Importance of the van Hove singularity in superconducting PdTe$_2$

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We have investigated the electronic, phononic, and superconducting properties of the transition-metal dichalcogenide superconductor PdTe$_2$, and explored the origin of different superconducting behaviors between PdTe$_2$ and its isostructural PtTe$_2$ that is nonsuperconducting. We have found that the saddle-point van Hove singularity (vHs) near the Fermi level, which interacts strongly with Te phonon modes, plays an important role in the BCS-type superconductivity of PdTe$_2$. We show that, with electron doping, the vHs in PdTe$_2$ shifts down toward the Fermi level to enhance $T_c$, as is consistent with the observed enhancement of $T_c$ in Cu-doped PdTe$_2$. We ascribe the absence of superconductivity in PtTe$_2$ to the different dispersion behavior of the saddle-point vHs band from that of PdTe$_2$. We also suggest that this difference in the vHs band behaviors is responsible for the different structural responses of PdTe$_2$ and PtTe$_2$ to external pressure.

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I. INTRODUCTION

Layered transition-metal dichalcogenide (TMD) systems have been studied extensively in many fields since the work of Wilson and Yoffe [1,2]. The two dimensionality of TMD material is of particular importance to bring about a variety of interesting physical properties, such as superconductivity, charge density wave (CDW), quantum criticality, and so on [3–5]. The simple structure of TMD, mainly composed of layers connected by a weak van der Waals interaction, makes the TMD a suitable platform for two-dimensional (2D) quantum materials. Namely, the TMD reveals the unique features of a 2D system, such as the simple structural variation by intercalation and possible exfoliation, which facilitates its fabrication for practical applications. In fact, a group of TMDs, such as MoS$_2$, WTe$_2$, and MoTe$_2$, has been intensively studied for spintronic materials, superconductors, and topological materials.

Recently, the topological surface state in PdTe$_2$ that is a CdI$_2$-type TMD was identified by using angle-resolved photoemission spectroscopy [6]. Furthermore, PdTe$_2$ and its isostructural materials [see Fig. 1(a)] were found to be type-II Dirac materials [7–11]. PdTe$_2$ exhibits superconductivity with $T_c \sim 1.78$ K [12], and so it is naturally anticipated that PdTe$_2$ would be a good candidate for a topological superconductor. Also, it was experimentally observed that Cu doping could enhance the $T_c$ of PdTe$_2$ [13]. Intriguingly, its isostructural TMD, PtTe$_2$, is not a superconductor. The superconducting properties of PdTe$_2$, however, are rarely studied. It has been once proposed that a softened $\Gamma$ phonon interacting with electrons in a tubelike Fermi surface (FS) is responsible for the superconductivity in PdTe$_2$ [14].

In this paper, we have investigated the electronic, phononic, and superconducting properties of PdTe$_2$, and compared its properties with those of PtTe$_2$ [9,14–24]. Using density functional theory (DFT) and density functional perturbation theory (DFPT), we have examined the electronic structures and the phonon dispersions, and electron-phonon interactions of PdTe$_2$ and PtTe$_2$. We have found that a dip structure in the phonon dispersion near $\Gamma$ is important for the superconductivity, as Finlayson et al. [14] reported. However, we have identified that the electrons coupled with this mode are not the ones in the tubelike FS, as claimed by Finlayson et al. [14], but other ones in the band near the Fermi level ($E_F$) having the saddle-point van Hove singularity (vHs). The main difference in the electronic structures of PdTe$_2$ and PtTe$_2$ is found to be the behavior of this vHs band along the $k_z$ direction, which indicates that the lack of superconductivity in PtTe$_2$ is related to the broad $k_z$ dispersion of the vHs band. According to a pressure study by Soulard et al. [22], the structural response (structural rearrangement) to pressure was found to be abrupt for PdTe$_2$ but mild for PtTe$_2$. We suggest that this difference also comes from the different behaviors of the vHs band dispersions.

II. COMPUTATIONAL DETAILS

We have employed the full-potential linearized augmented plane-wave band method with local orbitals, implemented in WIEN2K for the band-structure calculations [25]. For the exchange-correlation potential, the Perdew-Burke-Ernzerhof (PBE) functional has been used. To take into account the relativistic effects of Pd (Pt) and Te, the spin-orbit interaction is included in a second variational manner with a large enough

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FIG. 1. (a) CdI₂-type structure of PdTe₂ and PtTe₂. Cyan-colored atoms denote Pd or Pt, while gray-colored atoms denote Te. (b) Fermi surface of PdTe₂. (c) Fermi surface of PtTe₂. Red dotted lines in (b) and (c) locate the position of saddle-point van Hove singularities in the BZ. (d) Band structure of PdTe₂, and (e) that of PtTe₂. Pd (Pt) and Te band components are represented by red and blue thick bands, respectively. Saddle points are seen near M just above EF in the Pd (Pt)-Te hybridized band. Note that PtTe₂ has a larger bandwidth due to larger Pt-Te hybridization.

energy window up to 5 Ry and 19 × 19 × 13 k points in the full Brillouin zone (FBZ) are used.

To study the phonon spectra and electron-phonon interaction, we have used the pseudopotential plane-wave band method implemented in QUANTUM ESPRESSO [26]. For phonon calculations, 5 × 5 × 5 q points are used, and 10 × 10 × 10 k points are used in the FBZ to get converged charge. For the calculation of the electron-phonon coupling constant λ, 40 × 40 × 40 k points are used in the FBZ to get converged charge. We have fully relaxed the structure first using the VASP pseudopotential plane-wave package [27], and then the internal parameters of Te are optimized by using QUANTUM ESPRESSO prior to the calculation of the electron-phonon interaction. The spin-orbit interaction is considered for all calculations.

III. RESULTS AND DISCUSSIONS

A. Fermi surfaces and band dispersions

In Fig. 1, FSs and the band dispersion along the high-symmetry k points in the hexagonal Brillouin zone (BZ) for PdTe₂ and PtTe₂ are presented. Both compounds have six bands crossing EF, which are grouped as three FS sheets with Kramers degeneracy: Γ-centered magenta- (blue-) colored FSs (hereafter B₁ FSs), K-centered cyan- (green-) colored FSs with tubelike branches (B₂), and small pockets near K in blue (cyan) color (B₃) for PdTe₂ (PtTe₂).

The topologies of FSs of two compounds are quite similar except for a few features. For PdTe₂, K-centered B₂ FSs are not connected, while for PtTe₂, the corresponding B₂ FSs are connected to each other [see the FSs along the red guidelines in Figs. 1(b) and 1(c)].

While this feature is not clearly seen in the band dispersions in Figs. 1(d) and 1(e), we will explain this feature more in Figs. 3 and 4 below. In the band dispersion, it is also seen that the bandwidth in PtTe₂ is larger than that in PdTe₂, despite the large lattice constant of PtTe₂, which is expected to originate from the more extended 5d band of Pt than the 4d band of Pd. Near EF, the Te character is dominant except for the M-K path, where Pd(Pt)-Te hybridization is large.

B. Phonon spectra and electron-phonon coupling constants

We have calculated phonon spectra and electron-phonon coupling constants, utilizing the DFPT implemented in QUANTUM ESPRESSO [26]. Figures 2(a) and 2(b) show the phonon dispersion and phonon density of states (DOS) of PdTe₂. The size of the red circles is proportional to the phonon linewidth. Optical phonon modes are labeled as O₁,₂, O₃, O₄, O₅. (b) Phonon density of states. (c) Eliashberg function α²F(ω) (blue) and λ(ω) (red) as a function of phonon frequency. (d)–(f) are corresponding figures for PtTe₂. (g) Normal modes of optical phonons O₁,₂, O₃ at q = Γ. Red and blue arrows indicate Te and Pd displacements, respectively.
phonon frequency,

$$\omega^2 F(\omega) = \frac{1}{2\pi N(\epsilon_F)} \sum_{\mathbf{q} \eta} \lambda_{\mathbf{q} \eta} \delta(\omega - \omega_{\mathbf{q} \eta}),$$

(1)

and $$\lambda(\omega) = 2 \int_0^\infty d\omega' \frac{2\omega^2 F(\omega')}{\omega'^2}.$$ Here, $\eta$ denotes the phonon mode, and $\lambda_{\mathbf{q} \eta}, \omega_{\mathbf{q} \eta}$ are the electron-phonon coupling constant and phonon frequency for mode $\eta$ at wave vector $\mathbf{q}$, respectively. We estimated the superconducting $T_c$ from the Allen-Dynes equation [28]

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left( -1.04(1 + \lambda) \frac{\lambda - \mu^*(1 + 0.62\lambda)}{\lambda} \right),$$

(2)

where $\omega_{\log}$ is the logarithmic averaged frequency, $\omega_{\log} = \exp(\frac{1}{2} \int d\omega \log \omega^2 F(\omega))$.

Note that doubly degenerate phonon modes at $\Gamma$ near 15 meV provide a large contribution to $\lambda(\omega)$, indicating their large contribution to superconductivity. These modes are the ones with the dip structure, pointed out by Finlayson et al. [14]. With the obtained $\lambda = 0.53$ in Fig. 2(c) and $\mu^* = 0.1$, $T_c$ is estimated to be 1.79 K for PdTe$_2$, which is comparable to the experimental $T_c$ of 1.78 K [12].

The overall features of the phonon dispersion and DOS for PtTe$_2$ in Figs. 2(d) and 2(e) are essentially the same as those of PdTe$_2$. But, compared to PdTe$_2$, the contribution of $O_{1,2}$ modes to $\lambda(\omega)$ is smaller for PtTe$_2$, and so $\lambda = 0.35$ is obtained, which is smaller than $\lambda = 0.53$ for PdTe$_2$ [see Fig. 2(f)]. The estimated $T_c$ of PtTe$_2$ is 0.22 K, which is consistent with the fact that $T_c$ of PtTe$_2$ is not observed down to $T = 1.2$ K.

Finlayson et al. [14] claimed that phonon modes with the dip structure are coupled with electrons in the tubelike FSs that span from K to near A in the hexagonal BZ. To identify which electronic bands are really coupled with these phonon modes, we have performed the DFT calculations for PdTe$_2$ with an electronic bands are really coupled with these phonon modes, for mode $\eta$ at wave vector $\mathbf{q}$, respectively. We estimated the superconducting $T_c$ from the Allen-Dynes equation [28]

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left( -1.04(1 + \lambda) \frac{\lambda - \mu^*(1 + 0.62\lambda)}{\lambda} \right),$$

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As we mentioned earlier, this modulation changes Pd-Te distances as well as the Te-Te distance. To check which structural character is more important, we have carried out similar calculations to those in Fig. 3 for the modulated monolayer systems PdTe$_2$ and PtTe$_2$. We get the same responses to normal modes for the monolayers, too, which implies that the intralayer Pd(Pr)-Te interaction is more important than the interlayer Te-Te interaction in tuning the energy positions of the saddle points. Note that the reduced Pd(Pr)-Te distance moves the vHs downward for both PdTe$_2$ and PtTe$_2$.

We mentioned in the Introduction that there exists a type-II Dirac point in PdTe$_2$, which might produce topological superconductivity. Note that the superconductivity in the above discussion arises mainly from the electrons at the vHs band near $E_F$, not from those at the type-II Dirac points that are located about 0.55 and 0.8 eV below $E_F$ for PdTe$_2$ and PtTe$_2$, respectively [7–11]. This point has been explored recently by experiments, which manifest that the superconductivity in the type-II Dirac-semimetallic PdTe$_2$ is just a conventional one [12,29]. Nevertheless, the search for topological superconductivity in PdTe$_2$ and PtTe$_2$ will be quite interesting by tuning the binding energy of the Dirac points with external pressure or doping.

The strong electron-phonon coupling of the vHs electronic states shown in Figs. 2 and 3 suggests possible anharmonic responses to $O_{1,2}$ modes as in the case of MgB$_2$ [30]. To examine the possibility, we calculated the energy difference ($dE$) as a function of $d\epsilon$ from the equilibrium position for the $O_1$ normal mode in Fig. 3(g). The curve is fitted with a function of $dE = A_2 d\epsilon^2 + A_4 d\epsilon^4$. The harmonic coefficient $A_2$ and quadratic anharmonic coefficient $A_4$ are 2.549 eV/Å$^2$ and 9.359 eV/Å$^4$, respectively. Although the anharmonic term is not as large as that of MgB$_2$ [30], for which the whole boron $p_s$ band near $E_F$ is strongly coupled with the $E_{2g}$ phonon mode, the anharmonic contribution in PdTe$_2$ is not
negligible either. This anharmonic contribution originates from the electron-phonon interaction at the vHs points. However, for PdTe₂, the anharmonic contribution to the total energy is only about 1% of the harmonic contribution, so that the error from employing the standard Eliashberg theory for an anharmonic material PtSe₂ was studied [33]. The theoretical Tc of PtSe₂ was estimated to be 0.002 K. With an electron doping of 0.5e⁻ per formula unit cell, Tc increases up to 2.15 K. They claimed that the mechanism of the superconductivity in doped PtSe₂ is related to the softening of acoustic phonon modes. We noticed that the vHs at the K point is about 0.5 eV above EF for pristine PtSe₂. However, with doping, the vHs point becomes close to EF, and the band dispersion becomes similar to that of PdTe₂. Therefore, there is still a possibility that the contribution of O₁,₂ optical phonon modes to superconductivity is as important as that of the softened acoustic phonon modes. Actually, in Fig. S4(d) of Ref. [33], the contribution of phonons with ω ~ 100–150 cm⁻¹, where O₁,₂ modes reside, to λ is seen to be considerable. Further study is needed on this aspect.

D. Structural responses to pressure

Souillard et al. [22] showed that, under pressure, the structural parameters change abruptly at around 20 GPa, which corresponds to a 10% volume contraction in PdTe₂, while in PtTe₂, the changes are mild up to 30 GPa. They claimed that this difference comes from the difference in the hybridization between Pd-Te and Pt-Te. According to our calculation, when we contract the volume of PdTe₂ by 15%, all the saddle points shift down to EF and the M-centered FSs start to merge together [see Fig. 3(f)]. We suspect that the instability by the saddle-point vHs near EF might be a driving force for such an abrupt change in the lattice parameters of PdTe₂. However, for PtTe₂, the saddle points cross EF rather gradually with pressure, and so the change in lattice parameters also becomes mild. Even when the spin-orbit interaction of PtTe₂ is turned off, the energy positions of the saddle points do not change, indicating that the structure of the vHs points is correlated more to the size of Pt/Pd than to the spin-orbit interaction.

IV. CONCLUSION

Employing the DFT and DFPT, we have studied the electronic and phonon band structures, and the superconducting and structural properties of the layered TMDs, PdTe₂ and

![Image](https://example.com/image.png)

**FIG. 4.** (a) FSs for different kz planes for PdTe₂ (upper row) and PtTe₂ (lower row), respectively. Red contours are FSs at EF, while blue contours are FSs at the energy position of the vHs point E_vHs. (b) E_vHs positions of PdTe₂ and PtTe₂ for different k_z's. Note that E_vHs for PdTe₂ is less dispersive than that for PtTe₂. (c) Electron densities of states for PdTe₂ and PtTe₂ near the vHs points. Note that there is a pronounced peak structure only for PdTe₂.

In a recent work by Cheng et al. [33], the doping dependence of the superconducting temperature for an isostructural material PtSe₂ was studied [33]. The theoretical Tc of PtSe₂ was estimated to be 0.002 K. With an electron doping of 0.5e⁻ per formula unit cell, Tc increases up to 2.15 K. They claimed that the mechanism of the superconductivity in doped PtSe₂ is related to the softening of acoustic phonon modes. We noticed that the vHs at the K point is about 0.5 eV above EF for pristine PtSe₂. However, with doping, the vHs point becomes close to EF, and the band dispersion becomes similar to that of PdTe₂. Therefore, there is still a possibility that the contribution of O₁,₂ optical phonon modes to superconductivity is as important as that of the softened acoustic phonon modes. Actually, in Fig. S4(d) of Ref. [33], the contribution of phonons with ω ~ 100–150 cm⁻¹, where O₁,₂ modes reside, to λ is seen to be considerable. Further study is needed on this aspect.

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Employing the DFT and DFPT, we have studied the electronic and phonon band structures, and the superconducting and structural properties of the layered TMDs, PdTe₂ and
PtTe$_2$. Our study reveals that the saddle-point vHs near $E_F$ plays essential roles in both the BCS-type superconductivity of PdTe$_2$ and the abrupt change in the lattice parameters under pressure. We suggest that the absence of superconductivity and also the mild change in the lattice parameters under pressure in isostructural PtTe$_2$ are due to the different dispersion behavior of the near-$E_F$ saddle-point vHs band from that in PdTe$_2$.

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