Determination of the mosaic angle distribution of Grafoil platelets using continuous-wave NMR spectra

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Abstract We described details of a method to estimate with good accuracy the mosaic angle distributions of microcrystallites (platelets) in exfoliated graphite like Grafoil which is commonly used as an adsorption substrate for helium thin films. The method is based on analysis of resonance field shifts in continuous-wave (CW) NMR spectra of $^3$He ferromagnetic monolayers making use of the large nuclear polarization of the adsorbate itself. The mosaic angle distribution of a Grafoil substrate analyzed in this way can be well fitted to a gaussian form with a $27.5\pm2.5$ deg spread. This distribution is quite different from the previous estimation based on neutron scattering data which showed an unrealistically large isotropic powder-like component.

Keywords Two dimensional helium-3 · NMR · Substrate effects

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1 Introduction

Atomically thin $^3$He film adsorbed on graphite is an ideal model system for studying strong correlation effects in two-dimensional (2D) fermions. In this system, the correlation can be tuned in a wide range by changing $^3$He areal density ($\rho$). Intensive studies have been done especially in the density region around the 4/7 commensurate phase in the second layer \cite{1}. Grafoil, an exfoliated graphite, is an adsorption substrate commonly used in these kinds of experiments because of its large surface area ($\approx 20 m^2/g$) and moderate thermal conductivity. However, Grafoil consists of a lot of microcrystallites (platelets) with mosaic angle distributions. Thus, the experimental results
sometimes suffer from the heterogeneity effects of substrate. For example, the non-
exponential decay of NMR spin-echo signals recently observed near the 4/7 phase [2] and the linear Larmor frequency-dependence of transverse spin relaxation rate ($T_2^{-1}$) [3] are believed to be due to such heterogeneity effects. Therefore, it is important to obtain distributions of the platelet size and the mosaic angle spread accurately enough for each batch if possible. So far, there exist only a few experimental determinations of the platelet distributions, and it is desired to cross-check the results by different methods.

In this paper, we demonstrate that the mosaic angle distribution can be determined with good accuracy by analyzing continuous-wave (CW) NMR spectra and consequently that the distribution claimed by the previous neutron scattering experiments [4] is not correct.

2 Previous studies

The distribution of the platelet size in Grafoil estimated from scanning tunneling microscopy (STM) measurements [5] is widely spread below 100 nm. The mosaic angle distribution of platelets was determined by the neutron scattering experiments [4] as follows. For 2D crystals, the intensity diffracted at an angle $2\Theta$ by the Bragg reflection with the plane $(h,k)$ is represented as

$$I_{hk} = N m_{hk} |F_{hk}|^2 f(\Theta)^2 e^{-2W} \left( \frac{L}{\pi^{1/2}\lambda} \right)^{1/2} \mathcal{F}(a).$$

Here, $N$, $m_{hk}$ and $f(\Theta)$ are a normalization constant, the multiplicity of the $(h,k)$ reflection and the molecular form factor, respectively. $e^{-W}$ is the Debye-Waller factor, and

$$\mathcal{F}(a) \equiv \int_0^{\infty} e^{-(x^2-a)^2} dx,$$

where $a = (2\pi^{1/2}L/\lambda)(\sin\Theta - \sin\Theta_{hk})$ and $\Theta_{hk} = \sin^{-1} \lambda/2d_{hk}$. $\lambda$, $d_{hk}$ and $L$ are the wavelength, 2D plane spacing for the $hk$-reflection and a parameter defining the average size of the diffracting arrays, respectively. Using the orientational distribution

![Fig. 1](Color online) The orientational distribution of platelets in Grafoil derived from the neutron diffraction experiments [4].

![Fig. 2](Color online) The orientational distribution derived from analyzing CW-NMR spectra by our new method.
function of Grafoil platelets $H(\gamma(\Theta))$, the instrumental resolution factor $R(\Theta)$ and $I_{hk}$, the angle dependence of the scattering intensity $g_{hk}$ is expressed as

$$g_{hk} = \int R(\Theta - \Theta') H(\gamma(\Theta')) I_{hk}(\Theta') d\Theta'.$$

Thus $H(\gamma)$ can be determined by comparing measured diffraction peaks with ones calculated through eq. (3). Taub et al. [4] assumed $H(\gamma)$ as the sum of gaussian and some constant

$$H(\gamma) = H_0 + H_1 \exp\left(-\frac{\gamma^2}{2\delta^2}\right),$$

and obtained

$$H_0/H_1 = 0.78, \delta = 12.7 \text{ deg}$$

from their own neutron diffraction data for Ar monolayer adsorbed on Grafoil. As is shown in Fig. 1 this has a large isotropic powder-like component $H_0$ in addition to the angle dependent term with $H_1$. However, this is hard to believe since it is too isotropic judging from the existing ample experimental properties of thin films adsorbed on Grafoil and of the substrate itself, e.g., the thermal conductivity [6], that all show the significant anisotropy.

3 New analysis of the previous CW-NMR data

In this section, we introduce a quite different method to determine the mosaic angle distribution of Grafoil platelets based on an analysis of CW-NMR spectra of $^3$He thin films adsorbed on this substrate. Here we use the NMR data for the high density second-layer $^3$He at very low temperatures, where the nuclear spins are ferromagnetically aligned along the direction of applied magnetic field $B$, measured by Schiffer et al. [7]. The NMR frequency shift due to the demagnetization effect is expressed as $\Delta \nu =$

![Fig. 3](Color online) CW-NMR absorption spectra of the second-layer $^3$He adsorbed on Grafoil for two different field directions: (a) $B \parallel n$ and (b) $B \perp n$. The points are experimental data for the $\rho = 21.5 \text{ nm}^{-2}$ sample at temperatures indicated (from Ref. [7]). The solid and dashed lines are calculated spectra with eq. (7) and eq. (5), respectively.
\( \Delta \nu_{\text{max}} P(1 - 3 \cos^2 \alpha) \), where \( \Delta \nu_{\text{max}} \) is the maximum positive value of frequency shift, \( P \) is the degree of spin polarization and \( \alpha \) is the angle between \( B \) and the vector normal to the average plane of Grafoil \( n \) \([8]\). Since the inclination of each platelet about the average plane has two degrees of freedom, it is designated by two angular variables, \( \theta \) and \( \phi \), in the spherical coordinate with \( n \) being the positive direction of \( z \)-axis.

Then, the NMR line shape about the field corresponding to the Larmor frequency \( B_0 \) is represented as

**Fig. 4** (Color online) CW-NMR spectra of the second-layer \(^3\)He adsorbed on Grafoil. The dashed, solid and dash-dotted lines are calculated spectra with \( \delta = 25, 27.5, 30 \) deg, respectively. \( H_0/H_1 \) is fixed at 0.045. Otherwise, the same as Fig. 3.

**Fig. 5** (Color online) CW-NMR spectra of the second-layer \(^3\)He adsorbed on Grafoil. The dashed, solid and dash-dotted lines are the calculated spectra with \( H_0/H_1 = 0.03, 0.045, 0.06 \), respectively. \( \delta \) is fixed at 27.5 deg. Otherwise, the same as Fig. 3.
\[ I(x) \propto \begin{cases} \int_{-\pi/2}^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi \frac{H(\theta)}{2\pi} \frac{1}{1 + \left\{ \frac{x-M(1-3\sin^2 \theta \sin^2 \phi)}{A} \right\}^2} & (B \perp n) \\ \int_{-\pi/2}^{\pi/2} \sin \theta d\theta H(\theta) \frac{1}{1 + \left\{ \frac{x-M(1-3\cos^2 \theta)}{A} \right\}^2} & (B \parallel n). \end{cases} \]  

Here \( x \equiv B_0 - B \), and \( A \) is the intrinsic line width. Thus, \( H(\gamma) \) can be determined by fitting the measured NMR spectra to eq. (6). We note that similar analyses have been briefly reported by previous workers [9, 10] for the \( B \parallel n \) direction.

We fitted the NMR data at \( T = 0.28 \) mK for \( \rho = 21.5 \) nm\(^{-2}\) taken by Schiffer et al. [7] assuming the gaussian distribution (eq. (4)), and obtained

\[ \frac{H_0}{H_1} = 0.045, \delta = 27.5 \text{ deg.} \]

The mosaic angle distribution determined by this method is shown in Fig. 2, which is much more anisotropic than Fig. 1.

The fitted results are shown by the solid lines (red) in Fig. 3. The fitting quality is remarkably good both for (a) \( B \parallel n \) and (b) \( B \perp n \). In addition to this, the small fitted value for \( H_0/H_1 \) indicates the appropriateness of the gaussian functional form for \( H(\gamma) \). Note that there are small bumps near \( B_0 \) in the spectra for both \( B \) directions which are not reproduced by the fittings in Fig. 3. These are attributable to magnetization of the paramagnetic first-layer \(^3\)He [7].

On the other hand, the dashed lines (blue) in Fig. 3 are spectra calculated from eq. (5), the distribution claimed by Taub et al. [4]. They look nearly the same for both directions of \( B \) because of the large isotropic component \( H_0 \) and do not explain the experimental data at all. We noticed that, in Ref. [4], they represented the platelet inclination only with \( \theta \) without considering the \( \phi \) variation. We believe that is why their estimation of the mosaic angle distribution is unrealistically isotropic.

Note that the fitting for the \( B \parallel n \) direction is very sensitive to the presence of the isotropic component \( H_0 \), while that for the \( B \perp n \) is not. Let us estimate the sensitivity of CW-NMR spectra in determining the mosaic angle distribution in this method. In Figs. 4 and 5 we plotted the spectra calculated with slightly different \( \delta \) and \( \frac{H_0}{H_1} \) values from those of the best fitting by \( \pm 2.5 \) deg and \( \pm 0.015 \), respectively. The spectra are sensitive enough to discriminate such small variations of the distributions. The constraint that the spectra for both \( B \parallel n \) and \( B \perp n \) directions should be fitted simultaneously with the same parameters enhances the sensitivity.

4 Conclusions

In this paper, we proposed a useful method to estimate the mosaic angle distribution of Grafoil platelets from CW-NMR spectra of highly polarized monolayer \(^3\)He adsorbed on the substrate. By analyzing the NMR data taken by the Stanford group [7], we have proved that Grafoil used by them consists of two components. One is isotropic like powder (about 5 %) and the other is distributed in the gaussian function of inclination \( \theta \) with a standard deviation \( \sigma = 27.5 \pm 2.5 \) deg. These values are much more anisotropic (or 2D like) than ones determined from the previous analysis by Taub et al. [4] who used
the neutron diffraction data of Ar monolayer adsorbed on Grafoil. We have found that
their integration of the angular distribution is inappropriate. The results shown in this
paper will be valuable to elucidate intrinsic 2D properties from various experimental
data for monolayer systems adsorbed on Grafoil substrate. It is desirable to reanalyze
their data with the mosaic angle distribution of Eqs. (4) and (7) by taking account of
details of the experimental setup.

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