Dirac Point Degenerate with Massive Bands at a Topological Quantum Critical Point

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Dirac Point Degenerate with Massive Bands at a Topological Quantum Critical Point

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The quasi-linear bands in the topologically trivial skutterudite insulator $CoSb_3$ are studied under adiabatic, symmetry-conserving displacement of the Sb sublattice. In this cubic, time-reversal and inversion symmetric system, a transition from trivial insulator to topological point Fermi surface system occurs through a critical point in which massless (Dirac) bands appear, and moreover are *degenerate* with massive bands. Spin-orbit coupling, while small due to the type of band character, coupled with tetragonal strain opens the gap required to give the topological insulator. The mineral skutterudite ($CoSb_3$) is very near the critical point in its natural state.

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The topological properties of crystalline matter have become a central feature in characterizing the electronic structure of small gap, primarily binary, semiconductors.[1–4] Skutterudite compounds, many of which have small gaps, have received a great deal of interest in the past two decades. Most recently emphasis has been on the "filled" version in which atoms are incorporated in the large holes in the original skutterudite ($CoSb_3$) structure, which can become unusual heavy fermion correlated metals and even superconductors.[5] The earlier interest was in their transport properties.[6] As small gap semiconductors, many of them were of potential interest in solid state devices, and application as thermoelectric materials[7, 8] was a strong interest.

A study of the electronic structure[9] uncovered a very peculiar feature of some of them: there are linear valence and conduction bands that extended from well out in the Brillouin zone, changing to quadratic only very near the zone center k=0. This quasi-linear dispersion produces peculiar consequences: the density of states behaves as ε^2 near the band edge rather than the usual three dimensional (3D) form $\sqrt{\varepsilon}$; the carrier density scales differently with Fermi energy ε_F; the inverse mass tensor $\nabla\nabla\varepsilon_k$ is entirely off-diagonal corresponding to an "infinite" transport mass; the cyclotron mass is different from usual 3D behavior, etc. All of this was unique and was potentially very useful in applications, but theoretical excitement was tempered because the quasilinear dispersion, which was clearest in $IrSb_3$, finally became quadratic *very near* k=0, just as textbooks claim must be the case.

Since then, a 2D analog graphene has been isolated and its "Dirac point" with linear dispersion has been studied comprehensively.[10, 11] The Dirac point of graphene however occurs at a zone corner point where symmetry is much lower than at the zone center, and its occurrence does not violate textbook conventional wisdom. Here we show that in the skutterudite system small adjustments in the structure produce a critical point at which strictly linear bands extrude from $|\vec{k}|$=0. This does not violate any real principle, however it does violate the commonly used expansions. The linear behavior reflects non-analytic behavior in the $\vec{k} \to 0$ limit, resulting from an accidental (but tunable) degeneracy. In this paper we illustrate how to tune to this critical point, provide a simple model that reproduces the behavior, and demonstrate that the transition corresponds also to a trivial to topological insulator.

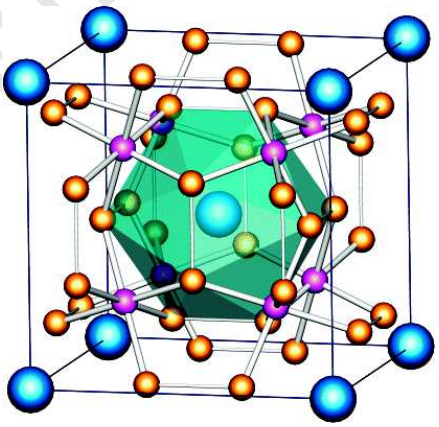

FIG. 1: (Color online) Crystal structure of skutterudite $CoSb_3$, space group $Im\bar{3}$ (#204). The experimental lattice constant is a=9.0385 Å and the internal position coordinates are u=0.335, v= 0.1575. The Co site (small pink sphere) is octahedrally coordinated to Sb atoms (small yellow spheres), each of which connects two octahedra. The large (blue) sphere denotes a large open site which is unoccupied in $CoSb_3$; the surrounding solid (center of figure) gives an idea of the volume and shape of the empty region.

The skutterudite structure, pictured in Fig. 1, in the space group $Im\bar{3}$ (#204), has a simple cubic Bravais lattice, and is comprised of a bcc repetition of three formula units (f.u.) when expressed as TPn_3. The pnictide (Pn) atoms form bonded units (nearly square but commonly designated as rings) which are not required by local environment or overall symmetry to be truly square; there-

fore they are not although very nearly so. The three Pn_4 squares in the primitive cell are oriented perpendicular to the coordinate axes. Transition metal (T) atoms (Co, Ir, ...) lie in six of the subcubes of the large cube of lattice constant a^3; the other two subcubes (octants) centered at sites $2a$ are empty. The structure is symmorphic, with 24 point group operations; the one that is missing is reflection in (110) planes. This space group leads to some interesting band behavior but is not relevant to the behavior we discuss in this paper. The related filled skutterudites XT_4Pn_{12} have an atom X incorporated into the large $2a$ site of $3\bar{m}$ symmetry.

A relevant structural feature is that skutterudite is related to the perovskite structure $\Box T Pn_3$ ($\Box$ denotes an empty A site). Beginning from perovskite, a rotation of the octahedra keeping the Pn atoms along the cube faces and the octahedra connected results in the formation of the (nearly square) Pn_4 rings, and the Pn octahedra become distorted and less identifiable as a structural feature. The transformation is, in terms of the internal coordinates u and v,

$$u' = \frac{1}{2} + s(u - \frac{1}{2}); v' = \frac{1}{2} + s(v - \frac{1}{2}). \qquad (1)$$

The transformation path, from perovskite for s=0 to the observed structure for s=1, is pictured in Fig. 1 of Ref. 12. Below we make use of this transformation to understand the opening of the (pseudo)gap between occupied and unoccupied states and to tune an unusual transition.

Evolution through a critical point. The electronic structure of skutterudites has been of keen interest since the quasi-linear bands (QLB) near the zone center were uncovered by Singh and Pickett.[9] The skutterudites that are isovalent with $CoSb_3$ are very narrow gap semiconductors (or possibly very small negative gap semimetals, or point Fermi surface zero-gap materials, *viz.* $IrSb_3$ [9]). In following the band structure along the perovskite-to-skutterudite structural path given above, it is found that the gap at the Fermi level only opens up near the end of the transformation ($s \sim 0.90 - 0.95$), where the Sb_4 rings approach their equilibrium size and the empty $2a$ site is fully developed into a large interstice. Only near $s \sim 1$ does the quasilinear band emerge from the dense spaghetti of occupied valence Sb $4p$ and Co $3d$ bands. **Analysis of the band character, projected density of states (DOS), and charge density indicates no Co $3d$ character and very little Sb $4p$ character in the quasilinear bands, which arise from Bloch states (one on either side of the gap) associated with Sb $5s$ states with some charge extending into the large empty $2a$ site.**

To illustrate the progression of the band structure through a critical point at which a Dirac point (with Dirac hypercone) appears, we provide in Fig. 2 the behavior of the bands for s = 1.020, 1.023, 1.025, corresponding to just before, precisely at, and just beyond gap closing. At zero gap, the QLBs become precisely linear (Dirac) bands emanating from the zone center. Because one of them is degenerate (by crystal symmetry) with two other bands in a 3-fold set, this Dirac point is degenerate with two conventional (massive) conduction bands. Beyond the critical point s_{cr} = 1.023, the singlet lies above the triplet, and the Fermi level lies at a symmetry-determined, point FS energy comprised of one

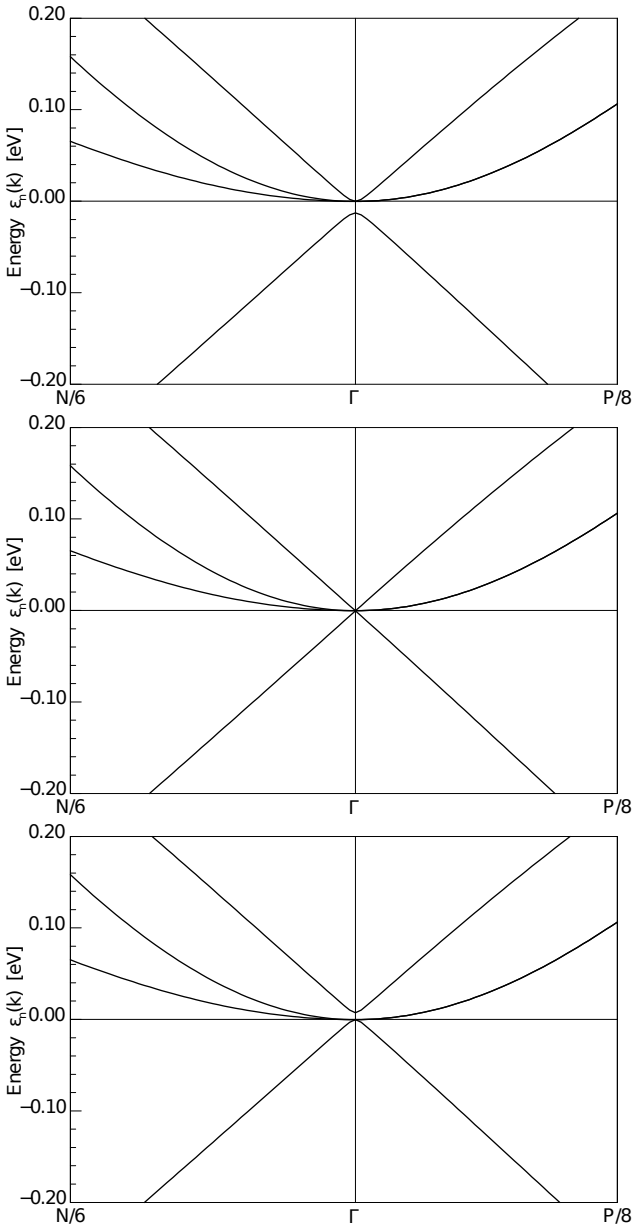

FIG. 2: Bands near k=0 in skutterudite $CoSb_3$, showing the band crossing as the valence band rises due to the variation of the Sb coordinate, through the critical point of quadruple degeneracy of a Dirac pair and a conventional band pair. Top: before transition, s=1.020. Middle: at the critical point, s=1.023. Bottom: just after the transition, s=1.025.

hole and two electron bands. While beyond the critical point these bands are all "massive" in the rigorous sense, immediately beyond the transition the masses of both quasilinear (valence and conduction) bands *arise continuously from zero mass* to the linear behavior that extends as far as the bands can be followed before they helplessly mix with and disappear into the background spaghetti.

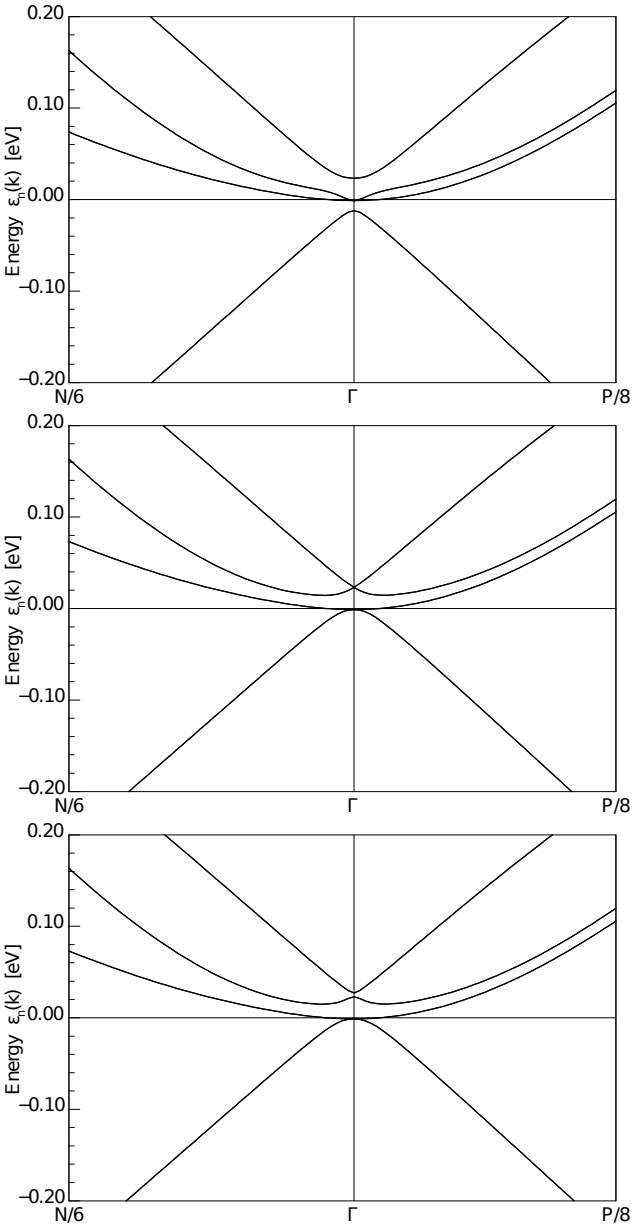

FIG. 3: Bands as in Fig. 2, with s=1.010, 1.019, 1.020 and with spin-orbit coupling included. Although the threefold "p" band degeneracy is split by SOC, the Dirac bands and hypercone survive, though the lower (hole) band mixes with one of the massive bands very close to k=0.

At first sight, the basic underlying feature seems to be provided by two states at $\pm\varepsilon_\circ$ on some scale, which will become degenerate ($\varepsilon_\circ = 0$) at the critical point. Although the two-band[13] Kane model has been used to represent the bands of $CoSb_3$, it fails to give the linear dispersion at *arbitrarily small* k as the gap vanishes, so some other picture must be constructed. While the bands are required to have only cubic – not spherical – symmetry, the linear bands for $CoSb_3$ are in fact isotropic well out into the zone, that is, the velocity is indistinguishable in all three high symmetry directions. The simplest viewpoint is that two bands are linearly coupled ($h_{ij} \propto v|\vec{k}|$ for $i \neq j$) at small $|\vec{k}| \equiv k$, in which case the eigenvalues are

$$\varepsilon_k = \pm\sqrt{\varepsilon_\circ^2 + (v|\vec{k}|)^2} \rightarrow \pm v|\vec{k}|, \tag{2}$$

giving the desired two linear bands upon degeneracy ($\varepsilon_\circ \rightarrow 0$).

So how does one obtain the desired coupling? The easiest way to get linear coupling at small k, in a tight-binding picture, is from a coupling such as $t(\sin k_x a + \sin k_y a + \sin k_z a)$ on the off-diagonal. However, expanding this coupling for small k ($k_x + k_y + k_z$) does not give isotropic coupling. What could give isotropic coupling?

The skutterudite structure, which has bcc translational symmetry with coupled Sb_4 ring $5p$ orbitals and large empty holes in the lattice that may harbor an s-like orbital in its well, can be modeled with a p triplet coupled to s-symmetry states on the bcc neighbors. Working in a picture where the p triplet is diagonalized at k=0, the coupling of the p_x function with the bcc-situated s orbitals gives

$$T_x \equiv T(k_x, k_y, k_z) = 8it\ sin\frac{k_x a}{2} cos\frac{k_y a}{2} cos\frac{k_z a}{2} \tag{3}$$

and symmetrically for coupling of p_y and p_z partners. Then using on-site energies ε_s and ε_p, the tight-binding Hamiltonian is

$$H = \begin{pmatrix} \varepsilon_s & T_x & T_y & T_z \\ T_x^* & \varepsilon_p & 0 & 0 \\ T_y^* & 0 & \varepsilon_p & 0 \\ T_z^* & 0 & 0 & \varepsilon_p \end{pmatrix} \tag{4}$$

with eigenvalues

$$\varepsilon_j = \varepsilon_p; \varepsilon_p; \frac{\varepsilon_s + \varepsilon_p}{2} \pm \sqrt{(\frac{\varepsilon_s - \varepsilon_p}{2})^2 + |T|^2}, \tag{5}$$

where $|T|^2 \equiv |T_x|^2 + |T_y|^2 + |T_y|^2$. To first order in k and and at the critical point $\varepsilon_s \rightarrow \varepsilon_p$, this result gives (1) 4-fold degenerate bands $\varepsilon = \varepsilon_p$ at k=0 (where T vanishes), (2) two bands have isotropic linear dispersion $\varepsilon_p \pm vk$ with $v = 4ta$, (3) the other two bands are flat in Eq. 4, but will acquire finite mass by the smaller $p-p$ hopping that has been neglected for simplicity. For $|\varepsilon_p \sim \varepsilon_s|$, three-fold degeneracy is preserved at k=0. This model

faithfully reproduces the behavior in $CoSb_3$ in Fig. 2 as the Sb rings are varied in size adiabatically.

A number of works[14–16] have pointed out that insulators in 3D, as well as in 2D, can be characterized by topological invariants, and Fu and Kane followed by demonstrating[17] that when inversion symmetry is present (as in space group $Im\bar{3}$), the Z_2 invariant can be obtained from the parities of the occupied states at the invariant momenta. Here only the Γ point requires consideration, since reoccupation occurs only there. The lower band in Fig. 2 has *odd* parity at Γ while the triplet is *even*. The product of parities (at Γ, and at all time-reversal momenta, is positive, so $CoSb_3$ is the expecte trivial insulator. As the critical point is crossed, the product of the parities of the occupied bands at Γ, and hence the Z_2 invariant, changes sign, the signal of a transition to a topological insulator. This change also reveals that the transition is associated with the entanglement of the odd symmetry valence band with an even parity conduction band that has the same symmetry away from Γ, and hence mixes with. The final state at this level is actually gapless; it is a (point Fermi surface) zero-gap semiconductor, with the mass of the lowest band rising from zero and giving rise to extremely light mass carriers in the limit of low hole doping. The system rendered a true topological insulator by strain (lifting of the band degeneracy).

Effect of Spin-Orbit Coupling and Tetragonal Strain. The system is rendered a true topoligical insulator by SOC and tetragonal strain. In Fig. 3 the effect of intrinsic (relativistic) SOC for the cubic system is shown. The triplet is split (by 40 meV) into a lower energy doublet and higher energy singlet. At the critical point $s_{cr}^{soc} = 1.019$ (it is slightly reduced by SOC) the (formerly) valence band singlet has crossed the two-fold level and become degenerate with the conduction singlet, giving rise to a Dirac point involving the two upper bands which are now separated from the doublet. **Thus the Dirac band behavior survives the inclusion of SOC. To make topological aspects completely clear, we have studied small tetragonal distortions ($c/a \sim 1.01$) that lift the last degeneracy at Γ (which pins the Fermi level in Fig. 3). This symmetry breaking opens a gap, and we have verified using the criterion of Fu and Kane[17] that s_{cr} indeed separates a trivial insulator from a topological insulator.**

Summary. We have established that the trivial insulator to topological zero-gap semiconductor occurs simultaneously with the appearance of a Dirac point at k=0, which is degenerate with conventional (massive) bands at the critical point. The appearance of the Dirac point at k=0 is clarified using a tight-binding model, being due to the tuning of a degeneracy of site energies of the orbitals that are involved. A small uniaxial strain, externally applied or resulting from epitaxial growth on a substrate with some lattice match, is required to lift the cubic-lattice degeneracy and produce the topological insulating state.

It is worthwhile to note that this "robust" topological state is delicate with respect to the Sb sublattice position: the transition occurs discontinuously at $s = s_{cr}$ upon continuous, symmetry-preserving change of the Sb coordinate. Such a situation will allow probing into just which (bulk or surface) properties are associated with the topological nature of the bulk electronic state. Of course, there are many properties that change discontinuously at an insulator-to-metal transition, so effects of topologicality will require more detailed study.

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