Supplemental Materials for:

"Six- or four-fold band degenerations in CoAs$_3$, RhAs$_3$ and RhSb$_3$ topological semimetals"

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1. Orbital-projected band structures for CoAs₃, RhAs₃, and RhSb₃ compounds

To provide further insight into the electronic properties of CoAs₃, RhAs₃, and RhSb₃ compounds, we have also calculated the orbital-projected band structures for these compounds, as shown in Fig. S1. In this case, we focus on the *d*-orbitals of metal atoms and the *p*-orbitals of pnictgon atoms. It can be inferred that the band around the six-fold degenerate point is mainly contributed by the *d*-orbitals of metal atoms with A_g symmetry, which is important information for deducing the EBRs of these compounds.
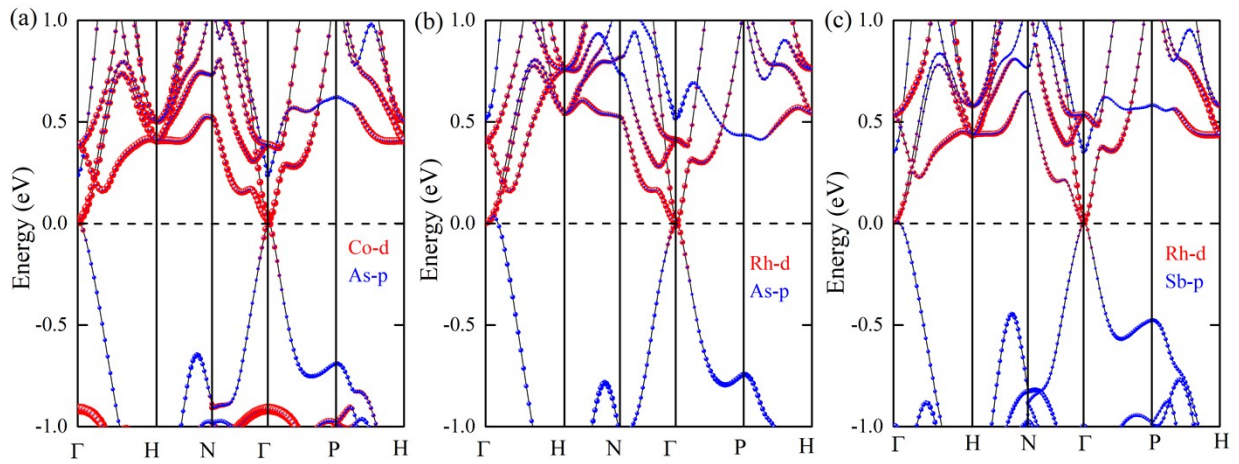

Figure S1: Orbital-projected band structures for CoAs₃ (a), RhAs₃ (b), and RhSb₃ (c) compounds. Red and blue colors correspond to the *d*-orbital of the Metals atoms and *p* orbital of pnictgon atoms, respectively.

2. Tight-binding band structures for CoAs₃, RhAs₃, and RhSb₃ compounds

In order to further explore the topological electronic properties of CoAs₃, RhAs₃, and RhSb₃ compounds, we have constructed tight-binding (TB) models [1, 2] based on the *d*-orbitals of metal atoms and *p*-orbitals of pnictgon atoms with MLWF method. We have plotted the TB band structures as shown in Fig. S2. The TB band structures match well with the DFT band structures shown in the main text, thus confirming the validity of our constructed TB models.
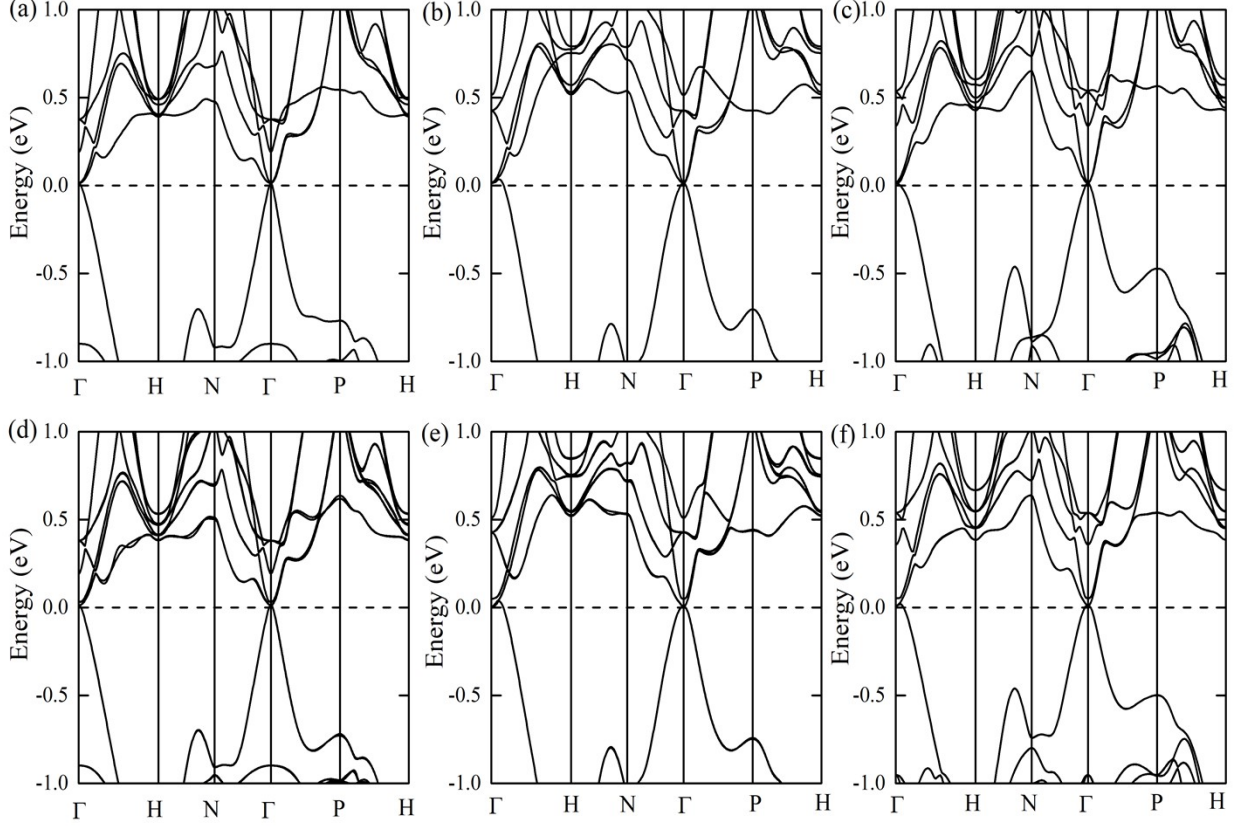
Figure S2: (a-c) Calculated TB band structures for CoAs$_3$ (a), RhAs$_3$ (b), and RhSb$_3$ (c) without SOC. (d-f) Calculated TB band structures for CoAs$_3$ (d), RhAs$_3$ (e), and RhSb$_3$ (f) with SOC.

3. Three-band $k \cdot p$ model for the case without SOC

In order to better understand the electronic properties of these binary Skutterudite compounds, we build up a three-band $k \cdot p$ models based on the theory of invariant:

$$D(R)H(k)D(R)^{-1} = H(Rk) \tag{S1}$$

where R is the symmetry operation and $D(R)$ is its corresponding irreducible representation. Here we focus on the bands around the Γ point, inversion symmetry (P), time-reversal symmetry (T), two-fold rotational symmetry (C_{2i}, $i = x, y, z$), and mirror symmetry (M_i, $i = x, y, z$), these symmetry operations read as the following:

$$T: \left(k_x, k_y, k_z\right) \rightarrow \left(-k_x, -k_y, -k_z\right),$$

$$P: (x, y, z) \rightarrow (-x, -y, -z), \tag{S2}$$

$$C_{2x}: (x, y, z) \rightarrow (x, -y, -z),$$

$$C_{2y}:(x,\ y,\ z)\to(-x,\ y,\ -z),$$

$$C_{2z}:(x,\ y,\ z)\to(-x,\ -y,\ z),$$

$$M_x:(x,\ y,\ z)\to(-x,\ y,\ z),$$

$$M_y:(x,\ y,\ z)\to(x,\ -y,\ z),$$

$$M_z:(x,\ y,\ z)\to(x,\ y,\ -z).$$

Then since irreps for the three bands is $\Gamma_4^+(3)$ we have the following representation matrices for these symmetry operators:

$$\mathcal{D}(T) = K,$$

$$\mathcal{D}(P) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathcal{D}(C_{2x}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$\mathcal{D}(C_{2y}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathcal{D}(C_{2z}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$ (S3)

$$\mathcal{D}(M_x) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$\mathcal{D}(M_y) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$(M_z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

Combining these symmetry operations and expand the Hamiltonian up to the second-order, we can have the following three-band $k \cdot p$ Hamiltonian:

$$H(k) = c_0 + c_1\left(k_x^2 + k_y^2 + k_z^2\right) + c_2 \begin{pmatrix} 0 & k_x k_z & k_y k_z \\ k_x k_z & 0 & k_x k_y \\ k_y k_z & k_x k_y & 0 \end{pmatrix},$$ (S4)

which can be expressed with a 3×3 unit matrix and three Gell-Mann matrices:

$$H(k) = c_0 + c_1\left(k_x^2 + k_y^2 + k_z^2\right)I_{3\times 3}$$
$$+ c_2 k_x k_z \lambda_1 + c_2 k_y k_z \lambda_4 + c_2 k_y k_x \lambda_6, \tag{S5}$$

Where λ_1, λ_4 and λ_6 are :

$$\lambda_1 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\lambda_4 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \tag{S6}$$

$$\lambda_6 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

Solving the eigenvalues of the Hamiltonian, we can know that when the three bands have a cross, there should be:

$$\left[E - c_0 - c_1\left(k_x^2 + k_y^2 + k_z^2\right)\right]\left(k_x^2 k_z^2 + k_y^2 k_z^2 + k_y^2 k_x^2\right) + 2k_x^2 k_y^2 k_z^2 =$$
$$\left[E - c_0 - c_1\left(k_x^2 + k_y^2 + k_z^2\right)\right]^3, \tag{S7}$$

obviously when k_x, k_y, $k_z = 0$, the three bands cross at $E = c_0$. Since we focus only on the energy bands around the Γ point, the $k_x^2 k_y^2 k_z^2$ term may be dropped, then the approximate eigenvalues of the three-band model may be written as:

$$E_1 = c_0 + \sqrt{\left(k_x^2 + k_y^2 + k_y^2\right)}$$
$$E_2 = c_0 + \sqrt{\left(k_x^2 + k_y^2 + k_y^2\right)} + \sqrt{\left(k_x^2 k_z^2 + k_y^2 k_z^2 + k_y^2 k_x^2\right)} \tag{S8}$$
$$E_3 = c_0 + \sqrt{\left(k_x^2 + k_y^2 + k_y^2\right)} - \sqrt{\left(k_x^2 k_z^2 + k_y^2 k_z^2 + k_y^2 k_x^2\right)},$$

Since the diagonal terms do not change the eigenvectors of the Hamiltonian, we can linearize the Hamiltonian as:

$$H(k) = c_2\left(k_x k_z \lambda_1 + k_y k_z \lambda_4 + k_y k_x \lambda_6\right). \tag{S9}$$

One can choose a sphere enclosing the $kk = 0$ point and the topological charge C is calculated as:

$$C = \frac{1}{2\pi}\oint_S \Omega(k) \cdot dS =$$
$$\frac{1}{2\pi}\Sigma_{occ}\oint_S i\langle u_{occ}(k)|\frac{\partial}{\partial k}|u_{occ}(k)\rangle \tag{S10}$$
$$= 0,$$

$\Omega(k)$ is the Berry curvature and $u_{occ}(k)$ is the wave function for the occupied states

4. Four-band $k \cdot p$ model for the case with SOC

In order to better understand the electronic properties with SOC, we need a four-band $k \cdot p$

model. In this SOC case, we still focus on the bands around the Γ point, considering the system has P, T, M_i and $(C_{2i}, i = x,\ y,\ z)$ symmetries, and in the SOC case, the irreps for the four-bands around the Γ point are $\Gamma_6(2)$ and $\Gamma_7(2)$, which means the basis are decoupled, then for simplicity, we focus firstly on the two-bands with $\Gamma_6(2)$ irrep, then we have the following representation matrices for the symmetry operators:

$$\mathcal{D}(T) = i\sigma_y K,$$

$$\mathcal{D}(P) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

$$\mathcal{D}(C_{2x}) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = -i\sigma_x,$$

$$\mathcal{D}(C_{2y}) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = -i\sigma_y,$$

$$\mathcal{D}(C_{2z}) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = -i\sigma_z,$$ (S11)

$$\mathcal{D}(M_x) = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} = -i\sigma_x,$$

$$\mathcal{D}(M_y) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = -i\sigma_y,$$

$$\mathcal{D}(M_z) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = -i\sigma_z.$$

Combining these symmetry constraints and expand the Hamiltonian up to the second-order, we have the following $k \cdot p$ model:

$$H_{dn}(k) = d_o + d_1\left(k_x^2 + k_y^2 + k_z^2\right) + d_2(k_y k_z \sigma_x + k_x k_z \sigma_y + k_x k_y \sigma_z),$$ (S12)

The $\Gamma_7(2)$ representation matrices are listed as the following:

$$\mathcal{D}(T) = i\sigma_y K,$$

$$\mathcal{D}(P) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\mathcal{D}(C_{2x}) = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} = i\sigma_x,$$ (S13)

$$\mathcal{D}(C_{2y}) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = i\sigma_y,$$

$$\mathcal{D}(C_{2z}) = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = i\sigma_z,$$

$$\mathcal{D}(M_x) = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} = i\sigma_{x'}$$

$$\mathcal{D}(M_y) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = i\sigma_{y'}$$

$$\mathcal{D}(M_z) = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = i\sigma_{z'}$$

Then since the $\Gamma_7(2)$ representation matrices take the same form as in Eq. S10, but just with opposite values, then we can easily solve the $H_{up}(k)$ and couple them together as:

$$H(k) = \begin{pmatrix} H_{up}(k) & 0 \\ 0 & H_{dn}(k) \end{pmatrix} = \begin{pmatrix} -H_{up}(k) & 0 \\ 0 & -H_{dn}(k) \end{pmatrix}$$

$$= \left[d_o + d_1\left(k_x^2 + k_y^2 + k_z^2\right) + d_2(k_y k_z \sigma_x + k_x k_z \sigma_y + k_x k_y \sigma_z) \right] \tau_z, \tag{S14}$$

the eigenvalues show that:

$$E = \pm \left[d_o + d_1\left(k_x^2 + k_y^2 + k_z^2\right) \right] \pm d_2\sqrt{\left(k_x^2 k_z^2 + k_y^2 k_z^2 + k_y^2 k_x^2\right)}, \tag{S15}$$

which gives us a quadratic four-fold Dirac point when $d_o = 0$. Again since the diagonal terms have no influence on the eigenvectors, the model Hamiltonian can be reduced as:

$$H(k) = (k_y k_z \sigma_x + k_x k_z \sigma_y + k_x k_y \sigma_z)\tau_z. \tag{S16}$$

Then we turn to the discussion of the topological charge; for simplicity, we still focus on the two down bands and take them as the occupied states, one can easily calculate the topological charge as

$$C = \frac{1}{2\pi}\oint_s \Omega(k) \cdot dS =$$

$$\frac{1}{2\pi}\Sigma_{occ}\oint_s i\langle u_{occ}(k)|\frac{\partial}{\partial k}|u_{occ}(k)\rangle = 0. \tag{S17}$$

The above results show that the topological charge is conserved as 0 for both cases without or with SOC.

References

1 A. A. Mostofi, J. R. Yates, Y. S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comput. Phys. Commun.*, 2008, **178**, 685.
2 N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys., 2012, **84**, 1419.