STS Observations of Landau Levels at Graphite Surfaces

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Scanning tunneling spectroscopy (STS) measurements were made on surfaces of two different kinds of graphite samples, Kish graphite and highly oriented pyrolytic graphite (HOPG), at very low temperatures and in high magnetic fields. We observed a series of peaks in the tunnel spectra associated with Landau quantization of the quasi-two-dimensional electrons and holes. A comparison with the calculated local density of states at the surface layers allows us to identify Kish graphite as bulk graphite and HOPG as graphite with a finite thickness of 40 layers. This explains the qualitative difference between the two graphites reported in the recent transport measurements which suggested the quantum-Hall effect in HOPG. This work demonstrates how powerful the combined approach between the high quality STS measurement and the first-principles calculation is in material science.

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Graphite is one of the best studied materials concerning its electronic properties both experimentally and theoretically. It is a semimetal or zero gap semiconductor with a unique *massless* linear dispersion relation for the conduction band. Graphite is also an important mother system for technologically attractive materials such as carbon nanotubes, fullerene, nanographites, etc., Thus, any new insight into this material should have broad impacts.

Recently, graphite has been attracting renewed fundamental interest particularly for its transport properties in magnetic fields. Kopelevich and co-workers [1] observed a plateau in the Hall resistance for highly oriented pyrolytic graphite (HOPG) in the quasiquantum limit, which suggests the quantum-Hall effect (QHE) characteristic of the 2D electron systems (2DES) with high mobility. But this behavior was not observed for a Kish graphite sample [1]. Although the QHE is theoretically predicted for a 2D graphene sheet [2], graphite is a far less ideal 2D conductor in spite of its layered structure. Reentrant field-driven metal-insulator transitions were also reported [1,3] for both types of graphites. Theories [4] predict the electron-hole pairing as a possible mechanism. Even for zero field properties, the gapless spin-1 neutral collective mode has been recently suggested from the view point of the resonating valence bond [5].

The aim of this work is to investigate the electronic states of Kish graphite and HOPG in high fields and low temperatures by scanning tunneling spectroscopy (STS). The STS technique, which probes the local density of states (LDOS), should potentially be a powerful tool to study the Landau quantization in 2DES in magnetic fields. This was recently demonstrated for the adsorbate-induced 2DES at the surface of InAs(110) with evaporated Fe submonolayers [6]. For both types of graphites, we observed clear peak structures in the tunnel spectra associated with the Landau levels (LLs). This is the first STS observation of the LLs in bulk materials. Comparisons with our LDOS calculations reveal that HOPG has a rather distinct 2D electronic state due to the effective finite thickness, but Kish graphite does not. This provides a spectroscopic explanation for the qualitatively different transport properties between the two types of graphites and the possible QHE in HOPG. More generally, it is an important achievement that in combination with the theoretical calculations we could determine the surface and underneath electronic states in layered materials in quantitative manners from the STS measurements.

The STS data were taken with a recently constructed ultralow temperature STM [7] at temperatures below 50 mK and in magnetic fields up to 6 T. The Kish graphite sample [8] is single crystalline graphite grown as precipitation from molten iron. The HOPG sample [9] is synthesized by chemical vapor deposition and subsequent heat treatment under high pressures. HOPG is polycrystalline graphite with ordered c-axis orientation. The typical microcrystallite (platelet) size is of the order of 1 μm. The samples were cleaved in air and then quickly loaded into an ultrahigh vacuum chamber ($P < 2 \times 10^{-8}$ Pa) of the STM. The differential tunnel conductance (dI/dV), which is proportional to the sample density of states (DOS), was measured by the lock-in technique with a bias modulation of $V_{\mathrm{mod}} = 0.6$ or 1.4 mV at a frequency of 131 or 877 Hz. Here V is the bias voltage applied to the sample relative to the tip.

Figure 1(a) shows measured tunnel spectra for Kish graphite at several different fields. Each spectrum at a given field is an average of raw data taken at 400 different positions over a 2×2 nm^2 area which is much smaller than the platelet size. The "V" shaped spectrum with a nonzero DOS at $V = 0$, i.e., $E = E_F$, in zero magnetic field is characteristic of semimetallic properties of graphite. To our knowledge, the DOS of graphite has never been measured with such a high energy resolution before.

In finite fields (B), several peaks appear superimposed onto the V-shaped base line [the open triangles in Fig. 1(a)]. The peaks become more pronounced at higher

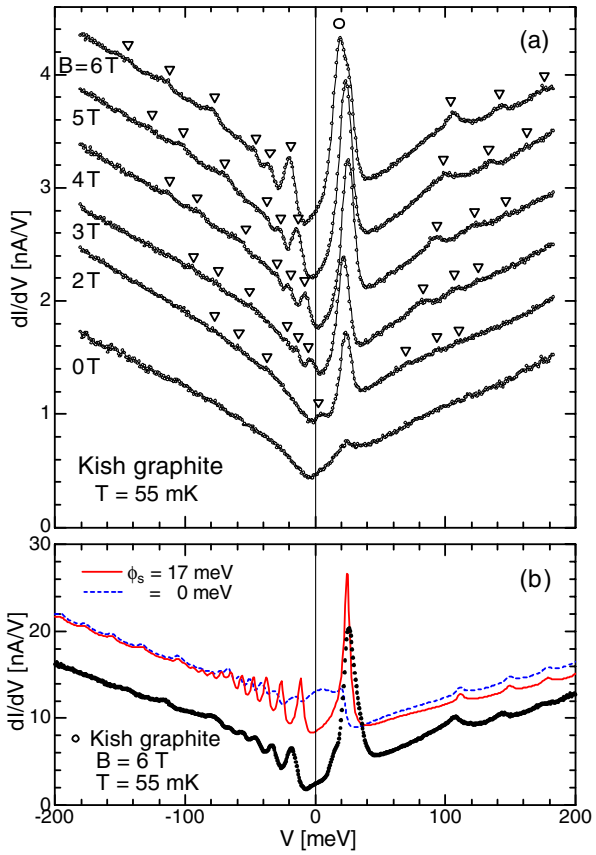

FIG. 1 (color online). (a) Tunnel spectra measured at $T = 55$ mK for Kish graphite in several different fields applied perpendicular to the basal plane ($V = 0.2$ V, $I = 0.24$ nA). Each spectrum is vertically shifted by 0.5 nA/V for clarity. (b) Comparisons between the calculated LDOS ($\eta = 5$ meV) for the surface layer of bulk graphite with (solid line) and without (dashed line) the surface potential ($\phi_s = +17$ meV), and the measured tunnel spectrum for Kish graphite at $B = 6$ T (dots; $V = 20$ mV, $I = 0.1$ nA).

fields, and the peak energies are roughly in proportion to B. A typical energy separation between the two successive peaks is 20–40 meV at $B = 6$ T, which is in the same order as ω_c for the electrons (= 12 meV) and holes (= 18 meV) calculated from the in-plane effective masses ($m_e^* = 0.057m_e$, $m_h^* = 0.039m_e$). Here $\omega_c = eB/m^*$ is the cyclotron frequency and m_e is the bare electron mass. Thus, we believe that these peaks are associated with the LLs in graphite. In addition to the field dependent small peaks, there exists a much pronounced peak just above E_F ($V = +20$ mV) for each spectrum. The peak energy is nearly field independent, but the amplitude grows rapidly with increasing field. The absence of field dependence of the peak energy strongly suggests that it originates from the $n = 0$ (electron) and -1 (hole) LLs [10]. These levels are characteristic of the graphite lattice structure [10,11] and have been known so far only indirectly. The important point is that this peak almost disappears in zero field.

Let us now compare the observed tunnel spectra with theoretically expected LLs in bulk graphite. Figs. 2(a) and 2(b) show Landau subbands calculated from the Slonczewski-Weiss-McClure (SWMcC) model [12] along the Brillouin zone edge (K-H axis) at $B = 2$ and 6 T. We followed here Nakao's method [10], which avoided the infinite dimension problem of the magnetic Hamiltonian matrix by grouping it into three submatrices and then truncating them at finite dimensions. We truncated them at 240 and 60 dimensions for $B = 2$ and 6 T, respectively, which are sufficiently large for studying the DOS in the energy range interested here. The seven band parameters in the SWMcC model were fixed to those used in Ref. [10], and small Zeeman energies are neglected throughout this Letter. As seen in Fig. 2(b), the doubly degenerated narrow bands across E_F, i.e., the lowest order LLs ($n = 0, -1$), are nearly unchanged even by applying the field of 6 T due to the strong interband interaction. The DOS calculated from these subbands are shown in Fig. 2(c) where we applied a Lorentzian smearing of $\eta = 5$ meV. There are general similarities between the experimental data (Fig. 1) and the theoretical DOS, for instance the existence of a field independent peak just above E_F and the asymmetry of peak structures above and below E_F. However, we also notice several quantitative disagreements: First, the peak energy separations in the theoretical DOS are much smaller than those observed experimentally. Second, the relative height of the field independent peak to the others is much smaller in the theory.

These discrepancies can be resolved by calculating the local DOS (LDOS) at the surface layer of bulk graphite. We decomposed the SWMcC Hamiltonian into a Hamiltonian for successive layers and calculated the surface LDOS by the Green's functions method [13,14]. The result of the calculation with the surface potential (ϕ_s) of +17 meV is shown as the solid line in Fig. 1(b) for the case of $B = 6$ T. The agreement between the experiment and theory is now excellent. This means that what is measured

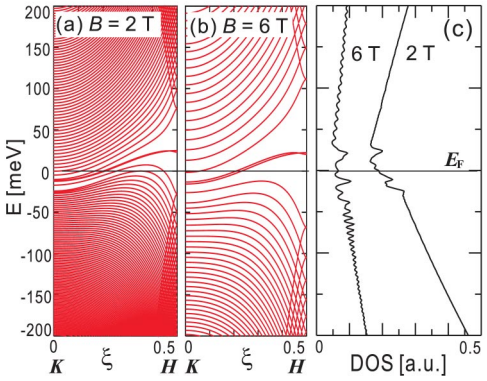

FIG. 2 (color online). Calculated Landau subbands along the graphite Brillouin zone edge (K-H axis) at (a) $B = 2$ T and (b) 6 T. (c) The density of states calculated from the subbands at $B = 2$ and 6 T with $\eta = 5$ meV.

with STS is the surface LDOS reflecting the bulk electronic state behind. This was confirmed by the fact that peak patterns calculated for underlayers rapidly change and approach that for bulk graphite shown in Fig. 2(c). The physical meaning of ϕ_s is band bending near the surface. Its possible origin is a local electrostatic potential induced by the tip. In the calculations, we added ϕ_s to on-site atomic levels at the surface layer in the Hamiltonian matrix. Note that the surface potential affects mostly the $n = 0, -1$ LLs and not the larger n LLs [see the dashed line in Fig. 1(b)].

Next we show tunnel spectra obtained for the HOPG sample in Fig. 3(a). Each spectrum is an average of the raw data at 100 different positions over a 90×42 nm^2 area.

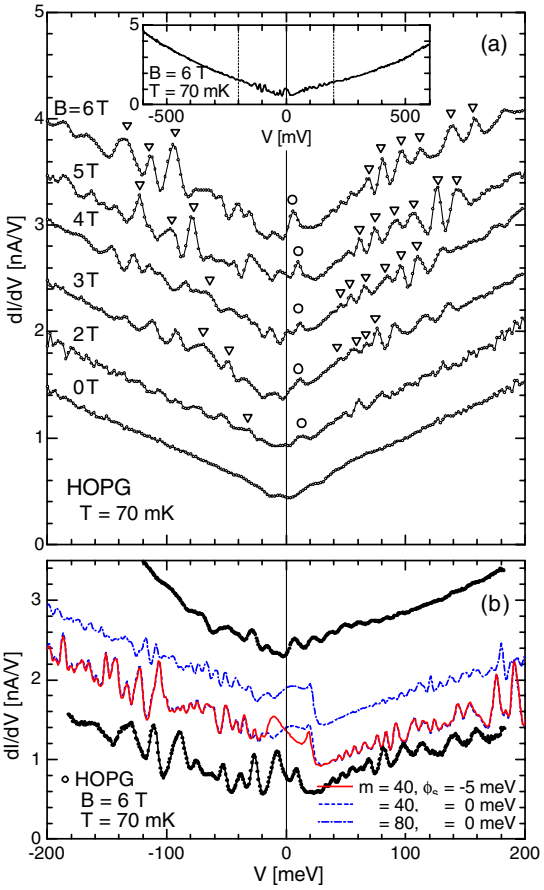

FIG. 3 (color online). (a) Tunnel spectra measured at $T = 70$ mK for HOPG in several different fields ($V = 0.2$ V, $I = 0.24$ nA). Each spectrum is vertically shifted by 0.5 nA/V for clarity. The inset shows the spectrum at $B = 6$ T in a wider energy range. (b) Comparisons between the calculated LDOS ($\eta = 5$ meV) for the surface layer of graphite with $m = 40$ layers with (solid line) and without (dashed line) the surface potential ($\phi_s = -5$ meV) and the measured tunnel spectrum for HOPG at $B = 6$ T (dots; $V = 0.2$ V, $I = 0.24$ nA). The dash-dotted line is the calculation for $m = 80$ layers without ϕ_s. The topmost spectrum shows experimental data ($V = 0.2$ V, $I = 0.24$ nA) for a HOPG sample with a smaller α value ($= 1.9 \times 10^3$) than that for the other data.

Again, we saw a series of growing and separating peaks with increasing field, as well as a nearly field independent peak just above E_F. The peak structures are, however, much more pronounced and complicated than those for Kish graphite except for the $n = 0, -1$ LLs. The peak amplitudes are comparable to those observed in the 2DES at the Fe/InAs(110) surface [6]. All these indicate that in HOPG an effectively 2D electronic state is created unlike in Kish graphite.

The somewhat irregular LL peak pattern for HOPG is explained by calculated LDOS at the surface of graphite with finite layer thickness (l^*). We calculated the LDOS at each atomic site and each layer by diagonalizing the decomposed Hamiltonian matrices. As can be seen in Fig. 3(b), the experimental data for HOPG at $B = 6$ T are reproduced reasonably well by the calculation for $m = 40$ layers, where m is the number of graphene layers ($m \equiv l^*/0.335$ nm). We assumed here $\phi_s = -5$ meV. The many irregular peaks are results of complicated phase interference between the incoming and outgoing wave functions at the surface. The calculations show that the peak amplitudes at high energies decrease with increasing m [cf. the dash-dotted line for $m = 80$ in Fig. 3(b)] and that, of course, the peak pattern approaches the result for bulk surface as $m \to \infty$ [14]. It is also shown that the peak structure near E_F due to the $n = 0, -1$ LLs does not depend appreciably on m.

The electronic identification of HOPG as graphite with finite thickness is consistent with the fact that it contains a much higher stacking fault density than Kish or natural graphite. This fact was checked by measuring the ratio (α) of the in-plane electrical conductivity to the out-of-plane one. The α values for Kish graphite and HOPG are 190 and 3.1×10^3, respectively. Furthermore, another HOPG sample with a lower α value shows less corrugated tunnel spectra [the topmost spectrum in Fig. 3(b)] in accordance with the above mentioned calculations.

In the following, we discuss the origin of ϕ_s. Experimentally, although the tunnel spectra within ± 30 meV of E_F changed significantly depending on the tip condition, those at higher energies were always unaffected. In addition, the overall spectra were stable for many hours unless we changed the tip condition intentionally, for example, by applying high voltage pulses (≈ 8 V). Thus the origin is attributable to the electrostatic potential caused by the tip. Note that, in graphite, the DOS in the vicinity of E_F should be very sensitive to ϕ_s, since the $n = 0, -1$ subbands are much narrower compared to the others [see Figs. 2(a) and 2(b)]. In other words, the LDOS peak associated with the $n = 0, -1$ LLs can easily be enhanced even by a small amount of ϕ_s like in Fig. 1. This is also seen in Figs. 1(b) and 3(b) where the calculated LDOS peaks near E_F are quite different between with and without the small surface potentials, while little is different for the higher energy peaks. We did not see a clear correlation

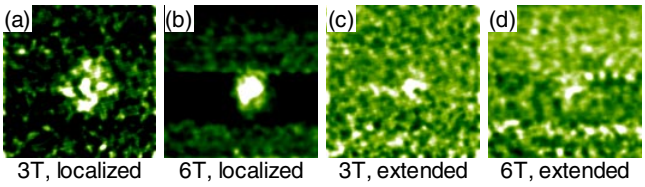

FIG. 4 (color online). dI/dV images (80×80 nm^2, $I = 0.2$ nA) near point defects at the HOPG surface at $T = 30$ mK. (a) $V = 30$ meV, $B = 3$ T and (b) 36 meV, 6 T corresponding to energies in between $n = 1$ and 2 LLs. (c) 33 meV, 3 T and (d) 43 meV, 6 T corresponding to energies of the $n = 2$ LL. The contrast in all images is identical.

between ϕ_s and the tip material (W or PtIr) which may suggest the importance of the work function difference between the tip and sample [15]. The relatively small effects on the LL structure (except for the $n = 0, -1$ LLs) caused by the tip compared to the 2DES in semiconductors are presumably due to the higher carrier densities and, hence, the more effective screening effect in graphite.

We observed a circular distribution of the LDOS around point defects on the HOPG surface in the dI/dV image at an energy in between $n = 1$ and 2 LLs at $B = 3$ T as shown in Fig. 4(a). The radial extension is roughly equal to the magnetic length, $\sqrt{\hbar/eB}$ (= 15 nm at 3 T), of the 2DES, and decreases as B increases to 6 T [see Fig. 4(b)], suggesting localization of the electronic wave function along an equipotential contour around the defects. In contrast, the dI/dV images at energies corresponding to the $n = 2$ LL do not show such a distribution but complicated nonlocal networks of the wave function in addition to moderately bright local spots at different positions from the defects [Figs. 4(c) and 4(d)]. These observations [16] indicate the existence of the 2DES in HOPG and likely the drift and extended states previously observed in the Fe/InAs(110) system [6].

It is generally expected that the LL structure will have a rather strong atomic-site dependence. Actually, the calculated LDOS peak structures are qualitatively different between the A and B sites in the case of graphite with finite thickness [14]. Note that the calculated LDOS shown in Fig. 3 is the sum of LDOS on the two sites. However, experimentally, averaged tunnel spectra on the B sites differ from those on the A sites only within the experimental errors. We speculate that the expected site dependence was masked by dominating tunnel currents from neighboring B-site atoms even when the tip is just above an A-site atom.

In conclusion, we succeeded in observing clearly the Landau quantization in bulk material (graphite) with STS in high magnetic fields and very low temperatures. By comparing with calculated LDOS, we found that the measured tunnel spectra for Kish graphite and HOPG well represent the LDOS at the surface layers of bulk graphite and graphite with finite thickness of about 40 layers, respectively. The more pronounced LL structure in HOPG indicates the much stronger 2D nature of the electronic state than previously thought. Our results provide a spectroscopic statement that HOPG has a high-mobility quasi-2DES which is eligible to show the quantum-Hall effect as was conjectured by the recent transport measurements [1]. This was supported by the wave function mappings near surface defects which show the localization and extension of the electronic state depending on energy relative to the LL structure. The present work is the first example to extract quantitative information on the electronic states in bulk or finite thickness layered material from the surface LDOS measured with STS. This further expands the potentialities of the STS technique for material science.

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