Unique Dirac and Triple point fermiology in transition metals and their binary alloys

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In this letter, we show the existence of Dirac like excitations in the elemental noble metal Ru, Re and Os based on symmetry analysis, first principle calculations and angle resolved photoemission (ARPES) experiment. This is the first report where unique Dirac surface states driven Fermi arcs are identified in Ru by ab-initio calculations, which are further confirmed by ARPES. We attribute these Dirac excitation mediated Fermi arc topology to be the possible reasons behind several existing transport anomalies, such as large non-saturating magneto resistance, anomalous Nernst electromotive force and its giant oscillations, magnetic breakdown etc. We further show that the Dirac like excitations in these elemental metal can further be tuned to three component Fermionic excitations, using symmetry allowed alloy mechanism for the binary alloys such as RuOs, ReOs and RuRe.

Symmetry protected multifold band crossings in momentum space often exhibit strong topological response in the transport measurement. A four-fold Dirac node[1] splits into a pair of two-fold Weyl node[2] under magnetic field, which in turn shows several anomalous transport signatures; such as anomalous Hall effect (AHE)[3][4] anomalous Nernst effect (ANE)[5][6] non-saturating large magneto-resistance (LMR)[7][8][9] chiral anomaly[10] etc. A pair of opposite monopole charges are created upon the separation of Weyl nodes under either inversion or time reversal symmetry (TRS) breaking conditions. Each of the Weyl nodes are associated with the source or sink of the Berry curvature in momentum space[11][12]. While this fictitious magnetic field like Berry curvature couples to the external magnetic field, it gives rise to such anomalous response in materials. Several Dirac and Weyl semi-metals (DSM and WSM) have been proposed and their topological signatures have been extensively investigated through photoemission and transport measurements[13][14][15][16]. Another type of quasi-particle excitation, different from DSM and WSM is triple point semi-metal (TPSM) states[17][18]. TPSM is believed to be an intermediate phase of relatively higher symmetric DSM and lower symmetric WSM. The topological index for TPSM is still a matter of debate[17][18] and lower symmetric WSM. The topological index for intermediate phase of relatively higher symmetric DSM metal (TPSM) states[17][18].

One of the main motivation to choose these systems is to understand the rich physics behind the various anomalous existing experimental results such as anomalous magneto transport effect[19] anomalous Nernst emf (and their giant quantum oscillation)[20] etc. Close inspection of these experimental results made us speculate the topological origin of the electronic structure of these systems to be responsible for such anomaly. Indeed, our detailed calculations confirmed by ARPES experiments and group theoretical analysis unambiguously indicate the existence of symmetry protected multiple Dirac Fermionic excitations near the Fermi level (E_F).

We choose Ru as a case study and investigate both the bulk and surface band topology in details. Our calculated surface states (SSs) and Fermi surfaces (FS) for Ru matches excellently well with our experimental results.

Ru has been extensively studied for its unusual magneto-transport properties under the so called neckless magnetic breakdown[21][22]. For instance, it shows non-saturating LMR in perpendicular magnetic field[23] which is somewhat similar to these in topological semi-metals. Several theories have been proposed to address the origin of such LMR. They are—(i) linear band crossing[24][25] in momentum space as in the case of Cd3As2, Na3Bi and so on, (ii) perfect electron-hole (e-h) compensation[26][27] in WSMs; WTe2, MoTe2, PtSn4 and LaSb (although LaSb has trivial band ordering, multiple Weyl type nodes are present in its band dispersion)[26], and (iii) Lifshitz transition (LT) of Fermi surface (FS) (recently, LT has been found in several topological materials where the phase transition does not break any symmetries but can be described by topological invariants). Apart from aforementioned theories, a topology driven non-trivial origin for the non-saturating LMR has also been predicted by Tafti et al[28]. Another interesting feature of Ru is that it shows finite Nernst emf which shows giant oscillation in high filed regime[29]. The characteristic curve and the oscillation patterns are quite similar to the non-trivial material Bi2Se3 and very different from the Drude like behavior[30][31].

In this letter, we have investigated the topological electronic structures of hexagonal noble metals ruthenium (Ru), rhenium (Re) and osmium (Os) based on symmetry analysis, first principle calculations and ARPES measurements (see sec. I & II of Supplementary mate-
Our study reveals the appearance of Dirac surface states (SSs) mediated Fermi arcs on the surface of noble metals (Ru, Re and Os) which is found to be the key origin in understanding the existing problem of transport anomalies. We use the crystalline symmetry breaking argument to tune the DSM phase to TPSM phase using alloy composition. Our study indicates the emergence of new Dirac nodal lines in this class of metals. The presence of Dirac nodal lines in these metals can be understood from the non-trivial Berry phase in topological electronic structure. Shockley SSs have previously been explained from the free electron theory, but recent studies reveal some of these SSs can be understood from the topological consideration, with the knowledge of global properties of symmetry elements, the elements Ru, Re and Os also holds structural inversion. Interplay of inversion symmetry and TRS further ensures Kramer’s double degeneracy throughout the BZ. Hence, two doubly degenerate bands belong to different irreducible representations while crossing each other along C6 rotation axis form a Dirac node and hence the hybridization at the nodal point is prohibited by group orthogonality relations. As such, presence of inversion center provides extra crystalline symmetry protection to the Dirac nodes in addition to C6v symmetry. Therefore, the Dirac nodes are stable against inversion breaking perturbation in the presence of C6v symmetry.

The origin of the surface states (SSs) in noble metals (Au, Ag and Cu etc.) can be traced back to Shockley’s prediction of SSs which appear inside an inverted energy gap due to band crossing. Although, these Shockley SSs have previously been explained from the free electron theory, but recent studies reveal some of these SSs can be understood from the topological consideration, with the knowledge of global properties of electronic structure. Recently, Zak phase driven large surface polarization charge and flat SSs have been understood from the non-trivial Berry phase in topological Dirac nodal line fcc alkaline earth metals; calcium (Ca), strontium (Sr) and ytterbium (Yb). Topological nature of Beryllium (Be) have also been explored, which indeed shed light on the long standing controversial issues of Be, such as strong deviations from the description of the nearly free-electron theory, anomalously large electron-phonon coupling effect, and large Friedel oscillations etc. Hence, a rigorous topological understanding is required to capture various other anomalous surface behaviors.

In the above context, Ru, Re and Os are unique as their Dirac like bulk band crossing suggests the appearance of non-trivial surface dispersion and Fermi arc topological...
FIG. 2. (Color online) For Ruthenium, (a) Calculated surface dispersion for (0001) miller plane. (b-d) Fermi surface maps on (0001) surface at different energy cuts. (e, f) The second derivative images (with respect to the energy axis) of the ARPES intensity of Ru(0001) along \( \bar{K}-\bar{\Gamma}-\bar{K} \) measured at 40K using (e) He I (\( h\nu=21.2 \) eV) and (f) He II (\( h\nu=40.8 \) eV) photon energies. The black dashed lines (arrows) represent the Dirac surface states. The red lines indicate the calculated bulk bands along \( K-\Gamma-K \) direction at \( k_z = 1.7c^* \) in (e) and \( k_z = 2.2c^* \) in (f), where \( c^* = 2\pi/c \). (g, h) Raw ARPES images corresponding to (e) & (f), respectively, where the blue dashed lines represent the calculated Dirac surface state. (i) The constant energy contour of Ru(0001) at -0.7 eV obtained from ARPES. The inner hexagonally warped Fermi contour (red hexagon) represents the Dirac arcs.

An experimental investigation of the electronic band structure of Ru(0001) surface using ARPES supports our theoretical results as shown in Fig. 2(e-i). Figure 2(e, f) show the second derivative ARPES band structure of Ru(0001) surface measured along \( \bar{K}-\bar{\Gamma}-\bar{K} \), while the corresponding raw spectra are shown in Fig. 2(g, h). Figure 2(e), the band with an inverted parabolic shape dispersing from \( \bar{\Gamma} \) at -0.5 eV to \( k_\parallel \approx 0.45 \) Å\(^{-1}\) at -1 eV exhibits an excellent agreement with the theoretically calculated DSS along the \( \bar{\Gamma}-\bar{K} \) direction (indicated by blue dashed line). These are distinct from the bulk bands (shown by red lines). As expected for surface states, this band exhibits similar dispersion with different photon energies that is evident from the comparison of Fig. 2(e & f).

The FS maps on (0001) surface have been simulated and the evolution of FS topology is investigated at three different energy cuts (E1, E2 and E3) as shown in Fig. 2(b-d). At energy cut E1, the Dirac SSs, DSS1 and DSS2 are somewhat immersed by bulk bands near \( \bar{\Gamma} \), hence we do not observe the clear signature of Dirac SSs mediated FS map at this constant energy cut. However, the signatures and contour patterns of DSSs mediated FS maps are clearly observed for other two energy cuts at E2 and E3 as described in Fig. 2(c, d). The two concentric Fermi arcs in Fig. 2(d) are indicated by arc1 and arc2. Furthermore, the DSSs mediated Fermi arc topology can also be observed on the side surface (01 \( \bar{1} \)0 plane) of Ru. These are shown in Fig. S3 of SM. A further experimental confirmation of our theoretically predicted Dirac FS is provided in Fig. 2(i) where the constant energy contour of Ru(0001) at -0.7 eV is shown. A comparison with the E3 cut in Fig. 2(d) shows gratifying agreement: the flower shaped hexagonally warped outer arc and an inner arc that originate due to DSS are clearly visible at similar \( (k_x, k_y) \) values.

We now discuss the origin of these SSs and arcs from the topological perspective. A DSM phase is the parent state of WSM and topological insulator (TI). TI phase can...
be achieved by opening up a non-trivial gap at the nodal points. In such a case, presence of SSs is guaranteed by topological Z$_2$ index. On the other hand, two Weyl nodes with opposite Chern number sit together to form a Dirac node in momentum space under the precise symmetry enforcement. Such degeneracies of Weyl nodes form a "doubly-degenerate" Fermi arc in DSM phase. However, such type of Fermi arcs may not be protected by topological index. Nevertheless, a crystalline symmetry protected three dimensional DSM phase is stable as long as the symmetries are intact.

Further, the alloy driven crystalline symmetry breaking allows us to realize three component Fermionic excitation near $E_F$, which is different from the Dirac excitation in pure metals Ru, Os and Re. For the binary alloys, e.g. RuOs, the point group symmetry reduces from D$_{6h}$ to D$_{3h}$ (space group group P6m2). Here, one Ru (out of two equivalent Ru site) is replaced by a Os in the unit cell. D$_{3h}$ allows it’s C$_{3v}$ subgroup symmetry along $\Gamma$-A direction. The symmetry elements that C$_{3v}$ contain are E, C$_3$ and three $\sigma_v$ (see Fig. S2 of SM). Similar to earlier case of C$_{6v}$ case, the non-commutation relation of $\tilde{C}_3$ and $\sigma_v$ (say, x-axis mirror) allows two singly degenerate states (denoted by $\Gamma_5$ and $\Gamma_6$) and one doubly degenerate state (denoted by $\Gamma_4$) along $\Gamma$-A direction in spin-orbit space. The operation of $C_3$ and $\sigma_v$ does not alter momentum co-ordinate along $k_z$-axis. Any accidental band crossing of $\Gamma_{5or6}$ with $\Gamma_4$ along $k_z$-axis forms a tripoly degenerate nodal point (TDNP). In particular, such an alloying, transforms the crystalline symmetry from C$_{6v}$ (elemental metal) to C$_{3v}$ and the corresponding band representation changes as; $\Gamma_{8,7} \rightarrow \Gamma_4$ and $\Gamma_9 \rightarrow \Gamma_5 \oplus \Gamma_6$. Further, the strength of $\Gamma_{5,6}$ band splitting and the slope of the $\Gamma_4$ band collectively determine the number of TDNP (two or four in our binary alloys) on the C$_3$ rotation axis. Figure 3(a) shows a case study of the bulk band structure of RuOs alloy along $\Gamma$-A direction. The band structure in full BZ of RuOs is shown in Fig. S4 of SM. Four triple points are observed along $\Gamma$-A in RuOs alloy and they are denoted by T1, T2, T3 and T4 in Fig. 3(a). Note that, TDNPs are protected by group orthogonality relations of different IRs. We have also simulated the Fermi arcs nesting on (0110) rectangular surface of RuOs alloy, which host triple point semimetallic state (see Fig. 3(b)). All the TDNPs are projected along the $\Gamma - Z$ axis on both sides of $\Gamma$ point. The Fermi arcs are originated and nested between the TDNPs as shown in Fig. 3(b). The existence of such TDNP induced Fermi arcs on a particular surface is a hallmark of TPSM state for their experimental detection.

To get the ideal candidates (in terms of the position of Dirac points (DPs) and TDNPs with respect to $E_F$), we have calculated the band structure of other metals (Os and Re) and their alloys (ReRu and ReOs). The band structures along the six (three) fold rotation axis are shown in Fig. 4. In Table I we have also listed the compounds with the number of nodal points and their relative position in terms of energy. The spin-orbit coupling strength of Os is highest among these three pure metals, hence the splitting between $\Gamma_7$ and $\Gamma_9$ is largest which in turn results in a larger separation of DPs for Os in momentum space as shown in Fig. 4(b). For ReOs alloy, the nodal points (TDNPs) lie close to $E_F$ as compared to other two alloys, ReRu and RuOs. Furthermore, ReOs only has a single pair of TDNPs, as shown in Fig. 4(d).

![Figure 3](image1.png)

**FIG. 3.** (Color online) For RuOs binary alloy, (a) bulk band structure along $\Gamma$-A indicating band IRs (shown by $\Gamma_i$). Triply degenerate nodal points TDNPs (shown by T’s). (b) Fermi arc on (0110) side surface at -0.5 eV binding energy.

![Figure 4](image2.png)

**FIG. 4.** (Color online) Electronic structure (along $\Gamma$-A) for (a) Re, (b) Os, (c) ReRu, and (d) ReOs. Dirac points and TDNPs are represented by DP’s and T’s respectively.

| Metal | DPs # | $\Delta \epsilon$ (eV) | Alloy | TP’s # | $\Delta \epsilon$ (eV) |
|-------|-------|------------------------|-------|--------|------------------------|
| Ru    | 2     | -0.45                  | RuOs  | 4      | 0.60                   |
|       |       |                        |       |        | -0.29                  |
|       |       |                        |       |        | -0.47                  |
|       |       |                        |       |        | -0.57                  |
| Os    | 2     | -0.50                  | ReOs  | 2      | 0.17                   |
|       |       |                        |       |        | 0.09                   |
| Re    | 2     | 0.41                   | RuRe  | 4      | 0.94                   |
|       |       |                        |       |        | 0.23                   |
|       |       |                        |       |        | 0.06                   |
|       |       |                        |       |        | -0.35                  |

**TABLE I.** Number (#) of DPs or TDNPs and their positions ($\Delta \epsilon$) with respect to $E_F$ for pure metals and their binary alloy.

The conclusions of this work are three fold: (i) we predict the existence of symmetry protected Dirac sates.
in pure elemental metals Ru, Os and Re. We find the unique Dirac like Fermi arc topology on the (0001) and (0110) surfaces of these metals. Our calculated SSs and Fermi arcs for Ru are in excellent agreement with our ARPES results. (ii) The presence of such topological character confirmed from both theory and experiments can provide deeper understand of the several anomalous properties of these metals reported in literature such as as magnetic break down, large mageto-resistance similar to DSM compound Cd₃As₂, and giant Nernst oscillation (similar to Bi₂Se₃). (iii) By precise symmetry breaking through intermixing of these transition metals, the Dirac excitations can be tuned to three component fermion excitations. Depending on the combinations, we get two or four triply degenerate nodal points (TDNPs) along Γ-A directions. The positions of TDNPs are closer to E_F for RuRe and ReOs, which should definitely enable strong topological response in transport experiments.

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