Graphene analogues in bulk: the prediction and observation of 3D Dirac semimetals

M. Neupane et al., arXiv:1309.7892; S. Borisenko et al., arxiv:1309.7978; Z. K. Lu et al., arXiv:1310.0391 (experiment)
S. M. Young et al., PRL **108**, 140405 (2012); Z. Wang et al., PRB **85**, 195320 (2012) and PRB **88**,125427 (2013). (theory)

Recommended with a Commentary by Joel E. Moore, UC Berkeley and LBNL

A large part of the enthusiasm for graphene studies stems from that material's unusual electronic structure. Undoped graphene is a two-dimensional "Dirac" semimetal, meaning that at low energies and neglecting spin-orbit coupling, its electrons are effectively relativistic but with a velocity about 300 times smaller than the velocity of light. The Dirac nature of the band structure is protected by symmetries of the graphene lattice: adding spin-orbit coupling, for example, may open a gap and make graphene into a 2D topological insulator [1] at very low temperatures. A more conventional band gap is opened by going from pure carbon to boron nitride, which also has a 2D honeycomb lattice; the inequivalence of the ions on the two sites in the unit cell lowers the symmetry and opens a large gap.

Three recent preprints [2, 3, 4] report success in the search for a 3D Dirac semimetal. All use angle-resolved photoemission to characterize the band structure of fairly obscure compounds, but before explaining a few more details, it is useful to understand some theoretical background for why 3D Dirac materials are rare and considerably more complicated chemically than graphene. The key theoretical work that simulated these experimental searches was a 2012 PRL [5] that asked the question of when a 3D Dirac point could be stabilized by space group symmetries in the way that the honeycomb lattice of identical atoms stabilizes graphene's 2D Dirac point.

More precisely, the effective Hamiltonian of a 2D Dirac point can be taken to be (setting velocity equal to 1)

$$H = k_x\sigma_x + k_y\sigma_y, \tag{1}$$

whose degeneracy is broken by a perturbation proportional to σ_z. The most direct generalization of this to 3D is a Weyl point of two bands, such as

$$H = k_x\sigma_x + k_y\sigma_y + k_z\sigma_z. \tag{2}$$

This is robust to perturbations, but that robustness results from a topological consideration (a Chern number ± 1) which means that there cannot be only one Weyl point on the Fermi surface as the total Chern number must be zero. In materials with both time-reversal and inversion symmetry, Weyl points must come together in pairs and form 3D Dirac points; to see this, note that time-reversal symmetry means that a Weyl point at k must be paired with one at $-k$ with the same Chern number. A center of inversion pairs a Weyl point at k with one with the *opposite* Chern number at $-k$. Hence isolated Weyl points are

forbidden when both time-reversal and inversion are present. The Hamiltonian at a Dirac point is a 4 by 4 matrix as now four bands are involved. These Dirac points are not topologically protected as their total Chern number is zero, and the question is whether they can be protected by crystalline symmetries.

This mechanism for protection is different from creating a 3D Dirac point by tuning to a phase transition (e.g., the transition between ordinary and Dirac semimetals): the goal is to have the Dirac semimetal as a "phase" (an extended region of parameter space, at least when crystalline symmetries are respected), rather than as an isolated point. It turns out that only non-symmorphic space groups can stabilize a Dirac point, and there are many subtle requirements that appear, such as the absence of 3-fold rotations in the little group at the possible Dirac point. The second part of this theoretical tour de force was to search the literature and use ab initio calculations to find candidate materials in which the Dirac point might be isolated in energy (i.e., not overlap other bands) and in which the stoichiometric electron density would put the Fermi level right at the Dirac point, again as happens in graphene. The chief example discussed by these authors is an unusual form ("β-cristobalite") of BiO_2, but the experiments so far have all been on other materials.

Both of the materials in the current experimental papers were proposed as candidates by a group at the Chinese Academy of Sciences using ab initio electronic structure methods [6, 7]. Two of the new experimental preprints [2, 3] are on cadmium arsenide (Cd_3As_2), which has been studied for some years but without a clear understanding of its full bulk band structure. The Dirac velocity appears to be quite large (1.6×10^6 m/s, more than an order of magnitude larger than in graphene). The Dirac point physics may explain the previously known fact that the mobility in this compound is unusually high. The third experiment [4] is on Na_3Bi and reports velocities closer to those in graphene, and the authors deliberately modified the surface of their sample *in situ* in order to verify that the observed Dirac dispersion is a bulk rather than a surface property.

This prediction of 3D Dirac semimetals reflects a resurgence of interest in the area of unusual semimetallic band structures that began a few years earlier. An important trigger was the observation that pyrochlore iridates might support a Weyl semimetal phase [8] and that this phase had an interesting Fermi-arc surface state (in ideal crystals) that had previously been overlooked. (An analogue of this surface state may exist in some of the 3D Dirac materials.) Topological classifications of metallic systems (see [9, 10], among others) and various examples of interesting metallic states had been proposed, but the understanding of how to connect these to crystalline symmetries in general required the sort of detailed investigation carried out in Ref. [5].

The reader may ask how much we learn on a fundamental level from finding examples of these semimetallic band structures, given that the essentials of graphene's electronic structure were pointed out in 1947, and the possibility of a Weyl semimetal goes back at least to Conyers Herring's thesis work [11]. Leaving aside potential applications, one answer is that the absence of a conventional Fermi surface means that most of the conventional physics of metals is

invalidated: a wide variety of new phases and effects appear that are difficult or impossible to create in standard metals. In the same spirit, the metallic surface state of a 3D topological insulator, even away from the massless point when it has a Fermi surface (with an odd number of sheets), requires a "chiral" version of Fermi liquid theory in which some standard assumptions break down [12].

So the next question is whether these 3D semimetals will support as many interesting phenomena as graphene does. The Dirac semimetals can be a starting point for other states of matter, such as Weyl semimetals if the materials can be modified to break time-reversal or inversion. The chief consequences discussed so far theoretically for Dirac and Weyl semimetals, aside from the band structure probed by ARPES, are in transport. Already transport experiments seeking to observe theoretically predicted anomalies are underway and find high conductivity and large magnetoresistance in single-crystal Cd_3As_2 [13]. This flurry of new examples of Dirac semimetals should lead to a broader consideration by theorists of what interesting physics this class of materials might enable.

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