On the Commensurate Phase in the Second Layer of Helium on Graphite: A New Quantum Phase?

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The second-layer phase diagrams of $^4$He and $^3$He adsorbed on graphite are investigated from heat-capacity measurements below 2 K at densities where He films solidify due to strong correlations and a periodic potential created by underlayers. In contrast to a recent first-principles simulation, we observed large heat-capacity anomalies in both isotopes which indicate unambiguously the existence of a distinct phase stabilized by the weak periodic potential, most likely a commensurate solid, over an extended density region between liquid and incommensurate solid phases. We propose novel states of matter including a quantum solid with zero-point defects for this phase where exotic ground states such as supersolid or gapless quantum spin-liquid are expected.

Helium (He) monolayers adsorbed on an atomically flat and strongly attractive graphite surface provide unique arenas to investigate low-dimensional effects and resultant novel quantum phases. One important example is the gapless quantum spin-liquid state found in the commensurate phase in the second layer, hereafter the C2 phase, of $^3$He with nuclear spin 1/2. This is a two dimensional (2D) fermionic quantum solid with a triangular lattice structure. The commensurability here is with respect to the triangular lattice of the compressed first layer. Since several promising electronic counterparts have been found during the last decade, this new magnetic state is now attracting much attention. Further novel strong-correlation effects are discussed in the supposed hole-doped C2 phase of $^3$He. In the second layer of $^4$He, a 2D bosonic system, two previous tor- sional oscillator experiments observed a reentrant superfluid response as a function of density below 400 mK. The supersolidity in the C2 phase, in which both lattice translational and gauge symmetries are spontaneously broken, is one of exciting possibilities to explain the observations.

Compared to the low temperature properties, details of the phase diagram around the C2 phase particularly structural information are quite limited. Neutron scattering experiments failed to detect Bragg peaks from the C2 phase. Heat capacity data for $^3$He and $^3$He films show rounded peaks at 1.4 and 0.9 K, respectively, at densities between the liquid (L2) and incommensurate solid (IC2) phases. The peaks are assigned to melting transitions of the C2 phases. Since they are found at similar density ratios around 4/7 between the first and second layers, the phase is called the “4/7 phase” or more specifically the $\sqrt{7} \times \sqrt{7}$ phase (see the inset of Fig. 1(c)). Such structural assignment has been confirmed by several computational simulations.

In addition, the 4/7 phase is also found in $^3$He monolayers adsorbed on graphite preplated with monolayer of $^4$He ($^3$He/$^4$He/gr) or a bilayer of HD molecules ($^3$He/HD/HD/gr).

The previous belief on the 4/7 phase has recently been seriously thrown into doubt by the path integral Monte Carlo (PIMC) calculation for $^4$He by Corboz et al. They claimed that the C2 phase is not stabilized against the L2 and IC2 phases if zero-point vibrations of the first layer atoms are explicitly taken into account. They also found that the 7/12 phase (not the 4/7 phase) can be stabilized only when (i) the first layer atoms are held fixed or (ii) they assume a 10% deeper He-graphite potential than widely accepted one and a rather high first-layer density ($= 12.7 \text{ nm}^{-2}$) compared to the second-layer promotion density ($= 11.7 \text{ nm}^{-2}$) calculated by themselves. The absence of the C2 phase was also reported in recent calculations on graphene which has 14% shallower potential than graphite. The apparent discrepancy between the previous understanding and the recent PIMC calculation raised serious questions: Is the C2 phase stabilized artificially, for example, by finite size effects due to the microcrystalline (platelet) structure of exfoliated graphite substrate used in the previous experiments? Are the heat capacity peaks observed in $^4$He and $^3$He the same phenomenon and related to melting transition?

In this Letter, we report results of new heat capacity measurements of the second layers of pure $^4$He and $^3$He films in a temperature range between 0.1 and 1.9 K using a ZYX exfoliated graphite substrate. ZYX is known to have ten times larger platelet size (100–300 nm) than Grafoil, a substrate used in all previous works. We obtained unambiguous thermodynamic evidences for the existence of a distinct phase (C2 phase) between the L2 and IC2 phases and that the phase exists in an extended density window. Novel possibilities such as quantum solid with zero-point defects are suggested for this phase, which provides a key basis for the emergence of the currently discussed exotic ground-states.

The experimental setup used here has been described in detail elsewhere. The heat capacity was measured by the heat pulse method with variable constant heat flows. In the following we show only the heat capaci-
ity of adsorbed He films after subtracting the addendum (empty cell) and the desorption contribution (see below). The surface area of the ZYX substrate is 30.5 ± 0.2 m². The vapor pressure of sample is monitored with an in situ capacitive strain gauge.

The much larger platelet size of our ZYX than Grafoil is well demonstrated by observing a two times higher specific heat peak at the order-disorder transition ($T = 2.9$ K) for the $\sqrt{3} \times \sqrt{3}$ commensurate phase of $^4$He adsorbed directly on graphite (see Figs. 1 and 2 of Ref. 25). The critical region is also wider in ZYX being consistent with the finite size scaling. Here the commensurability of this phase is with respective to the graphite honeycomb lattice. Despite the larger platelet size, ten times smaller specific surface area (2 m²/g) of ZYX causes much larger desorption heat-capacity contribution. This prevents us from analyzing experimental data with reasonable accuracies at temperatures higher than 1.8–1.9 and 1.3–1.4 K for $^4$He and $^3$He, respectively.

Let us first show $T$-dependencies of measured heat capacities ($C$) of $^4$He films at densities of $17.50 \leq \rho \leq 19.73$ nm⁻² in Fig. 1(a) and $19.73 \leq \rho \leq 21.01$ nm⁻² in Fig. 1(b). Here $\rho$ is the total areal density. Since the first-layer has a much higher density or Debye temperature than the second layer, its heat capacity contribution is less than 3% in the $T$-range we studied. At the lowest $\rho$ ($17.50$ nm⁻²) the system is a uniform 2D liquid. At high $T$, this phase is characterized by a nearly constant $C$ slightly less than the $N_2$KB expected for an ideal 2D gas as well as a broad maximum near 0.9 K below which $C$ rapidly falls down [11, 26]. Here $N_2$ is the number of He atoms in the second layer estimated by assuming a constant first-layer density ($\rho_1$) of 12.2 nm⁻². This $\rho_1$ value is evaluated from the second-layer promotion density ($=11.8\pm0.3$ nm⁻²) [25] and the subsequent compression of the first layer by 3% [10]. As $\rho$ increases above $18.70$ nm⁻², a new $C$ anomaly starts to develop near $T = 1.4$ K whereas the liquid component gradually decreases. The two features coexist until $19.47$ nm⁻². Above $19.64$ nm⁻² the liquid component completely disappears leaving only the rounded peak at 1.4 K which corresponds to the C2 peak observed by Greywall [11] using Grafoil substrate. As we further increase $\rho$, the heat-capacity peak height ($C_{\text{peak}}$) becomes largest at $19.73$ nm⁻² ($\equiv \rho_{C2}$) and then turns to decrease. In Fig. 1(c) the specific heat data at $\rho_{C2}$ obtained with ZYX and Grafoil are compared. They look similar each other except that the ZYX data give a slightly larger specific heat around and above $T_{\text{peak}}$ by about 13%. Above $20.44$ nm⁻² a new peak appears near 0.8 K. With increasing $\rho$, the peak grows rapidly in height and temperature up to 1.2 K coexisting with the C2 anomaly which diminishes gradually keeping $T_{\text{peak}}$ fixed. The two features apparently coexist at least until $20.80$ nm⁻². This last peak is associated with melting transition of the IC2 solid [11, 26]. The third layer promotion occurs at densities above $21$ nm⁻² [11] after the major compression of the second layer.

In Fig. 1(d) we plot density variations of $C_{\text{peak}}$ and $T_{\text{peak}}$ as well as those of Greywall [11] (dashed lines) who used Grafoil substrate. The phase diagram determined in this work is also shown on the top. Unambiguously, there exists a distinct C2 phase over an extended density region from 19.6 to 20.3 nm⁻² where we observed only the C2 anomaly (closed circles). The C2 phase is not an experimental artifact caused by finite size effects of substrate since the specific heat anomaly is even enhanced slightly with increasing the platelet size by an order of magnitude. Within this C2 region, $T_{\text{peak}}$ increases by 10% almost linearly with increasing $\rho$. The C2 phase is well separated from the L2 and IC2 phases by L2-C2 ($18 < \rho < 20$).
19.6 nm$^{-2}$) and C2-IC2 (20.3 $< \rho < 20.9$ nm$^{-2}$) coexistence regions where we observed the double anomaly feature (open circles). This feature is also seen in Greywall's data at 19.00 and 20.30 nm$^{-2}$ (see Fig. 3 of Ref. 11). However, thanks to finer $\rho$- and $T$-grids and the better substrate quality, we could obtain much more informative data. For example, the L2-C2 and C2-IC2 coexistence regions share a remarkable feature as follows. When $\rho$ approaches $\rho_{C2}$, the L2 and IC2 anomalies destruct preferentially from higher-$T$ envelopes keeping common low-$T$ envelopes, while the C2 anomaly grows without changing its $T_{\text{peak}}$ so much. This strongly suggests the commutersure nature of the C2 phase and non-macroscopic two phase coexistence perhaps with domain wall structures, since only the more compressible L2 and IC2 phases seem to be changing their excitation spectra.

Next we show heat capacity data of the second layer of $^3$He films at densities of $17.50 \leq \rho \leq 19.00$ nm$^{-2}$ in Fig. 2(a) and 19.00 $< \rho < 20.40$ nm$^{-2}$ in Fig. 2(b). The density evolution is qualitatively similar to that in $^4$He. We observed again a clear C2 peak which becomes maximum at $\rho_{C2} = 19.1 \pm 0.1$ nm$^{-2}$ and $T_{\text{peak}} = 1.0-1.1$ K. This peak is very similar to that observed by Van Sciver and Vilches using Grafoil [12] as compared in Fig. 2(c), indicating almost no size effects. Here we estimated $N_2$ assuming $\rho_1 = 11.6$ nm$^{-2}$. This $\rho_1$ value is evaluated from the second-layer promotion density ($\approx 11.2 \pm 0.2$ nm$^{-2}$) [26] and the subsequent first-layer compression of 4% [10]. We should also point out that their data have slightly larger specific heats at low-$T$ due to a small amount of remnant L2 phase (see below). In Fig. 2(d) we plot density variations of $C_{\text{peak}}$ and $T_{\text{peak}}$ for $^3$He as well as a proposed phase diagram at $T = 0$. The determination of each phase boundary is somewhat ambiguous compared to $^4$He. This is partly because the density grid of measurement is not fine enough here, and partly because the double peak feature in the coexistence regions is hardly observable due to weakly $T$-dependent large $C$ contributions from Fermi liquids in the second and third layers. These contributions are represented by the heat capacity isotherm at $T = 0.2$ K plotted in Fig. 2(d). The previous workers’ data with Grafoil seem to be consistent with our phase diagram if their density scales are multiplied by 1.015 for Refs. 12, 26 and 1.04 for Ref. 30. The third layer promotion in $^3$He occurs at a relatively low density ($\approx 19.3$ nm$^{-2}$) before the C2-IC2 coexistence starts [26, 30].

The low-$T$ specific heat of the $^3$He-C2 phase is well fitted to $C/N_2k_B = \alpha T^2 + \beta \exp(-E_k/T)$ below 0.7 K, where $\alpha = 0.14$ K$^{-2}$, $\beta = 4.1 \times 10^2$ and $E_k = 6.2$ K, as shown in Fig. 3(a). The $C \propto T^2$ behavior is expected from 2D phonon excitations. The coefficient $\alpha$ is only $9 \pm 3\%$ smaller than that estimated from the known relation between $\alpha$ and $T_{\text{peak}}$ for the IC solid $^3$He in the first layer [12] suggesting the 2D solid nature. Unfortunately, we could not conclude if the $^4$He data follow the $C \propto T^2$ behavior or not mainly due to limited accuracies of the data below 0.6 K.

The overall $T$-dependencies of the anomalies look reasonably similar between the two isotopes as shown in Fig. 3(b), suggesting a common phenomenon behind, though the $^3$He anomaly is slightly narrower. Also considering the apparent scalability of $C_{\text{peak}}/N_2k_B$ with

FIG. 2. (a) (b) Heat capacities of the second layer of $^3$He on ZYX. (c) Specific heat of the C2 phase obtained with ZYX (filled circles: this work) and Grafoil (crosses: Ref. [12]). (d) Density variations of $C_{\text{peak}}$ (lower panel) and $T_{\text{peak}}$ (upper panel). The dashed line is a heat capacity isotherm at $T = 0.2$ K. The triangles (Refs. 12, 26) and squares (Ref. 27) are the data with Grafoil adjusted to our surface area and density scale (see text). Other details are the same as Fig. 1.

FIG. 3. (a) Low-$T$ specific heat of the C2 phase of $^3$He plotted as a functions of $T^2$. The crosses are the data in the L2-C2 region from Ref. 12 where a liquid-like nearly $T$-independent contribution coexists with a $T^2$ contribution. (b) Comparisons between the $^4$He- and $^3$He-C2 anomalies on ZYX.
This gives rise to "fluidity" to crystal even at mechanically with atoms occupying commensurate sites. In this connection, we should point out that the recent calculation \[20\]. The most probable assignments or disclinations. Eventually, the experimental C2 phase is compressed, while \(\rho_4\) than the critical temperature \(T_c\) for \(\rho_4\) to \(\rho_3\), respectively, regardless of the platelet size. Within this region \(T_{\text{peak}}\) increases linearly with \(\rho\), i.e., the C2 phase is compressed, while \(C_{\text{peak}}\) has a maximum near the lowest density bound.

How can we explain the compressibility of commensurate solid? There seem to be two possibilities which explain the compressibility of commensurate solid \[31\]. (I) The C2 phase is a commensurate solid which can accommodate large amounts of interstitial particles (and perhaps some vacancies as well). Those interstitials should be zero-point defectons which exchange quantum mechanically with atoms occupying commensurate sites. This gives rise to “fluidity” to crystal even at \(T = 0\). The zero-point defectons in quantum solids were predicted long ago by Andreev \[8, 33\] but have never been found experimentally. (II) A quantum liquid crystal state, where translational or rotational symmetries are partially broken, may also be possible. In both cases, supersolidity will be expected for \(^4\text{He}\) at sufficiently low \(T\). In connection with this, we should point out that the \(T_{\text{peak}}\) vs. \(\rho_2\) data for \(^4\text{He}\) are in surprisingly close proximity to the \(T_c\) vs. \(\rho_3\) relation in the Kosterlitz-Thouless theory \[35\] for 2D superfluidity of the whole second layer (the dotted line in Fig. 4d) but not for \(^3\text{He}\). Here \(\rho_2\) is the second-layer density and \(\rho_3\) is the superfluid density.

In summary, we determined the phase diagrams of the second layer of \(^4\text{He}\) and \(^3\text{He}\) on graphite near solidification from heat capacity measurements below 2 K. We obtained experimental evidences for the existence of a distinct phase (C2 phase) at densities between the liquid and incommensurate solid phases in both isotopes unlike the recent calculation \[20\]. The most probable assignment for the C2 phase is a commensurate quantum solid with zero-point defectons, a new class of matter. The ground states of bosonic \(^4\text{He}\) and fermionic \(^3\text{He}\) C2 phases should be of great interest to investigate further.

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[31] We should, however, keep in mind that the $C_{\text{peak}}$ might not be the maximum one if we failed to pinpoint the true $\rho_{\text{C2}}$ in $^3\text{He}$.

[32] It is less plausible that intrinsically much sharper specific-heat anomalies, for example, due to order-disorder transitions are thermally smeared out by desorption because the $^3\text{He}$-C2 peak, for which the desorption contribution is larger, is sharper than the $^4\text{He}$ one. Instead, thermally-activated interlayer mixing may play some roles on the smearing or on the transition nature.

[33] One may consider that the apparent compression of the C2 phase is a result of the simultaneous compression of the first and second solid layers with increasing $\rho$ keeping the density ratio fixed. Eventually, the neutron scattering experiments of Ref. [10] revealed 2% increase of $\rho_1$ at corresponding densities both for $^4$He and $^3$He. However, this increase cannot explain $w = 0.10$ for $^4$He quantitatively nor the $\rho$-dependence of $C_{\text{peak}}$. Moreover, in $^3$He/HD/HD/gr where an even larger width ($w = 0.16–0.25$) has been reported in Refs. [18, 19], simultaneous compression is impossible by adding only $^3$He atoms.

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