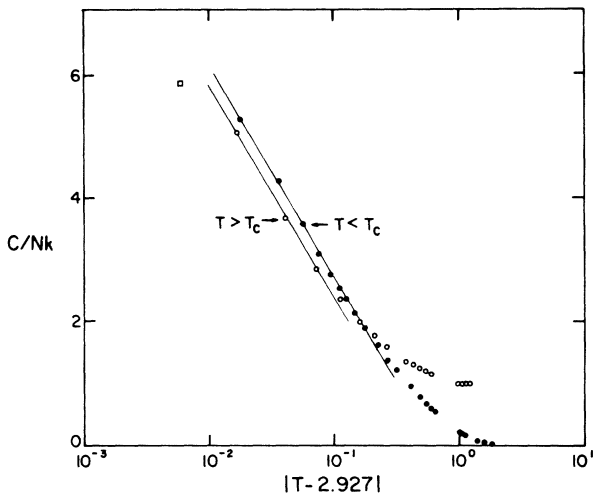

FIG. 3. Test of logarithmic law for He^4 data at $x=0.608$.

coverage, comparable to the sensitivity we observe for He^4.

Ordered states of physically adsorbed monolayers have been observed directly by low-energy electron diffraction (LEED). Lander and Morrison[8] used LEED to study a system quite similar to ours: Xe on graphite. They detected an ordered state at 90°K, the Xe forming an epitaxial triangular array at $x_g = \frac{1}{3}$, where x_g is the ratio of the number of adatoms to the number of hexagonal cells on the basal plane of the substrate. The Xe lattice became gradually disordered as the temperature was raised, and Lander and Morrison speculated that the transition to the 2D "liquid" state might be second order. We find the strong peak in He^4 at very nearly the same "critical coverage": With the measured substrate area, 240 m^2, and the crystallographic parameters of graphite[9] $x = 0.608$ is equivalent to $x_g = 0.35$.

The identification of the sharp peak as due to an ordering transition at density $x_g = \frac{1}{3}$ suggests further conclusions concerning the behavior at lower coverages. If we use the above value for x_g as an area calibration of greater accuracy than the Ar adsorption isotherm, the scaled density for $x = 0.452$ is $x_g = 0.248$ while $x = 0.51$ corresponds to $x_g = 0.28$. At $x_g = \frac{1}{4}$ there are two possible ordered arrays: rectangular, $\sqrt{3} \times 2$, and triangular, 2×2. The latter structure was observed by LEED in a monolayer of Cs on graphite.[8] Our heat-capacity peaks at $x_g \simeq \frac{1}{4}$ are relatively sharp and bear a closer resemblance to the shapes at $x_g = \frac{1}{3}$ than do those at $x_g = 0.28$ where the He^4 peak is rounded, and is centered at lower T than those for the higher and lower densities. The peak for He^3 at intermediate density is so diffuse that its maximum cannot be located to better than 0.1°. The peaks at $x_g \simeq \frac{1}{4}$ appear to be superimposed on smoother trends which retain characteristics of the 2D quantum gases described earlier.[1] The retention of mobility below the ordering temperature is consistent with the realtively low density and the possibility of two, distinct ordered structures. We are therefore led to a tentative identification of the sharp peaks of Fig. 1(a) as evidence of ordering or partial ordering at $x_g = \frac{1}{4}$ and the broad peaks at intermediate coverage in Fig. 1(b) as due to a mixture of $x_g = \frac{1}{4}$ and $x_g = \frac{1}{3}$.

Although the preceding arguments indicate correspondence with conventional theories of lattice gases, the actual situation must be much more complicated. Conventional models assume localized absorption, whereas there is strong evidence for mobility with respect to absorption sites. All samples near 4° have specific heats per atom tending toward the signature of a classical 2D gas. This is consistent with calculations by Hagen, Novaco, and Milford,[10] who find rapid tunneling of He on basal-plane graphite at all T and that the single-particle states of noninteracting He adatoms are virtually the same as for He on a smooth plane. Our results suggest that tunneling remains important at low temperatures. At $x_g \simeq \frac{1}{4}$ the low-T signals retain some quantum-gas characteristics of low-coverage films. The persistence of tunneling seems crucial to the formation of an ordered array in He at $x_g = \frac{1}{3}$. The ordered state of Xe at this density can be understood to arise from the blocking of adjacent sites by the relatively large diameters of the adatoms. He atoms are considerably smaller; classical hard disks with diameters equal to the Lennard-Jones value 2.556 Å might almost fit in a dense array with every hexagon occupied. But if the He tunnels rapidly through substrate potential barriers, such high densities would be prevented by the zero-point kinetic energy due to adatom scattering.

Our arguments as to the nature of the high- and low-temperature regimes can be put to a partial test by an entropy check. If the films near 4° are indeed similar to ideal classical 2D gases, then their entropies must be given by $S/Nk = 2 + \ln(2\pi mAkT/Nh^2)$, whatever the nature of their states at lower T. If the films were ideal all of the quantities would be known, but interactions cause m and A to be replaced by their effective values. Since the recent band calculation[10] shows that the states of He on graphite are essentially two-dimensional, we take $m^* = m_4$. The effective area is reduced by the area "occupied" by films atoms: In the simplest approximation, $A = A_0 - Nb$, where A_0 is the area of the substrate and b is the effective area per adatom. The Fermi temperatures measured for He^3 films at lower coverages[1] indicate that b is itself density dependent.[7] At present, our best independent estimate for the effective atomic area is obtained from the He^3 monolayer capacity at 4.2°, yielding $b = 9.9$ Å^2. The entropies at high T of all samples can be obtained by integrating the measured heat capacities. The most precise value is obtained for He^4 at $x_g = \frac{1}{3}$ since the heat capacity per atom falls to extremely small values within the experimental range (less than $0.006k$ at 0.5°). Assuming a smooth extrapolation to 0

at 0°, we obtain for this sample $S = 1.129Nk$ at 4.21°K, while the 2D hard-disk gas calculation yields $S = 0.969Nk$. The b for which the formula agrees with the experimental entropy is 8.8 Å^2, which lies well within its range of uncertainty. The entropy comparison indicates that the assumptions of a 2D gas state at 4° and of essentially complete order at low temperatures are correct. The transition at $x_g = \frac{1}{3}$ thus appears to involve a change from a 2D gaslike state at high temperatures to an ordered array at low temperatures; and since He^4 at "critical coverage" follows the logarithmic dependence of lattice-gas theory, the extinction of thermal mobility must in some sense be proportional to the degree of spatial order. If mobility is so intimately related to the spatial order, it is a collective property of the system and cannot be treated in terms of noninteracting single-particle Bloch states. The transitions therefore bear some resemblance to the metal-insulator transition of certain three-dimensional electronic systems.[11]

We wish to thank C. E. Campbell, M. Schick, and P. R. Zilsel for continuing stimulating conversations and the free exchange of ideas. Their current study of the theoretical implications of these experiments has made important contributions to our present analysis.

*Research supported by The National Science Foundation.

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Spin Diffusion in Liquid ^{3}He: The Effect of Leggett and Rice*

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The effects in spin-echo experiments predicted by Leggett and Rice for Fermi liquids in large magnetic fields and at low temperatures have been verified for liquid ^{3}He. A preliminary value of the Fermi-liquid parameter $Z_1/4$ determined from this work is 0 ± 0.3 for the liquid at saturated vapor pressure.

Liquid ^{3}He at low temperatures is a highly degenerate Fermi liquid with strong magnetic interactions between the^{3}He quasiparticles. The molecular field associated with the quasiparticle interaction will permit the propagation of a large spin-density current in response to a pulse of rf energy at the Larmor frequency ω_0 if $\omega_0\tau_D \geq 1$, where τ_D is the magnetic collision lifetime. Leggett and Rice[1] predicted that the effect of the spin current upon the diffusion coefficient measured in a spin-echo experiment with small-angle tipping pulses φ in the pulse sequence φ-180°-echo would be to cause the apparent diffusion coefficient, determined from the attenuation of the spin echoes, to have a maximum at the temperature at which $\omega_0\tau_D \sim 1$, rather than varying as T^{-2}. In subsequent work[2,3] Leggett showed that the attenuation of the spin echo will not be exponential in general but will depend upon both the initial pulse angle φ and the external field. For 90° initial pulses the molecular field is rotated perpendicular to the external field, creating the maximum spin-wave–like excitation; and the spin current, driven by an external field gradient, precesses about both the molecular field and the external field, giving large departures from the standard diffusion equation for the magnetization,

$$\partial\vec{M}/\partial t = D\nabla^2\vec{M}, \quad (1)$$