Degenerate $p$ orbitals flat band model and realization in two-dimensional materials

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We propose a flat band model based on degenerate $p$ orbitals at the centers of octahedrons which are closely-packed in a two-dimensional structure. Our theoretical analysis and first-principles calculations show that the proposed flat band can be realized in 1T layered materials of alkali-metal chalogenides and metal-carbon group compounds. Some of the former are theoretically predicted to be stable as layered materials here (e.g. K$_2$S), and some of the latter have been experimentally fabricated in previous works (e.g. Gd$_2$CCl$_4$). More interestingly, our calculations show that the Gd$_2$CCl$_2$ monolayer prefers ferromagnetic order and harbors a spin polarized nearly flat band. Our theoretical model together with the material predictions provide a realistic platform for the realization of flat bands and related exotic quantum phases.

The properties including the electronic bands of a material are codetermined by its structure and the component elements of which the outer-shell electrons usually matter most [1]. In the band theory regime, there are two limiting cases: the massless Dirac fermion in linear dispersion band [2,3] and infinitely heavy fermion in flat band [5,6]. Both of them harbor unique and fantastic properties. The Dirac fermion has been experimentally realized in a graphene monolayer [3,4]. For the flat band, the density of states is impressive and well-isolated from other orbitals [15–22]. Yet to date, definitive experimental demonstrations of electronic flat bands in realistic materials are still lacking. It is still challenging to realize the previous theoretical proposals.

In this Letter, we propose a more realistic flat band model based on the degenerate $p$ orbitals when they sit at the centers of octahedrons which are closely-packed to form a 2D structure. Our theoretical analysis and first-principles calculations show that the proposed flat bands can be realized in 1T layered materials of alkali-metal chalogenides and metal-carbon group compounds. The calculated flat bands of these materials can be well-described by our theoretical model with physically meaningful parameters. Some of the former materials are theoretically predicted to be stable in layered structure here (e.g. K$_2$S), while some of the latter have been experimentally fabricated in previous works (e.g. Gd$_2$CCl$_4$) [25,27]. More interestingly, our calculations show that the Gd$_2$CCl$_2$ monolayer prefers ferromagnetic order and harbors a spin polarized nearly flat band. Our theoretical model together with the material predictions provide a realistic platform for the realization of flat band and related exotic quantum phases.

We first discuss the tight-binding (TB) model and its

![FIG. 1](color online). The structure and hoppings between $p$ orbitals in a 1T monolayer. (a) An octahedron formed by six cations with an anion at the center. The $p_{1,2,3}$ orbitals on the anion are represented by red, green, and blue arrows, respectively. (b) Schematic diagram of the effective crystal field $E$. The black rhombus represents one unitcell and black arrows are the lattice vectors $\vec{a}_{1,2,3}$. (c) Schematic diagrams of the hoppings between $p$ orbitals along $\vec{a}_1$ direction.
single-particle spectrum. In a 1T (tetragonal symmetry, octahedral coordination) layered structure, the octahedrons are closely-packed in 2D planes by sharing edges and corners, as shown in Fig. 1. We define the 2D plane formed by the centers of octahedrons as xy-plane. Three lattice vectors in the xy-plane are defined as \( \vec{a}_1 = \frac{\sqrt{3}}{2} a \hat{e}_x - \frac{1}{2} a \hat{e}_y \), \( \vec{a}_2 = a \hat{e}_y \), and \( \vec{a}_3 = -\vec{a}_2 - \vec{a}_1 \), where \( a \) is the lattice constant and \( \hat{e}_{x,y} \) are the unit vectors of the two orthogonal axes. When an anion locates at the center of an octahedron structure, its three \( p \) orbitals are energetically degenerate, as shown in Fig. 1(a). For convenience, we label \( p_{x,y,z} \) as \( p_{1,2,3} \) and align their polarization direction to the three diagonals of the regular octahedron. Cations locate at the corners of octahedrons to make the system electronically neutral. Here, lattice constant \( a \) is also the distance between nearest anions. The TB Hamiltonian \( H = H_0 + H' \) reads

\[
H_0 = t_0 \sum_{\vec{r},i,j,k} \{ p_{\vec{r},i}^{\dagger} p_{\vec{r}+\vec{a}_i,j} \epsilon_{ijk} | h.c. \};
\]

\[
H' = t_1 \sum_{\vec{r},i} \{ p_{\vec{r},i}^{\dagger} p_{\vec{r}+\vec{a}_i,i} + h.c. \}
+ t_2 \sum_{\vec{r},i,j} \{ p_{\vec{r},i}^{\dagger} p_{\vec{r}+\vec{a}_{i,j},i} (1 - \delta_{i,j}) + h.c. \}
+ t_3 \sum_{\vec{r},i,j} \{ p_{\vec{r},i}^{\dagger} p_{\vec{r}+\vec{a}_{i,j},i} + p_{\vec{r},i}^{\dagger} p_{\vec{r}+\vec{a}_{i,j},j} \} (1 - \delta_{i,j}) + h.c. \}
+ E \sum_{\vec{r},i,j} \{ p_{\vec{r},i}^{\dagger} p_{\vec{r},j} \} (1 - \delta_{i,j}).
\]

where \( i,j,k = 1-3 \); \( \vec{r} \) runs the locations of all anions in the xy-plane; \( t_0 \) describes the hopping between \( p \) orbitals on neighboring anions when their polarization directions cross at one corner of the octahedron, namely a cation; \( t_1 \) (\( t_2 \)) describes the neighboring hopping between the same \( p \) orbitals when they are (not) perpendicular to the connection direction \( \vec{a}_i \); \( t_3 \) is the hopping between different \( p \) orbitals when only one of them is perpendicular to the connection direction \( \vec{a}_i \). \( E \) describes the crystal field when the octahedrons are arranged in the 2D plane and the effect of structure adjustment. \( t_0 \) is negative due to the odd parity of the \( p \) orbitals and atomic potential of cations. The schematic diagrams of the crystal field \( E \) and hoppings along \( \vec{a}_i \) direction are shown in Fig. 1(b) and 1(c). The Hermitian conjugate (\( h.c. \)) describes the hoppings along \( -\vec{a}_i \) directions. Due to the existence of cations at the corners of octahedrons, the amplitude of \( t_0 \) is usually larger than \( t_1, t_2, t_3 \), and \( E \).

It is of practically guiding significance to consider a limiting case when only \( t_0 \) has nonzero value with \( t_1 = t_2 = t_3 = E = 0 \) and \( H = H_0 \). In momentum space, we define the three component basis as

\[
\psi(\vec{k}) = [p_1(\vec{k}), p_2(\vec{k}), p_3(\vec{k})]^T.
\]
(K$_2$S) monolayer and digadolinium monocarbide dichloride (Gd$_2$CCl$_2$) monolayer as two examples.

Our density functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP) [29], where the projector augmented plane wave (PAW) method [30, 31] is adopted, and the generalized gradient approximation (GGA) in the framework of Perdew-Burke-Ernzerhof (PBE) [32] is chosen for the exchange-correlation interaction. A specific semi-empirical scheme (DFT-D2) [33] is used to treat the van der Waals (vdW) type interaction. Phonon spectrum are obtained using the PHONOPY code [34].

Table I lists the comparisons of total energies of alkali-metal chalogenides in different structures. The energy difference $E_{\text{layered}} - E_{\text{cubic}}$ describes the relative structural stability of the 1T layered bulk materials to the cubic antifluorite structure. $E_{1T} - E_{\text{layered}}$ is the excitation energy of a 1T monolayer from its layered bulk. The energy difference $E_{2H} - E_{1T}$ is the relative structural stability of a 1T monolayer to its 2H (hexagonal symmetry, trigonal prismatic coordination) counterpart.

|       | Unit (eV) | O | S | Se | Se |
|-------|-----------|---|---|----|----|
| K     | $E_{\text{layered}} - E_{\text{cubic}}$ | 0.58 | 0.50 | 0.47 | 0.43 |
|       | $E_{1T} - E_{\text{layered}}$ | 0.01 | 0.18 | 0.22 | 0.27 |
|       | $E_{2H} - E_{1T}$ | 0.51 | 0.45 | 0.42 | 0.37 |
| Rb    | $E_{\text{layered}} - E_{\text{cubic}}$ | 0.41 | 0.44 | 0.40 | 0.33 |
|       | $E_{1T} - E_{\text{layered}}$ | 0.09 | 0.30 | 0.34 | 0.42 |
|       | $E_{2H} - E_{1T}$ | 0.43 | 0.39 | 0.37 | 0.33 |

Our DFT calculations predict that K$_2$S can be stabilized in the 1T phase as a monolayered material, which can be confined by the nonnegative phonon spectrum shown in Fig. 3(c). The structure refers to Fig. 1. One S atom sites at the center of an octahedron formed by K atoms. Due to the large difference in electronegativity between alkali metals and chalcogens, the 4s electron of K atom transfers to 3p orbital of S atom. The highest six valence bands with spin degeneracy included are totally contributed from the nearly flat band at Γ point. The right panel in (b) is the orbital projected DOS. The black solid curve is the total DOS and the red is contributions from the p orbitals of S atoms (S-p). (c) Phonon spectrum of a 1T K$_2$S monolayer.

![Figure 3](Link to the figure)[3]

**FIG. 3** (color online). Electronic and phonon bands of a 1T K$_2$S monolayer. Electronic bands (a) without SOC; (b) with SOC. Filled dots and solid curves represent the data from DFT calculations and TB fittings, respectively. The fitting parameters are: $t_0 = -83$, $t_1 = -19$, $t_2 = 0.13$, $t_3 = 5$, $E = 20$ meV. In (b), $\lambda = 20$ meV describes the SOC effect. Fermi level is set to be zero. The highest valence bands are nearly flat with bandwidth of 59 meV in (a) and 55 meV in (b), respectively. $\Delta_{\text{SOC}} = 53$ meV in (b) is the direct gap between the nearly flat band and dispersive band at Γ point. The right panel in (b) is the orbital projected DOS. The black solid curve is the total DOS and the red is contributions from the p orbitals of S atoms (S-p).
gap opens when the SOC is taken into consideration. A direct band gap $\Delta_{\text{SOC}}$ at $\Gamma$ point is about 53 meV, as shown in Fig. 3(c). The SOC also affects the dispersion of the bands. The bandwidth of the nearly flat band slightly decreases from 59 to 55 meV.

As another large family of materials, compounds of metal and carbon group elements can also adopt the 1T layered structure, some of which have been fabricated in experiments [24]. It provides more realistic platforms for the study of flat band. A 1T Gd$_2$CCl$_2$ monolayer is a typical example. Figure 4(a) shows the structure of a 1T Gd$_2$CCl$_2$ monolayer. In the 1T phase, one C atom sites at the inversion symmetry point of an octahedron formed by six Gd atoms, which is a constitutional unit of the 1T layered structure. On each side a 1T structure, there is one layer of Cl anions. The $p$ orbitals of C and Cl anions are full-filled via the electron transfer from Gd atoms, with the C’s 2$p$ orbitals at the highest valence bands. The 4$f$ orbitals of Gd cations are half-filled. Based on our DFT calculations, the half-filled 4$f$ orbitals of Gd prefers a ferromagnetic order. The spin polarized band can be described by adding a Zeeman term $M = \sigma_{3}M$ into the Hamiltonian, where $M$ describes the effective Zeeman field [15].

Figures 4(b) and 4(c) show the spin polarized band structures. The ferromagnetic order of half-filled 4$f$ orbitals of Gd cations has effects on the full-filled 2$p$ orbitals of C anions making the highest valence bands spin polarized. The effective Zeeman field $M$ is around 40 meV. The fitting parameters are listed in the caption. The highest three valence bands with spin up can be well-fitted by our TB model, as shown in Fig. 4(b). Similar to the case of K$_2$S, the highest valence band of the spin up electron in Gd$_2$CCl$_2$ is very flat with a bandwidth of 197 meV. From the orbital projected DOS, it is clear that the three highest valence bands are mainly contributed from the $p$ orbitals of C anions.

Figure 4(c) shows the band structure of spin down electrons. The trends of the three highest valence bands can be captured by our TB model. For the spin down $p$ orbitals, $t_1$ and $t_2$ is comparable to $t_0$. All the bands are relatively more dispersive than the spin up case. The highest valence band is partially flat along the path $\Gamma$-M. As shown in the orbital projected DOS in Fig. 4(c), the lowest conduction bands mainly contributed from the $f$ electrons of Gd, which is energetically close to the valence bands. The hybridization of C’s $p$ orbitals and Gd’s $f$ orbitals makes the valence bands slightly deviate from the $p$ orbital based TB model.

Here we emphasize the significance and novelty of our flat band model, its materials realization, and related properties. Unlike the challenging in experimental realization of previous models via designing an isolated isotropic orbital on special lattices (e.g. kagome lattice [5, 15, 24, 25], dice lattice [21], and Lieb lattice [20]), the degenerate $p$ orbitals flat band model predicted here can be easily realized. Beyond the two classes of materials predicted above, a lot of 1T layered materials may also have nearly flat band. Compared with the nearly flat band in graphene systems with moiré superlattices [35-37], the DOS around the flat band in the systems predicted here should be much larger making them more intriguing for the study of flat band physics. As the nearly flat band locates at the highest valence band in the K$_2$S systems, the emergence of magnetic properties can be expected under hole doping. It is worth noting that the Gd$_2$CCl$_2$ monolayer intrinsically prefers ferromagnetic order. It may exhibit spin polarized half-metallicity under hole doping [35-37]. The spin polarized flat band may benefit the equal-spin pairing and $p$-wave superconductivity [11, 12].

In summary, a new TB model with (nearly) flat bands is proposed based on the degenerate $p$ orbitals in 2D materials. Our theoretical analysis and first-principles calculations show that the proposed flat band can be realized in 1T layered materials of alkali-metal chalogenides and metal-carbon group compounds. The calculated flat bands of these materials can be well-described by our theoretical model with physically meaningful parameters. To be specific, we present 1T K$_2$S and Gd$_2$CCl$_2$ monolayers as two examples. The K$_2$S monolayer is theoretically predicted to be stable here and the Gd$_2$CCl$_2$ layered material has been experimentally fabricated [25]. More
interestingly, our calculations show that the Gd\(_2\)CCl\(_2\) monolayer prefers ferromagnetic order and harbors a spin polarized nearly flat band. Our theoretical model together with the material predictions provide a realistic platform for the realization of flat band and related exotic quantum phases.

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