Structural Study of Adsorbed Helium Films: New Approach with Synchrotron Radiation X-rays

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Abstract

A few atomic layers of helium adsorbed on graphite have been attracting much attention as one of the ideal quantum systems in two dimension. Although previous reports on neutron diffraction have shown fundamental structural information in these systems, there still remain many open questions. Here, we propose surface crystal truncation rod (CTR) scatterings using synchrotron radiation X-rays as a promising method to reveal surface and interface structures of helium films on graphite at temperatures below 2 K, based on the preliminary experimental results on a monolayer of ^{4}He on a thin graphite. Our estimation on heat generation by X-ray irradiations also suggests that CTR scatterings are applicable to even at system temperatures near 100 mK.

Keywords Two-dimensional helium film · Crystal truncation rod scattering · Surface X-ray diffraction · Graphite substrate

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1 Introduction

Adsorbed helium films on graphite are a unique system for studying two-dimensional (2D) quantum phenomena [1, 2]. This system has a rich variety of two isotopes (^{3}He and ^{4}He, corresponding to fermions and bosons, respectively), different numbers of atomic layers, and various condensed states such as 2D gas, fluid, and commensurate and incommensurate solids. Very recently, exotic 2D quantum phases such as a quantum liquid crystal phase [3] and an intertwined phase like a supersolid [4] have also been proposed to emerge below 1 K. These features, which are attributed to the strong quantum nature of helium atoms and low-dimensionality of the system, have attracted widespread experimental and theoretical attention. Since the appearance of such phases strongly depends on its areal density and layered structure of the helium atoms, structural information is crucial for deeper understandings of them.

Historically, neutron diffractions were performed from a structural point of view in 1980s to 1990s [5–10], for example, Lauter et al. investigated in-plane reflections from helium films on partially oriented exfoliated graphite substrates (Papyex and ZYX grade) at temperatures down to 60 mK [9, 10]. A large surface area per volume in these exfoliated substrates is advantageous to increase diffraction intensities from them; on the other hand, its wide mosaic spread of graphite microcrystallites makes it difficult to analyze the complete atomic structures within the layers. Currently, the process of layer promotions has been clarified for ^{3}He and ^{4}He [9, 10] and is widely accepted as a fundamental knowledge combined with comprehensive heat capacity data by Greywall, et al. [11–13].

However, there are still many open questions; nevertheless, neutron diffraction studies are pioneering and have played an important role in this research area. For example, the existence of a commensurate solid in the second layers of ^{3}He and ^{4}He is still controversial among experiments [3, 11, 13] and quantum Monte Carlo calculations [14, 15]. Therefore, diffraction studies are strongly awaited to extract structural information on these systems. Here, we propose a new approach to study atomic structures of helium adlayers using synchrotron radiation X-rays. We introduce crystal truncation rod (CTR) scatterings, which have been rapidly developed in recent years as one of the powerful methods to study surface structures. Based on the results of our preliminary study, we discuss the applicability of this method to very low temperatures below 2 K.

2 Crystal truncation rod scatterings

CTR scatterings are known as one of the surface structure analysis techniques [16]. Since, in general, a crystal is terminated at the surface, its crystallographic symmetry (crystal periodicity) is broken perpendicular to the surface, resulting in appearance of pseudo two-dimensional diffraction conditions in between the Bragg points in the reciprocal space. As a result, additional X-ray

scatterings are observed perpendicular to the surface, which is so called the CTR scatterings, as shown in Fig.1. The intensity of the CTR scatterings $I_{CTR}(l)$ is formulated in the following equations:

$$I_{CTR}(l) = \left| \sum_{n=-\infty}^{0} F_{hk}^{B}(l)e^{2\pi inl} + F_{hk}^{S}(l) \right|^{2}$$

$$= \left| \frac{F_{hk}^{B}(l)}{1 - e^{-2\pi il}} + F_{hk}^{S}(l) \right|^{2} \tag{1}$$

$$F(K) = \int_{cell} \rho(r)e^{2\pi iK \cdot r} dr. \tag{2}$$

Here, $F(K)$ is the crystal structure factor, $\rho(r)$ is the electron density in the unit cell at a position r, and $F_{hk}^{B}(l)$ and $F_{hk}^{S}(l)$ are a structure factor of the bulk substrate and that of the surface layers, respectively. Here, we omitted a prefactor in Eq. (1). A notable point is that $I_{CTR}(l)$ is not proportional to an individual sum of the contributions of bulk substrate and the surface layers, but to a squared absolute value of the sum of them. Since both $F_{hk}^{B}(l)$ and $F_{hk}^{S}(l)$ are complex numbers, interference is expected among them. From Eq. (1), it is derived that the bulk and surface contributions are nearly equivalent at points with fractional l in the reciprocal space. Consequently, the CTR scattering is quite sensitive to the adsorbed layers on the surface. Furthermore, by combining this technique with intense and highly parallel synchrotron radiation X-rays, it is possible to study the structure of helium films in spite of their small scattering factors.

In this work, we focus on scatterings from the 00 rod (or $hkl = 00l$ in the Miller indices), which contain surface structural information perpendicular to the surface. Typically, when the directions of incident X-rays and sample are set to the appropriate diffraction conditions, a striped ellipsoidal spot as illustrated in Fig. 1c is obtained at a 2D X-ray detector. By scanning in the L direction and integrating intensities of the spots, we obtain CTR data as shown in the right panel of Fig. 1b.
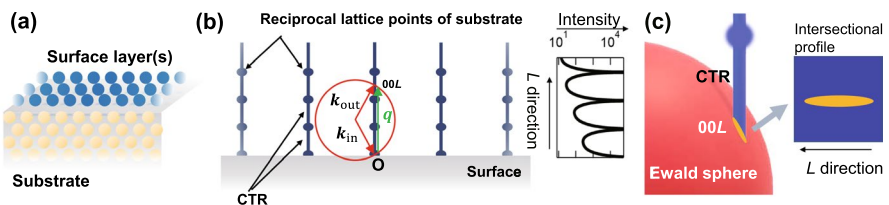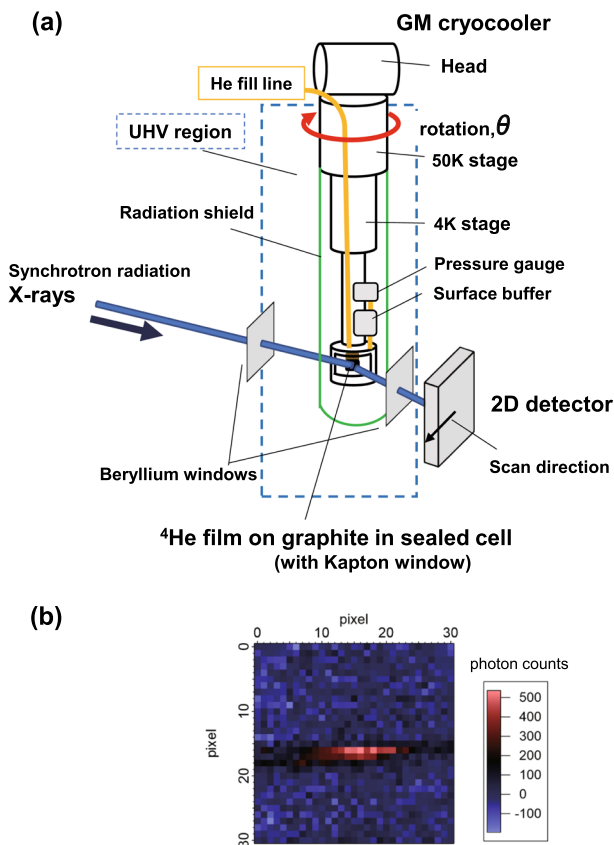

Fig. 1 (Color online) **a** Schematic view of a substrate surface with an adlayer in the real space. **b** Same in the reciprocal space with the Ewald sphere (a red circle). k_{in}, k_{out} and q are the incident, exit, and scattering wave-number vectors, respectively. The right panel represents a scattering intensity profile from both the Bragg reflections and CTR scatterings (intensity distributions in between Bragg reflections) along the 00 rod. (c) An enlarged view of the reciprocal space near $00L$ and a corresponding scattering profile projected to a 2D plane.

As mentioned above, the previous neutron studies have focused on in-plane structure only using in-plane reflections, except the one [6]. Our approach will provide us with new information on heights of helium adlayers.

3 Preliminary experiment

In order to evaluate the feasibility of the X-ray diffraction experiment we suggest, we have preformed a preliminary study at the surface and interface structures beamline (BL13XU [17, 18]) of SPring-8 in Japan. Figure 2a shows a schematic of the cryogenic part of the experimental setup. The refrigerator, which is based on a GM cryocooler (Sumitomo Heavy Industries, Ltd., RDK-101E), is designed to match

Fig. 2 (Color online) **a** Schematic view of the cryogenic part of the experimental setup. It is installed in the UHV chamber, represented by the blue dashed line. **b** Color plot of CTR scatterings with 00L ($L =$ 1.66) for a ^{4}He monolayer on graphite sample. The horizontal axis of the image is parallel to the surface normal. The pixel size is 100×100 μm^2. The color bar indicates photon counts at each pixel. A background scattering from misaligned microcrystallites which lies along the scan direction has already been subtracted.

the ultra-high-vacuum (UHV) chamber in the beamline. It is noted that the effect of mechanical vibration, which is often a problem in helium-free refrigerators, is not a serious issue if the substrate surface is homogeneous over a length scale sufficiently longer than the vibration amplitude. The refrigerator rotates 360° around the vertical axis, allowing us to perform, so called, θ scan. The bottom part of the refrigerator is equipped with a 1 K pot, which is used to cool the system further down to 1.6 K. A demountable sample cell was attached at the bottom of the 1 K pot, which is helium-leak tight with a large window made of a thin Kapton wall. The window is designed to let incident and reflected X-ray beams pass through it with reduced absorption. Beryllium X-ray windows for incident and reflected X-rays are equipped with the UHV chamber. Scatterings and absorption at the beryllium windows as well as aluminized-Kapton-film radiation shields attached to the 50 K stage were also sufficiently small. The scattering data were collected with a 2D detector.

We used a highly oriented pyrolitic graphite (HOPG) thin film of high quality as a graphite substrate in this experiment. The HOPG substrate with 50 μm thickness, which is fabricated on a 1.7 mm thick glass plate, was adhered to a small plate of copper with sliver paste from the graphite side, and the copper plate was thermally anchored to the 1 K pot. A notch was machined into the copper plate as a loophole of X-ray beams. Details of the substrate will be described elsewhere [19]. Since the surface area of the HOPG is small, we use a surface buffer made of Grafoil with a surface area of 5.4 m² in order to control the areal density and number of layers of ^{4}He. A cryogenic pressure gauge was installed to monitor the adsorption pressure during sample preparations.

Figure 2b shows a CTR scattering image at 00L ($L = 1.66$, $|q| = 1.55$ Å^{-1}) for ^{4}He monolayer on graphite obtained at 4.5 K. At this temperature, the ^{4}He film is in the fluid phase [12, 13]. X-rays of 20 keV in energy with the beam size of 0.3 mm in diameter, which corresponds to photon flux of 2×10^{11} photons/s, were used. The measurement time duration per each image was 10 s. In this condition, our measurement was successfully performed without significant heat generation, where the integrated photon counts of reflections were above 1000, indicating that the statistical error of each measurement is less than 4%.

4 Results and discussion

The major concern in cryogenic scattering experiments using synchrotron radiation X-rays will be the heat generation by X-ray irradiation. From the preliminary study, the photon flux of 2×10^{11} photons/s was found to be enough to obtain sufficient CTR scattering intensity. Here, we evaluate a temperature increase in the ^{4}He film with this irradiation intensity, assuming a simplified geometry, as shown in Fig. 3. In the geometry, the X-ray beam with 0.3 mm in diameter enters an circular HOPG substrate of 50 μm thick and 1 mm in diameter, surrounded by a copper plate of 50 μm thickness. We assume a perfect thermal contact between the HOPG film and the copper plate. The glass-supporting plate is omitted in the estimation for simplicity and the effect is discussed later. The temperature of the copper plate, T_{bath} is fixed (constant) as a thermal bath. From the photon energy
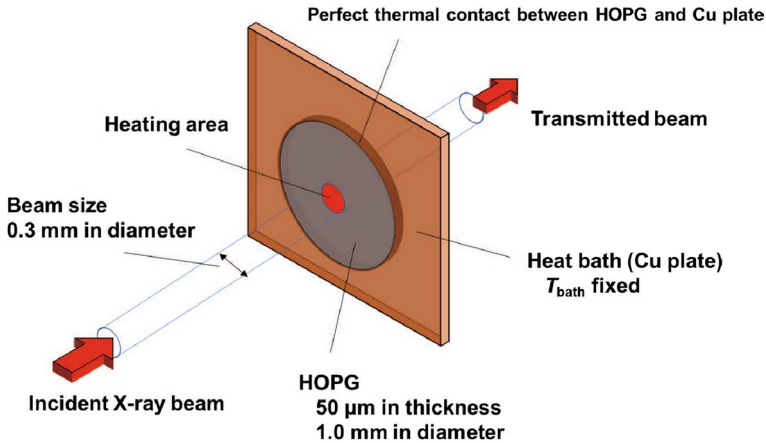
Fig. 3 (Color online) Thermal model for an estimation of the temperature rise at the graphite surface. See the text for details.

(20 keV) and flux intensity (2×10^{11} photons/s), the total power of the irradiation X-ray is calculated to be 640μW. Note that, since the incident X-rays are in the hard X-ray region, most of them pass through the graphite substrate film, and only 0.4% of the X-rays are absorbed in a 50 μm thick graphite film [20]. Furthermore, if the mass energy-transfer coefficient [21] is taken into account, only about 0.2%, namely, 1.3 μW of the energy is actually converted to heat in the graphite substrate. This heat is deposited on the red area in Fig. 3 and diffuses to the surroundings by heat conduction through the HOPG. First, we estimate the temperature rise at $T_{bath} = 1$K. The thermal conductivity of HOPG is highly anisotropic; the in-plane and out-of-plane thermal conductivities are $\kappa_\parallel = 1.0$ [22] and $\kappa_\perp = 1 \times 10^{-2}$ [23] W/(K·m) at 1 K, respectively. Because of the high in-plane thermal conductivity, the increase in temperature is only $\Delta T = 4.9$ mK at the graphite surface of the irradiation side, namely, at the position of the helium film. The result indicates that the CTR scattering experiment is feasible at $T = 1$ K with $\Delta T/T = 0.49\%$.

Similarly, at $T_{bath} = 100$ mK where $\kappa_\parallel = 6 \times 10^{-2}$ [22] and $\kappa_\perp = 2 \times 10^{-4}$ [23] W/(K·m), we estimate the temperature increase is 82 mK. This temperature increase can be reduced by one order of magnitude by deceasing the beam intensity and increasing the measurement time. For example, for a photon flux of 1×10^{10} photons/s and measurement time of 200 sec, it will be $\Delta T = 4.1$ mK at 100 mK ($\Delta T/T = 4.1\%$).

In reality, the 1.7 mm thick glass plate, which was attached on the back side of the HOPG film in the preliminary experiment, should have absorbed a large amount of X-rays and generated an enormous heat that is unbearable when the temperatures go down to subkelvin. However, this problem can be managed by shaving the glass plate mechanically down to about 100 μm thick. It is noted that this extra heat generation can be eliminated by using self-standing single crystal graphite, instead of the thin HOPG film. From the above discussion, we conclude that the CTR scattering experiment is quite feasible at least down to $T \sim 100$ mK.

Finally, we summarize the advantages of the proposed CTR scatterings. Compared with the conventional neutron diffraction using exfoliated graphite whose microcrystallites have wide spreads of mosaic angle and orientation, CTR scatterings are very effective to extract structural information on surface systems including helium layers on graphite by using a single crystal with very small mosaic spread. In addition, X-ray beam size can be reduced to a few micrometers in diameter at the state-of-the-art synchrotron facilities like SPring-8, which might be applicable, if proper mechanical vibration isolation is taken, to phase separation (or coexisting) phenomena with spatial resolution, such as the gas-liquid phase separation in 2D ^{3}He, one of interesting topics proposed recently [24]. Furthermore, the height information for each atomic layer in He multilayers has not been clarified so far, and thus, our approach using CTR scatterings offers novel experimental insight into them. Comparison between our expected structural data and the quantum Mote Carlo simulations, which have become progressively accurate in recent years [14, 15, 25], will produce fruitful discussion or novel findings.

5 Conclusion

We proposed a new approach for studying structures of 2D helium films on graphite using CTR scatterings with synchrotron radiation X-rays. In our preliminary study, we succeeded in detecting CTR scattering clearly from monolayer of ^{4}He films adsorbed on a thin HOPG surface at 4.5 K. From our estimation on the influence of heat, we concluded that CTR scattering measurements are possible even at temperatures down to near 100 mK.

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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