

Theoretical expectation of large Seebeck effect in PtAs₂ and PtP₂

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Motivated by a recent observation of good thermoelectric properties in PtSb₂, we theoretically study related pyrites in an attempt to seek for a material which overcomes the suppression of the Seebeck coefficient at high temperatures. We find that PtAs₂ and PtP₂ are good candidates, where a larger band gap than in PtSb₂ combined with the overall flatness of the band top gives rise to a monotonically increasing Seebeck coefficient up to high temperatures. This expectation has been confirmed quite recently for hole doped PtAs₂, where a very large power factor of $\sim 65\mu\text{W}/\text{cmK}^2$ at $T = 440\text{K}$ is observed.

Searching good thermoelectric materials is an challenging issue both from the viewpoint of fundamental physics and device applications. From the latter viewpoint in particular, the efficiency of thermoelectric materials is characterized by a dimensionless figure of merit, ZT with $Z = P/\kappa$, where $P = S^2\sigma$ is the power factor, T , S , σ and κ are the temperature, the Seebeck coefficient, the electric conductivity, and the thermal conductivity, respectively[1]. A large power factor requires simultaneously large S and σ , but usually materials with large Seebeck coefficient have small conductivity. As a general way to overcome this problem, one of the present authors along with Arita proposed that a band shape that has a flat portion at the top (or the bottom), connected to a dispersive portion, can give rise to large conductivity and Seebeck coefficient simultaneously. This band shape is referred to as the pudding-mold type, and the theory was applied to Na_xCoO₂, a thermoelectric material with large metallic conductivity and power factor, discovered by Terasaki *et al*[2].

Quite recently, Nishikubo *et al.* found that doping holes into a cubic pyrite material PtSb₂ (Fig.1(a)) by partially substituting Pt by Ir as Pt_{1-x}Ir_xSb₂ gives rise to a metallic conductivity, while exhibiting a large Seebeck effect below room temperature, thereby resulting in a large power factor of $\sim 40\mu\text{W}/\text{cmK}^2$ for $x = 0.01$ [4]. Referring to the band structure calculation in ref.[5], a possible relevance of the peculiar band structure has been pointed out. Succeedingly, we have analyzed the origin of this large Seebeck effect in PtSb₂, and concluded that a fairly flat band with dispersive portions, which we called the “corrugated flat band”, plays an important role[6]. In the study, we also found that the narrowness of the valence-conduction band gap results in a reduction of the Seebeck coefficient at high temperatures. We analyzed how the band gap is determined from a tightbinding viewpoint, and concluded that if we could increase the hopping integral between Pt 5*d* and Sb 4*p* orbitals, the band gap increases, and the Seebeck coefficient monotonically increases up to high temperatures.

In the present study, we theoretically search for related pyrite materials that can give a larger band gap

and hence a monotonically increasing Seebeck coefficient at high temperatures. We perform first principles band calculation for MPn_2 with $M = \text{Ni, Pd, Pt}$ and $Pn = \text{P, As, Sb}$, which shows that the band gap for PtAs₂ and PtP₂ is large compared to that of PtSb₂. By constructing a tightbinding model for the bands near the Fermi level exploiting maximally localized Wannier orbitals, it is found that the large band gap is indeed due to the large *d-p* hopping. Calculating the Seebeck coefficient using the obtained tightbinding model, we find a monotonically increasing large Seebeck coefficient against temperature for these two materials. For PtP₂, we find an ideal band shape in the conduction band structure, so that better thermoelectric properties are expected in the electron doped regime.

We start with the first principles band calculation for cubic pyrites MPn_2 with $M = \text{Pt, Pd, Ni}$ and $Pn = \text{Sb, As, P}$. We adopt the lattice structure parameter values taken from ref.[10], and the band structure is calculated using the Wien2K package[9]. Here we take $RK_{\text{max}} = 7$, 512 *k*-points. The results are summarized in Fig.1(b). It can be seen that in PtAs₂ and PtP₂, a large band gap opens, while in other materials the gap is narrow or absent.

To see the origin of this result in more detail, we obtain tightbinding models exploiting the maximally localized Wannier orbitals[11]. The bands near the Fermi level consist mainly of the *p* orbitals, but in order to see the *d-p* hybridization explicitly, we first construct a 44 orbital *d-p* model that considers 20 (5 orbitals \times 4 sites) *Mn d* orbitals in addition to the 24 *Pn p* orbitals. The parameters listed in table I are the lattice constant, the largest hopping integral t_{dp} between *M d* and *Pn p* orbitals, the level offset ΔE_{dp} between *d* and *p* orbitals, and the band gap E_g . As analyzed in our previous study[6], the band gap opens between the non-bonding (valence bands) and the antibonding bands (conduction bands), where non-bonding means that the band is almost solely constructed from *p* orbitals. Therefore, the magnitude of the band gap should roughly be proportional to $t_{dp}^2/\Delta E_{dp}$ in the large $\Delta E_{dp}/t_{dp}$ limit.

There are two competing effects that affect the magni-

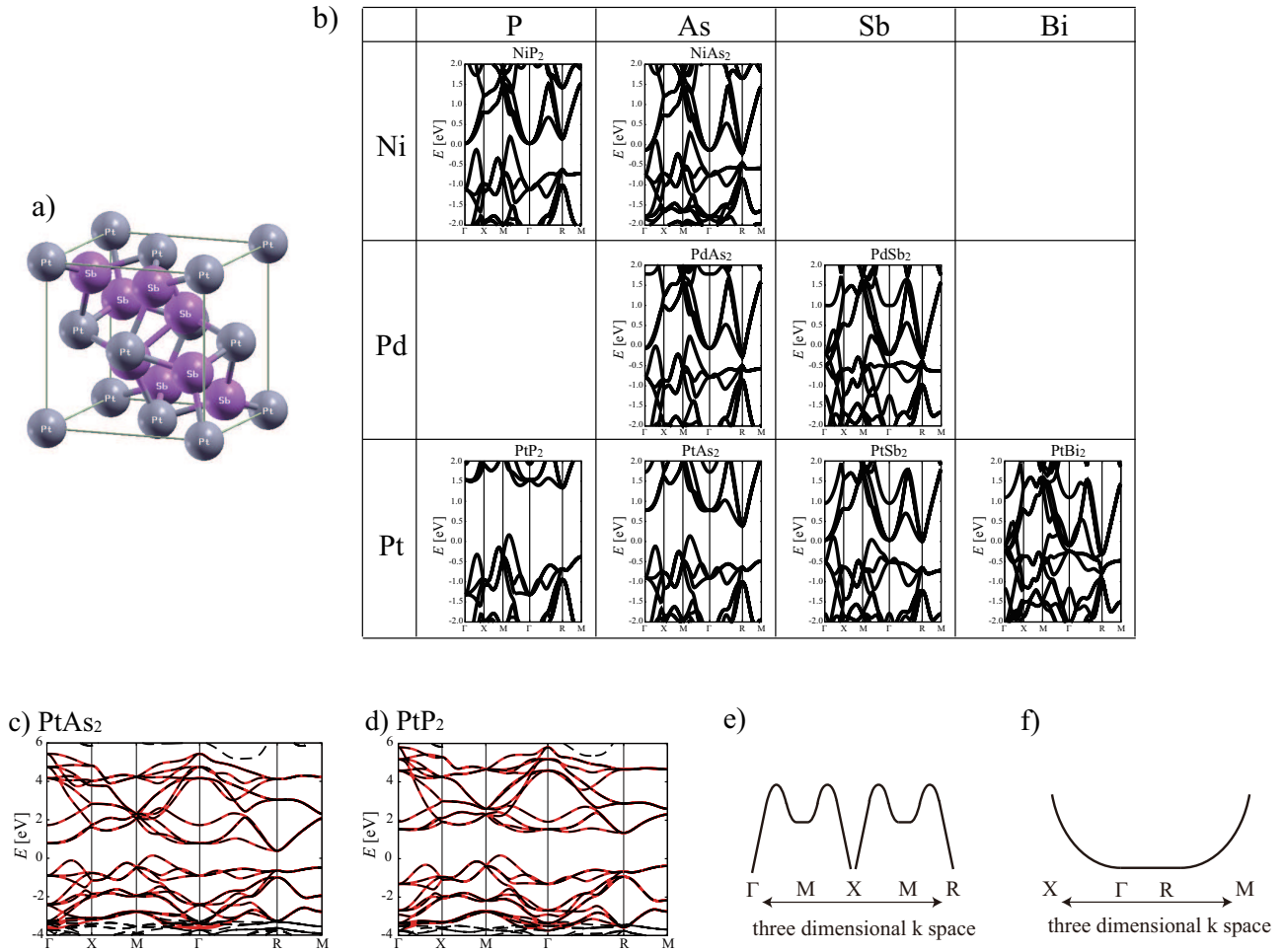


FIG. 1. (a) The lattice structure of PtSb₂. (b) Band structures of MPn_2 . The blanks indicate that experimentally determined lattice structures were not available. (c)(d) Tightbinding models of PtAs₂ and PtP₂. (e) Schematic figure of the valence band of PtAs₂ and PtP₂. (f) Schematic figure of the conduction band of PtP₂.

TABLE I. The lattice constant, the tightbinding parameters, and the band gap for the pyrite materials studied in the present paper. All the values are normalized by the corresponding values of PtSb₂.

	NiP ₂	NiAs ₂	PdAs ₂	PdSb ₂	PtP ₂	PtAs ₂	PtSb ₂	PtBi ₂
a	0.85	0.89	0.93	1.00	0.88	0.93	1.00	1.04
ΔE_{dp}	0.41	0.33	1.33	1.45	0.63	0.76	1.00	1.08
t_{dp}	0.81	0.72	0.97	0.86	1.22	1.13	1.00	0.88
E_g	0.96	0.87	0.86	0.69	1.46	1.27	1.00	0.81

tude of t_{dp} ; one is the unit cell volume (the lattice constant) and the other is the spread of the p or d orbitals. When Sb is replaced by As or P, the unit cell volume and the p orbital spread are both reduced, but the former effect overcomes the latter, thereby resulting in an enhanced t_{dp} . On the other hand, when Pt is replaced by Pd or Ni, the lattice constant barely changes, while the d orbital shrinks, giving a smaller t_{dp} .

Having seen that the band gap of PtAs₂ and PtP₂ is large compared to that of PtSb₂, we now analyze these two materials in more detail. To reproduce the band structure near the Fermi level, a 24 orbital model that

considers only the p Wannier orbitals (eight Pn per unit cell \times three p orbitals) suffices. The band dispersion of the model is shown in fig.1(c) and (d) superposed to the original first principles band. The Fermi surface of the two materials is obtained using these models for several hole or electron doping rates as shown in Fig.2. In the hole doped case, it can be seen that the Fermi surface pockets are scattered through the entire Brillouin zone except around the Γ and X points, indicating that the valence band is essentially flat (i.e. have similar energies) over a large portion of the zone with some corrugation. This can be seen in the band structure in Fig.1(c), in

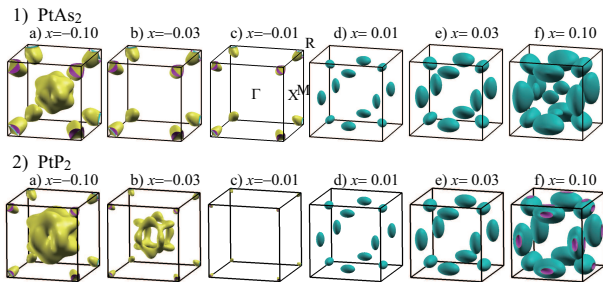


FIG. 2. Fermi surface of PtAs₂ and PtP₂. x denotes the doping rate, where the positive (negative) values imply hole (electron) doping.

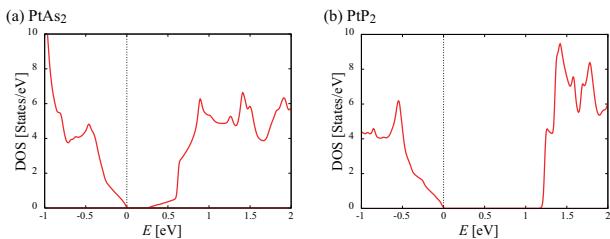


FIG. 3. The density of states of PtAs₂ and PtP₂.

which the top positions of the valence band at different k points have similar energies except around the Γ , X, and R points. Therefore, the band shape can be schematically captured as shown in Fig.1(e). This can be viewed as a combination of multiple pudding-mold type bands with a corrugated top. In the present case, the k axis extends through the *three dimensional* k -space, while in previous cases, the k axis was either two dimensional (k_x, k_y) like in Na _{x} CoO₂ or CuAlO₂[7], or one dimensional as in FeAs₂[8].

On the other hand, in the electron doped case, especially for PtP₂, the Fermi surface is gathered around the Γ point meaning that the portion of the bands around the zone center is flat in this case. As seen in Fig.1(d), the conduction band of PtP₂ indeed has a very flat bottom that extends over a large portion of the three dimensional Brillouin zone, as schematically depicted in Fig.1(f). This is also clearly seen in the density of states (DOS) of PtP₂ shown in Fig.3(b), which rises sharply at the conduction band edge, as if the material were a 2D system. Thus, the conduction bands of PtP₂ have an ideal three dimensional pudding-mold shape.

As discussed in ref.[3], pudding-mold type band is ideal for obtaining good thermoelectric properties, especially the power factor. A large thermopower is generally obtained when the velocity of electron (v_e) and hole (v_h) excitations near the Fermi level have large difference. When the Fermi level sits close to the band edge, the v_h/v_e ratio can in general be large, but the absolute values of the velocities are usually small and also the Fermi surface is small, so that the conductivity is small. For the pudding-mold type band, on the other hand, the large density of

states at the top of the band prevents the Fermi level from going down rapidly even when a large amount of carriers (holes in the present case) is doped. This is good for thermopower in that the Fermi level stays near the bending point of the band even when the Fermi surface volume is large. When the Fermi level sits close to the bending point of the pudding mold type band, v_h/v_e ratio is large, resulting in a large Seebeck coefficient. At the same time, the conductivity becomes large due to the large Fermi surface volume and the dispersive portion (mainly below the Fermi level) of the bands. In this manner, the coexistence of large Seebeck coefficient and large conductivity is realized for a wide range of hole doping rate.

We now proceed to the calculation of the Seebeck coefficient for PtAs₂ and PtP₂. The Seebeck coefficient is calculated within the Boltzmann's equation approach using the obtained tightbinding band structure. In this approach, tensors of the Seebeck coefficient \mathbf{S} and the conductivity $\boldsymbol{\sigma}$ are given as,

$$\mathbf{S} = \frac{1}{eT} \mathbf{K}_1 \mathbf{K}_0^{-1} \quad (1)$$

$$\boldsymbol{\sigma} = e^2 \mathbf{K}_0 \quad (2)$$

where $e (< 0)$ is the elementary charge, T is the temper-

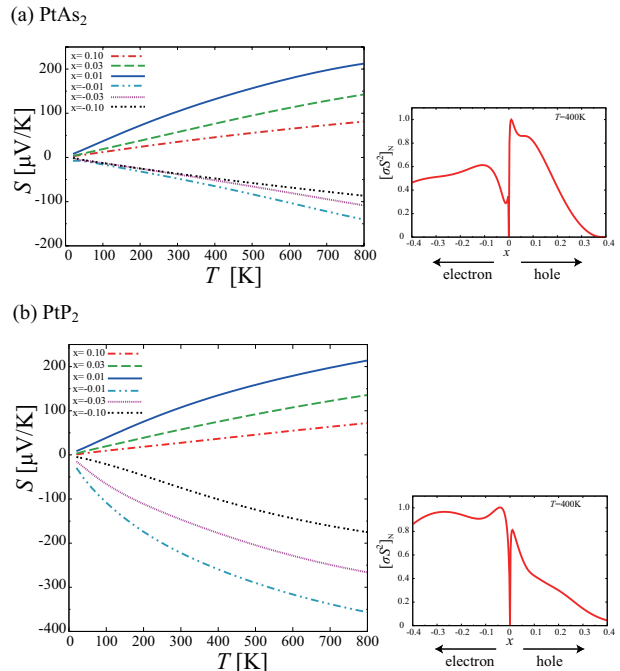


FIG. 4. (left panels) The calculated Seebeck coefficient plotted against temperature for PtAs₂ and PtP₂. $x > 0 (< 0)$ implies hole (electron) doping. (right) The power factor against the doping rate at $T = 400\text{K}$, normalized by its maximum value.

atretensors $\mathbf{K}_1, \mathbf{K}_2$ are given as

$$\mathbf{K}_n = \sum_{\mathbf{k}} \tau(\mathbf{k}) \mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k}) \left[-\frac{df(\epsilon)}{d\epsilon}(\mathbf{k}) \right] (\epsilon(\mathbf{k}) - \mu)^n. \quad (3)$$

Here, $\epsilon(\mathbf{k})$ is the band dispersion, $\mathbf{v}(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon(\mathbf{k})$ is the group velocity, $\tau(\mathbf{k})$ is the quasiparticle lifetime, $f(\epsilon)$ is the Fermi distribution function, and μ is the Fermi level (chemical potential). In the present study, we approximate τ as a constant, so that it cancels out in the Seebeck coefficient. We simply write σ_{xx} and S_{xx} as σ and S , respectively. σ and thus the power factor σS^2 contain the constant τ , whose absolute value is not determined. Therefore, we only discuss the values of the power factor normalized by its maximum value as a function of the doping rate.

In Fig.4, we show the Seebeck coefficient against temperature for the two materials. It can be seen that the Seebeck coefficient monotonically increases with temperature, in contrast to a similar calculation for PtSb₂[6], and reaches 200 μ V/K for both PtAs₂ and PtP₂, for the hole doping rate of $x = 0.01$ and at temperature $T = 800$ K. This is indeed due to the combination of the ideal band shape, together with the large band gap.

We also consider the case of electron doping, since the conduction band seems to have an ideal pudding mold type band structure for PtP₂. The Seebeck coefficient

for PtP₂ indeed exceeds -200μ V/K already at 300K, and reaches a very large value of -350μ V/K at 800K for $x = -0.01$ ("-" implies electron doping). The superiority of the electron doped PtP₂ can further be seen in the doping dependence of the normalized power factor at $T = 400$ K also shown in Fig.4. While the hole doped regime gives a better power factor for PtAs₂, in PtP₂ the electron doped regime gives larger and more persisting power factor compared to that in the hole doped regime. Based on these results, we expect good thermoelectric properties in PtP₂ once sufficient amount of electrons is doped.

To summarize, we have studied the band structure and the Seebeck coefficient of MPn_2 in an attempt to search for materials with thermoelectric properties better than PtSb₂. We find that PtAs₂ and PtP₂ are good candidates with larger band gap, while Pd and Ni based compounds are not expected to exhibit good performance. Quite recently, the thermoelectric properties of the hole doped Pt_{1-x}Rh_xAs₂ has been measured experimentally, in which a large and monotonically increasing Seebeck coefficient at high temperature is found[13]. The combination of this with the metallic behavior of the resistivity results in a very large power factor of $\sim 65\mu$ W/cmK² at $T = 440$ K.

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