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Observation of Van Hove singularities in twisted graphene layers

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Electronic instabilities at the crossing of the Fermi energy with a Van Hove singularity[1] in the density of states often lead to new phases of matter such as superconductivity[2,3], magnetism[4] or density waves[5]. However, in most materials this condition is difficult to control. In the case of single-layer graphene, the singularity is too far from the Fermi energy[6] and hence difficult to reach with standard doping and gating techniques[7]. Here we report the observation of low-energy Van Hove singularities in twisted graphene layers seen as two pronounced peaks in the density of states measured by scanning tunnelling spectroscopy. We demonstrate that a rotation between stacked graphene layers can generate Van Hove singularities, which can be brought arbitrarily close to the Fermi energy by varying the angle of rotation. This opens intriguing prospects for Van Hove singularity engineering of electronic phases.

In two dimensions, a saddle point in the electronic band structure leads to a divergence in the density of states, also known as a Van Hove singularity[1] (VHS). When the Fermi energy (E_F) is close to the VHS, interactions, however weak, are magnified by the enhanced density of states (DOS), resulting in instabilities, which can give rise to new phases of matter[2–5] with desirable properties. This implies the possibility of engineering material properties by bringing E_F and the VHS together. However, in most materials one cannot change the position of the VHS in the band structure. Instead, it may be possible to tune E_F through the VHS by chemical doping[8] or by gating[7]. In this regard, graphene, the recently discovered two-dimensional form of carbon, is quite special[5,9]. It has linearly dispersing bands at the K (K′) point in the Brillouin zone, the so-called Dirac points, and a DOS that is linear and vanishes at Dirac point. The fact that this material is truly two-dimensional and has a low DOS means that it cannot screen applied electric fields, allowing for strong gating and ambipolar behaviour[7]. However, although the band structure of graphene[5] contains a VHS, its large distance from the Dirac point makes it prohibitively difficult to reach by either gating or chemical doping. We show that by introducing a rotation between stacked graphene layers, it is possible to induce VHSs that are within the range of E_F achievable by gate tuning. As the samples studied here are not intentionally doped, E_F is within a few millielectronvolts of the Dirac point.

Rotation between graphene layers is often observed as a Moiré pattern on graphite surfaces[10], as illustrated in Fig. 1. Graphite consists of stacked layers of graphene, the lattice structure of which contains two interpenetrating triangular sublattices, denoted A and B. In the most common (Bernal) stacking, adjacent layers are shifted by one atomic spacing, so that B atoms of layer 2 (B2) sit directly on top of A atoms of layer 1 (A1) and B1 and A2 atoms are in the centre of the hexagons of the opposing layer. Assuming a rotation through an angle θ about an A1 (B2) site in bilayer graphene, a set of conditions for commensurate periodic structures leading to Moiré patterns is easily derived[11] $\cos(\theta_i) = (3i^2 + 3i + 1/2)/(3i^2 + 3i + 1)$, with i being an integer ($i = 0$, $\theta = 60°$ corresponds to AA stacking and $i \to \infty$, $\theta = 0°$ to AB stacking) and lattice constant of the superlattice $L = a_0\sqrt{3i^2 + 3i + 1}$, where $a_0 \sim 2.46$ Å is the atomic lattice constant. For the extended Moiré pattern in Fig. 1, $\theta_i = 1.79°$ is obtained from the superlattice period, $L = 7.7 \pm 0.3$ nm, corresponding to $i = 18$.

Thus far, most work on Moiré patterns focused on structural aspects revealed by scanning tunnelling microscopy (STM), but their effect on the electronic properties has not been addressed. By using scanning tunnelling spectroscopy (STS), we find that rotation markedly alters the DOS. Figure 2 shows the tunnelling differential conductance, dI/dV, a quantity proportional to the local DOS (ref. 12). In regions inside the Moiré pattern (M1 and M2), the spectra develop two sharp peaks flanking the Dirac points with energy separation $\Delta E_{vhs} \sim 82$ meV. Below, we show that these peaks correspond to rotation-induced VHSs. The effect of the VHS on the DOS is evident in the energy dependence of the dI/dV maps. Close to the VHS, the maps develop a strong density modulation (Figs 2f and 3c), characteristic of charge-density waves (CDWs), suggesting an impending Fermi-surface instability. In contrast, for energies away from the VHS, the charge density becomes nearly homogeneous.

To explore the angle dependence of ΔE_{vhs}, we studied graphene layers prepared by chemical vapour deposition[13] (CVD). CVD graphene layers have a strong twisting tendency revealed by Moiré patterns with a range of rotation angles. The example in Fig. 3a shows a pattern, corresponding to $\theta \sim 1.16°$. The STS spectra in this region reveal strong VHSs (Fig. 3b) with a much smaller $\Delta E_{vhs} \sim 12$ meV. The pronounced spatial modulation of the dI/dV maps at energies close to these VHSs (Fig. 3c), indicating the formation of a CDW, is significantly stronger than for the pattern in Fig. 2f, where the more widely separated VHSs are farther away from the Fermi energy. For a pattern with an even larger angle, $\theta \sim 3.4°$, and $\Delta E_{vhs} \sim 430$ meV, the localization is weaker still (see Supplementary Fig. S3), consistent with theoretical predictions[14].

We next show that the VHSs are induced by the rotation and use the model developed in ref. 11 to derive the angle dependence of ΔE_{vhs}. A rotation between two graphene layers causes a shift between the corresponding Dirac points in momentum space, so

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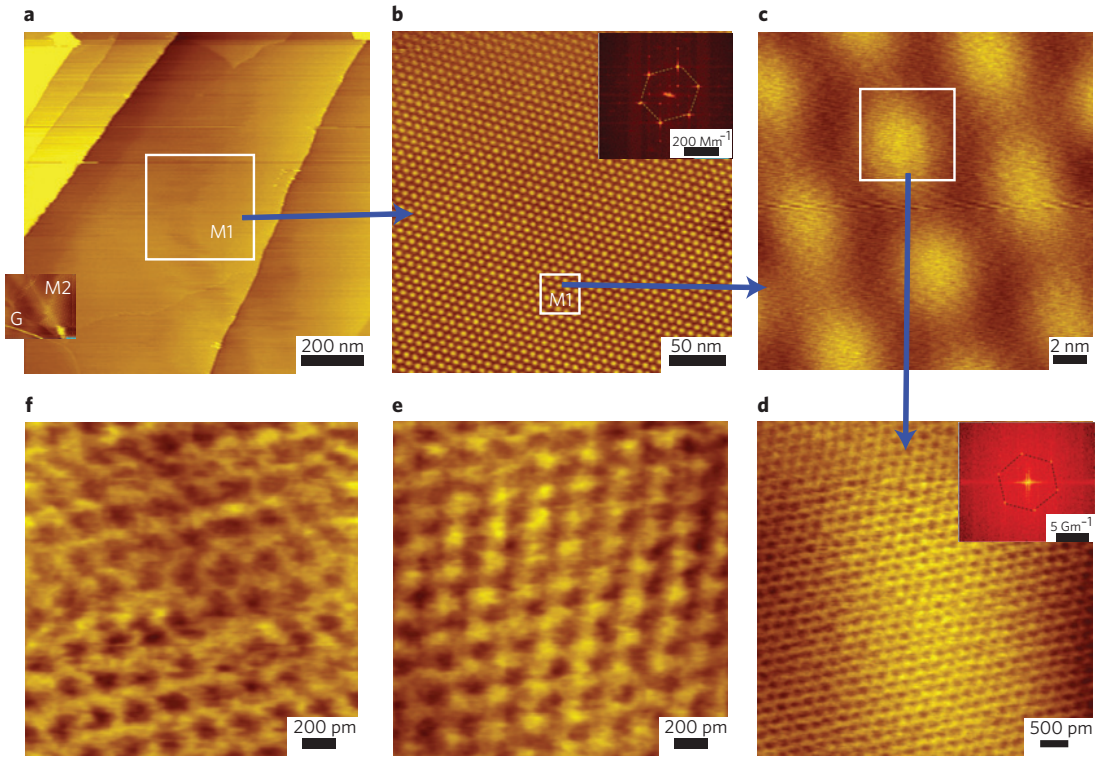

Figure 1 | STM of a graphene flake on a freshly cleaved surface of highly oriented pyrolitic graphite revealing a Moiré pattern. a, Large-area scan of a graphene flake. Regions M2 and G flank the boundary of the Moire pattern. **b**, Zoom-in of the frame in **a**, showing a Moiré pattern with period 7.7 ± 0.3 nm. Inset: Fourier transforms of the superstructure. **c**, Zoom-in to the centre of the pattern, region M1. **d**, Atomic-resolution image of a bright spot. Inset: Fourier transforms of the atomic-resolution image. **e**,**f**, Atomic-resolution image on bright and dark regions of the pattern, showing a well-ordered triangular lattice within the bright spots (**e**) and a less-ordered honeycomb-like structure in between (**f**). The former indicates Bernal-stacked layers[16,23], whereas the latter suggests slipped stacking, resulting from a small-angle rotation between layers. Tunnelling current 20 pA, sample bias voltage 300 mV.

that the Dirac wavevector of the rotated layer is $K^\theta = K + \Delta K$, where $\Delta K = K \times 2\sin(\theta/2)$. If we use the same origin of momentum for the two layers, so that a uniform hopping couples states of the same momentum in both layers, the zero-energy states do not occur at $k = 0$, but rather at $k = -\Delta K/2$ in layer 1 and $k = \Delta K/2$ in layer 2. Unlike in the AB stacked bilayer, there is no direct coupling of the zero-energy states of one layer to the zero-energy states of the other. As shown in ref. 11, the states near the Dirac cone of each layer couple with amplitudes of order $t_\perp^\theta \approx 0.4\, t_\perp$ to states of energy $\pm\hbar v_F \Delta K$ of the opposing layer and the linear dispersion is preserved near zero energy. Here, $t_\perp$ is the interlayer hopping for unrotated layers and $v_F \sim 10^6$ m s^{-1} is the Fermi velocity. The two Dirac cones intersect near the centre of the superlattice Brillouin zone and hybridize, resulting in a saddle point in the energy dispersion and in two symmetric VHSs (Fig. 4a).

This mechanism of rotation-induced low-energy VHSs is not restricted to the bilayer. We extended the calculation to a trilayer consisting of an AB stacked bilayer and a third rotated layer on top and again found two VHSs in the DOS (Fig. 4b). In both cases, ΔE_{vhs} is controlled by the energy scale $\hbar v_F \Delta K \propto \theta$. Figure 4c shows that this model accounts well for the experimental angle dependence of ΔE_{vhs}.

This analysis shows that the mechanism behind the formation of VHSs is quite robust, and we expect it to apply more generally whenever one layer is rotated with respect to the others, even for a graphene flake over graphite. The strong twisting-angle dependence of ΔE_{vhs} is its unmistakable signature.

In the bilayer, the two Van Hove peaks are exactly symmetrical, whereas in the trilayer, a slight asymmetry occurs because of the third layer, but not as large as that observed experimentally. The discrepancy can be attributed to two factors. First, the experiments probe the local DOS, which varies across the unit cell of the Moiré pattern, whereas the calculation refers to the total DOS. Averaging the data over several unit cells reduces the asymmetry. Second, a bias between the layers can also enhance the asymmetry. In the AB stacked bilayer, a perpendicular electric field opens a gap in the spectrum[15]; not so in the twisted bilayer. As states close to zero energy result from the hybridization of zero-energy states in one layer with states of energy $\pm\hbar v_F \Delta K$ in the other, the corresponding wavefunctions have different weights in the two layers; when an electric field is applied, the two Dirac points move in opposite directions in energy[11]. The positive and negative energy states at the saddle points now have different weights in the two layers. As the STM probes predominantly the top layer, we expect this asymmetry in the STS. This effect of the bias in the DOS of the bilayer is shown in Fig. 4b (mid-panel).

It is important to note that the VHSs can form only in the presence of finite interlayer coupling. For vanishingly small interlayer coupling, $t_\perp \sim 0$, as is the case when a detached graphene flake is found on a graphite substrate[16] (see also Supplementary Information), the VHSs will not form even though a Moiré pattern may be visible in the STM images[17] (Supplementary Information). It is well known that on the surface of graphite one often finds graphene flakes loosely bound to the surface where interlayer coupling is completely suppressed[16]. Such flakes, regardless of the presence or absence of rotation with respect to the underlying layer, show an uninterrupted honeycomb structure and a Landau-level sequence characteristic of massless Dirac fermions[16]. However, they do not show VHSs in their zero-field DOS.

The situation here is reminiscent of transition-metal dichalcogenides[14], which form triangular lattices where both CDWs and superconductivity are observed[18]. In fact, these materials have