



# 从能带非抛物性因子看热电输运

朱建博, 隋解和, 郭逢凯, 张永胜

2025 年 7 月 7 日



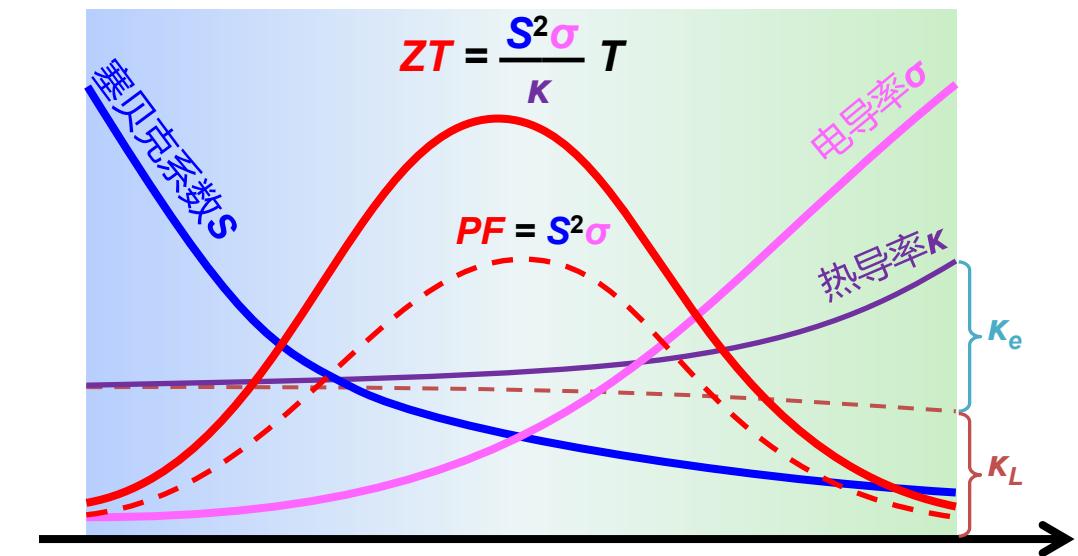
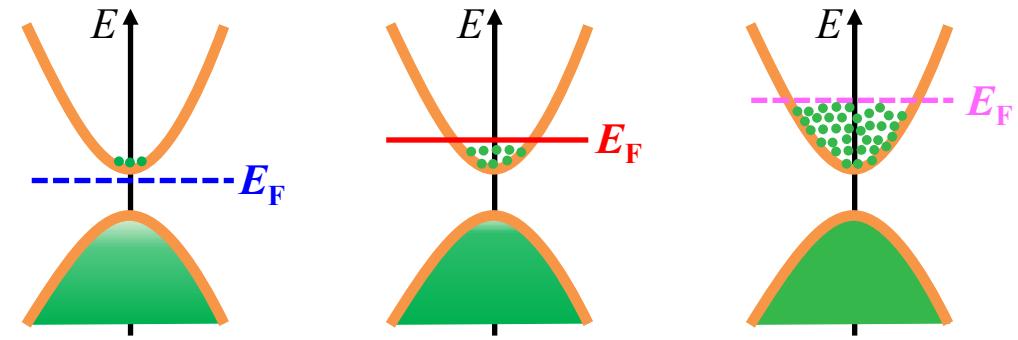
# 研究背景

## ● 热电优值

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_L} T = \frac{PF}{\kappa_e + \kappa_L} T$$

- $T$ : 绝对温度
- $PF$ : 功率因子
- $\sigma$ : 电导率
- $S$ : 塞贝克系数
- $\kappa_e$ : 电子热导率
- $\kappa_L$ : 晶格热导率

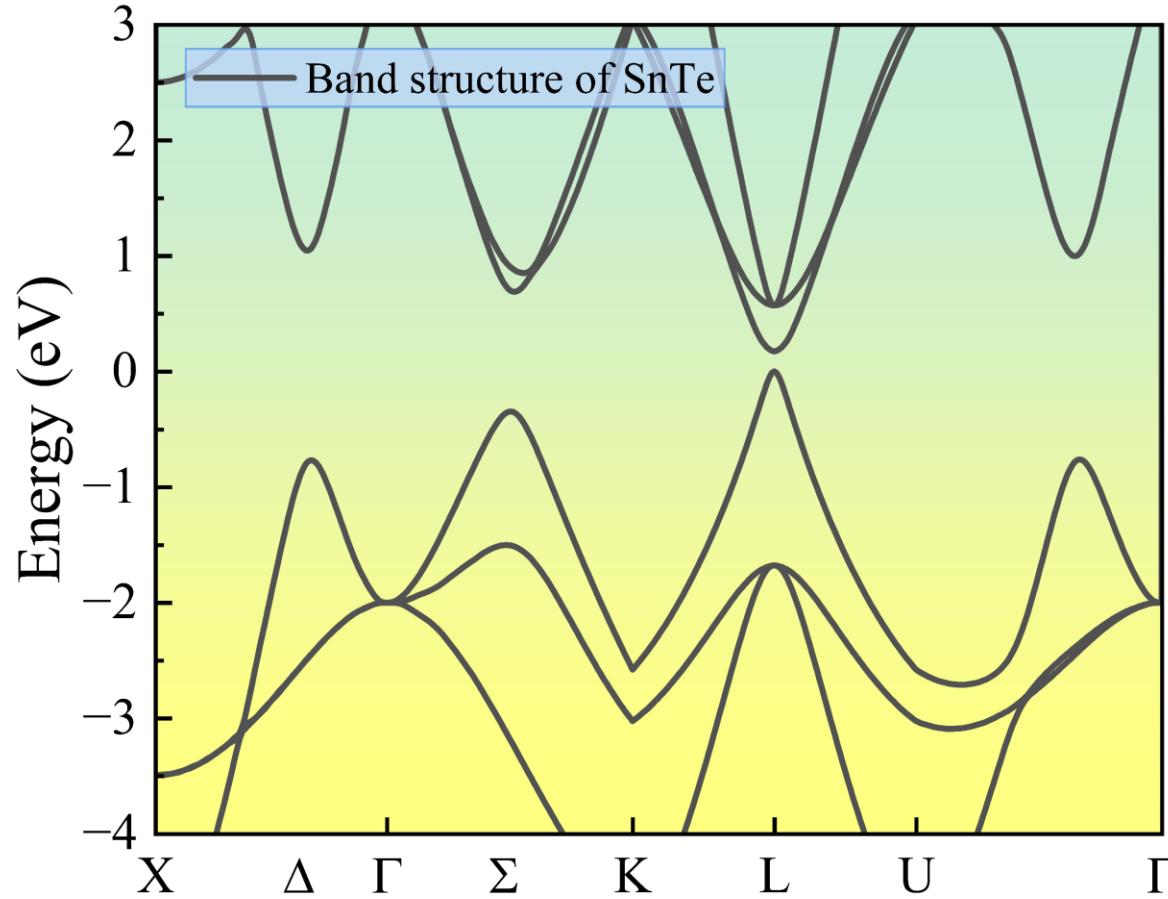
电输运  
热输运



## 载流子浓度增加 →

◆ 电输运性能参数之间复杂的耦合关系是提升  $ZT$  的重要阻碍之一

## ➤ 玻尔兹曼输运方程 + 驰豫时间近似



$$\tau \propto \frac{1}{g(E)}$$

$$\sigma = q^2 \int_{-\infty}^{+\infty} v^2(E) g(E) \tau \left( -\frac{\partial f_0}{\partial E} \right) dE$$

$$S = \frac{1}{qT} \left[ \frac{\int_{-\infty}^{+\infty} v^2(E) g(E) \tau E \left( -\frac{\partial f_0}{\partial E} \right) dE}{\int_{-\infty}^{+\infty} v^2(E) g(E) \tau \left( -\frac{\partial f_0}{\partial E} \right) dE} - E_F \right]$$

$$\kappa_e = \frac{1}{T} \int_{-\infty}^{+\infty} v^2(E) g(E) \tau E^2 \left( -\frac{\partial f_0}{\partial E} \right) dE$$

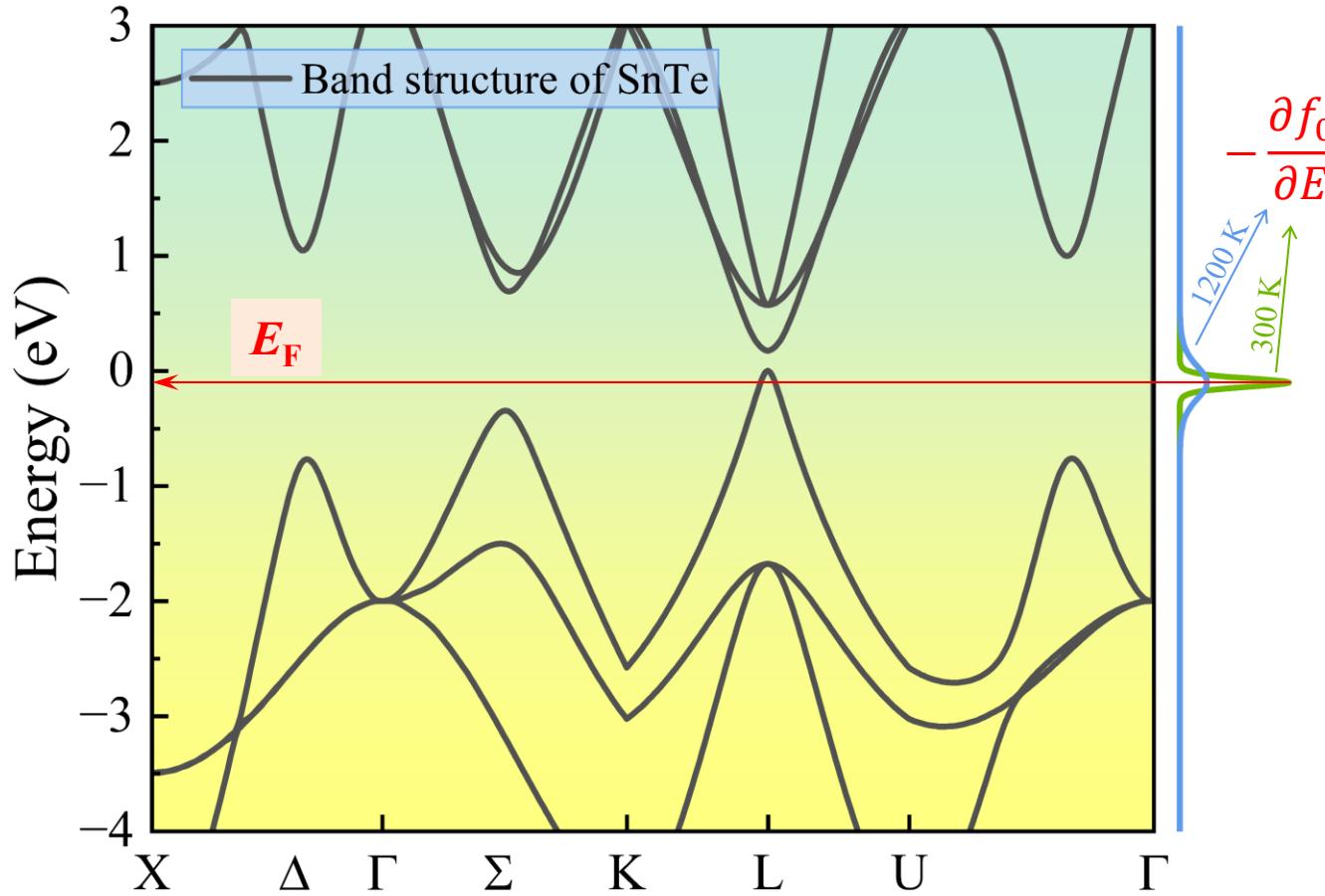
$$- \frac{\left[ \int_{-\infty}^{+\infty} v^2(E) g(E) \tau E \left( -\frac{\partial f_0}{\partial E} \right) dE \right]^2}{T \int_{-\infty}^{+\infty} v^2(E) g(E) \tau \left( -\frac{\partial f_0}{\partial E} \right) dE}$$

$$L \xleftarrow{\text{def}} \frac{\kappa_e}{\sigma T}$$

◆ 能带结构直接决定了晶体材料的电输运性能，为热电材料设计提供思路，但是可解释性较差

# 电输运性能计算

➤ 费米窗口函数:  $w_F = -\partial f_0 / \partial E$



$$f_0 = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

$$\tau \propto \frac{1}{g(E)}$$

$$\sigma = q^2 \int_{-\infty}^{+\infty} v^2(E) g(E) \tau \left( -\frac{\partial f_0}{\partial E} \right) dE$$

$$S = \frac{1}{qT} \left[ \frac{\int_{-\infty}^{+\infty} v^2(E) g(E) \tau E \left( -\frac{\partial f_0}{\partial E} \right) dE}{\int_{-\infty}^{+\infty} v^2(E) g(E) \tau \left( -\frac{\partial f_0}{\partial E} \right) dE} - E_F \right]$$

$$\kappa_e = \frac{1}{T} \int_{-\infty}^{+\infty} v^2(E) g(E) \tau E^2 \left( -\frac{\partial f_0}{\partial E} \right) dE$$

$$- \frac{\left[ \int_{-\infty}^{+\infty} v^2(E) g(E) \tau E \left( -\frac{\partial f_0}{\partial E} \right) dE \right]^2}{T \int_{-\infty}^{+\infty} v^2(E) g(E) \tau \left( -\frac{\partial f_0}{\partial E} \right) dE}$$

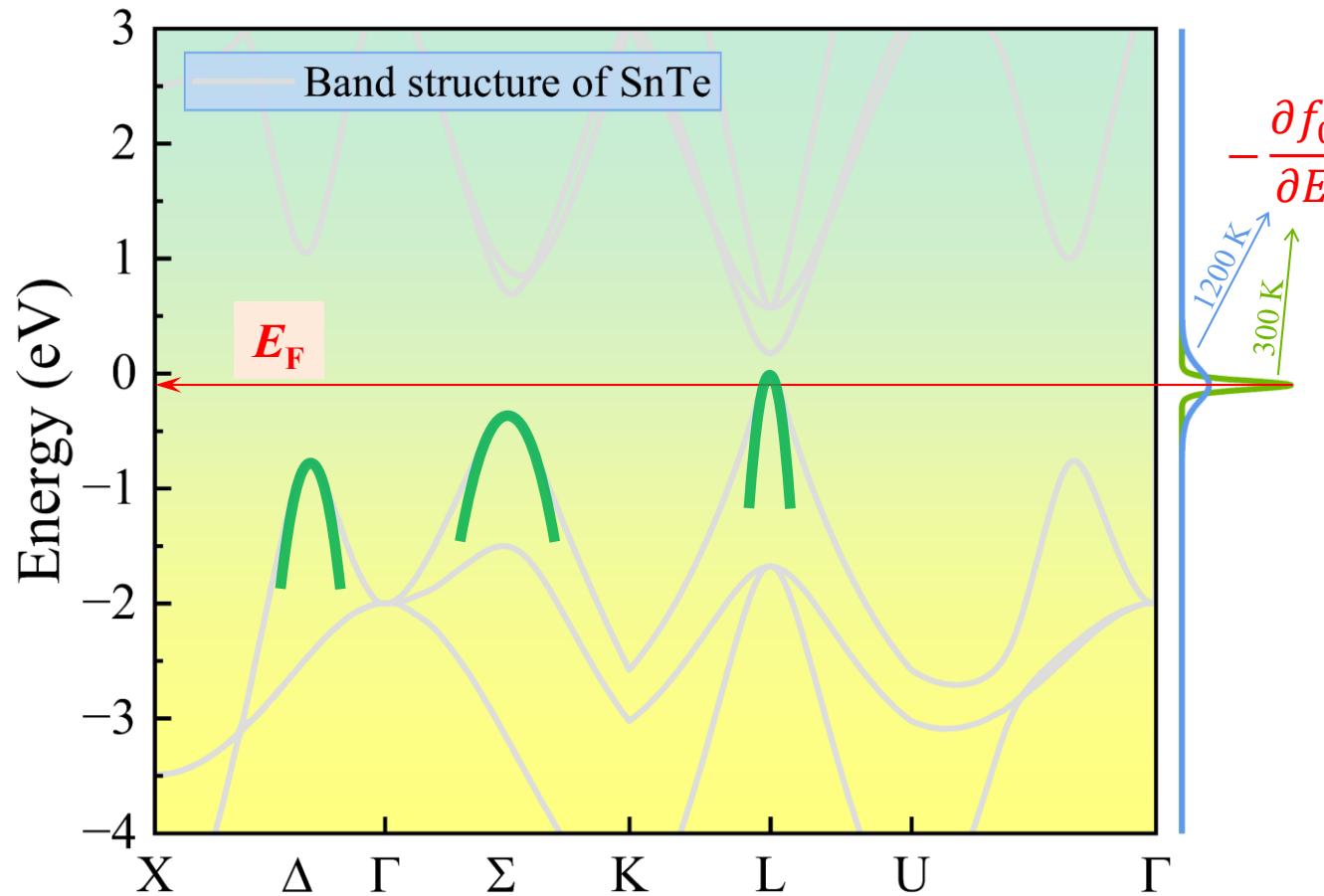
$$L \xleftarrow{\text{def}} \frac{\kappa_e}{\sigma T}$$

◆ 实际材料中只有费米面附近  $\sim k_B T$  范围内的载流子被激活 → 可以利用简化的解析式近似描述能带

# 电输运性能计算

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➤ 仅考虑价带顶/导带底局部性质 → 抛物带模型



$$E = \frac{\hbar^2 k^2}{2m^*} + \tau \propto \frac{1}{g(E)}$$

$$n = n_{m,0} \cdot \left( \frac{m^* T}{m_e T_r} \right)^{3/2} F_{1/2}(\eta)$$

$$\sigma = \sigma_0 \cdot F_0(\eta)$$

$$S = \frac{k_B}{q} \cdot \left[ \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right]$$

$$L = \left( \frac{k_B}{q} \right)^2 \cdot \left[ 3 \frac{F_2(\eta)}{F_0(\eta)} - 4 \left( \frac{F_1(\eta)}{F_0(\eta)} \right)^2 \right]$$

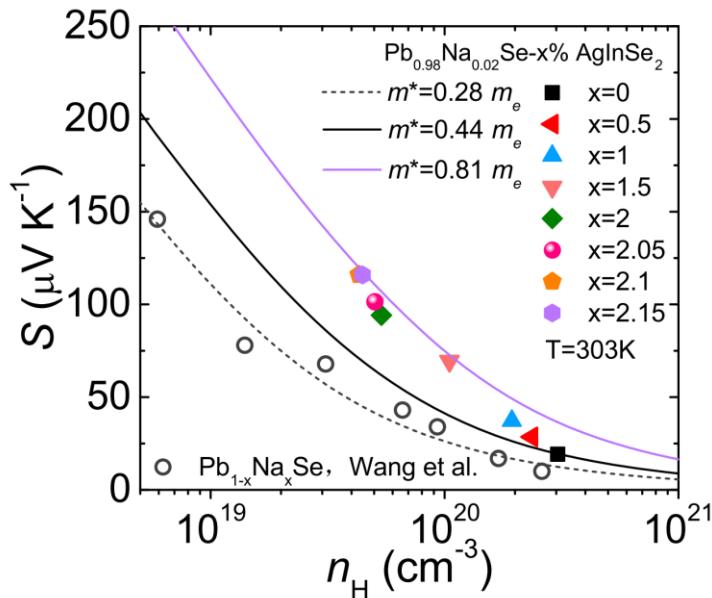
$$F_n(\eta) = \int_0^\infty \frac{x^n}{1+\exp(x-\eta)} dx, \eta = \frac{E_F}{k_B T}$$

◆ 能带结构由有效质量( $m^*$ )参数唯一描述, 与散射强度共同决定了材料的宏观电输运性能

# 电输运性能计算

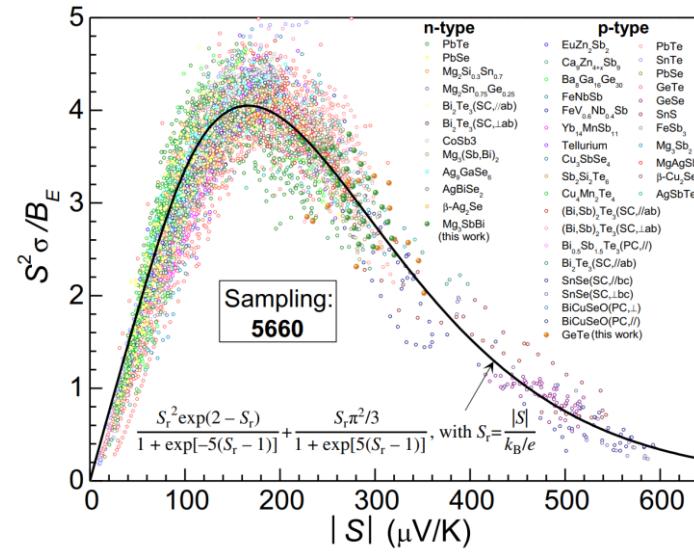
## ● 抛物带模型的应用

### ❖ 拟合态密度有效质量 (Pisarenko 关系)



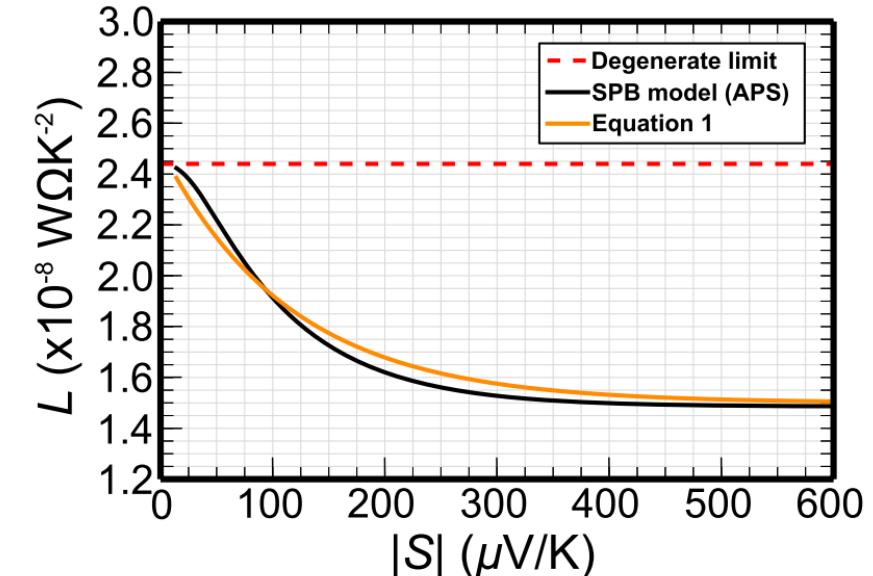
Y. Zhu *et al.*, *Nat. Commun.*, **13** 4179, 2022.

### ❖ 预测峰值功率因子和最优掺杂浓度 (电学品质因子 $B_E$ )



X. Zhang *et al.*, *Sci. Adv.*, **6** eabc726, 2020.

### ❖ 从塞贝克系数估计洛伦兹常数 (L – S 关系图)



H. Kim *et al.*, *APL Mater.*, **3** 41506, 2015.

◆ 抛物带模型已经广泛应用于热电材料的性能分析与新材料设计，是能带结构与宏观电输运参数之间的桥梁

# 电输运性能计算

## ● 抛物带模型的应用 → 重构单抛物带模型(rSPB)

❖ Excel® 计算模板: <https://gitee.com/joulehit/rSPB>

J. Zhu *et al.*, *Npj Comput. Mater.*, 7 116, 2021.

Information\_2021.7.24

If it works for you, please cite our paper. Thanks!

Title: Restructured Single Parabolic Band Model for Quick Analysis in Thermoelectricity

Author: Jianbo Zhu, Xuemei Zhang, Muchun Guo *et al.*

Journal: *npj Computational Materials*, 7, 116(2021).

DOI: 10.1038/s41524-021-00587-5

### How To Use

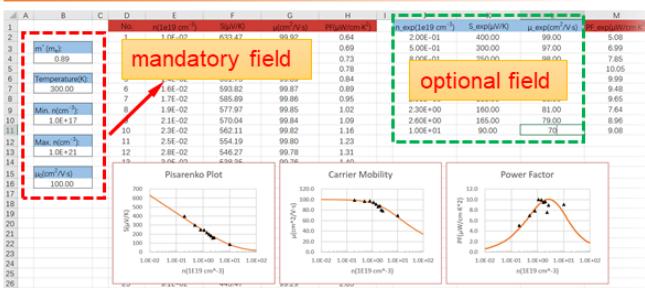
#### 1. Input experimental data

A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
Temperature(K)	$n(10^19 \text{ cm}^{-3})$	$\mu(\text{cm}^2/\text{V}\cdot\text{s})$	$S(\mu\text{V/K})$												
300.00	0.02	102.50	500.00	3.28	0.82	0.50	102.88	36.62	36.62	4.639					
300.00	0.05	99.50	500.00	73.00	1.24	0.70	99.97	70.47	70.47	8.5421					
300.00	0.08	96.50	460.00	12.37	2.62	0.93	97.07	86.71	86.71	10.5115					
300.00	0.11	93.50	440.00	16.48	3.19	0.98	94.20	91.61	91.61	11.1051					
300.00	0.14	90.50	420.00	20.30	3.58	0.99	92.30	89.50	89.50	10.8491					
300.00	0.17	87.50	400.00	23.20	3.81	0.96	88.54	83.33	83.33	10.3203					
300.00	0.20	84.50	380.00	27.08	3.91	0.96	85.76	75.09	75.09	9.1025					
300.00	0.23	81.50	360.00	30.03	3.89	0.86	83.04	66.06	66.06	8.0080					
300.00	0.26	78.50	340.00	32.70	3.78	0.80	80.36	57.05	57.05	6.9102					
300.00	0.29														

#### 2. Read average effective mass

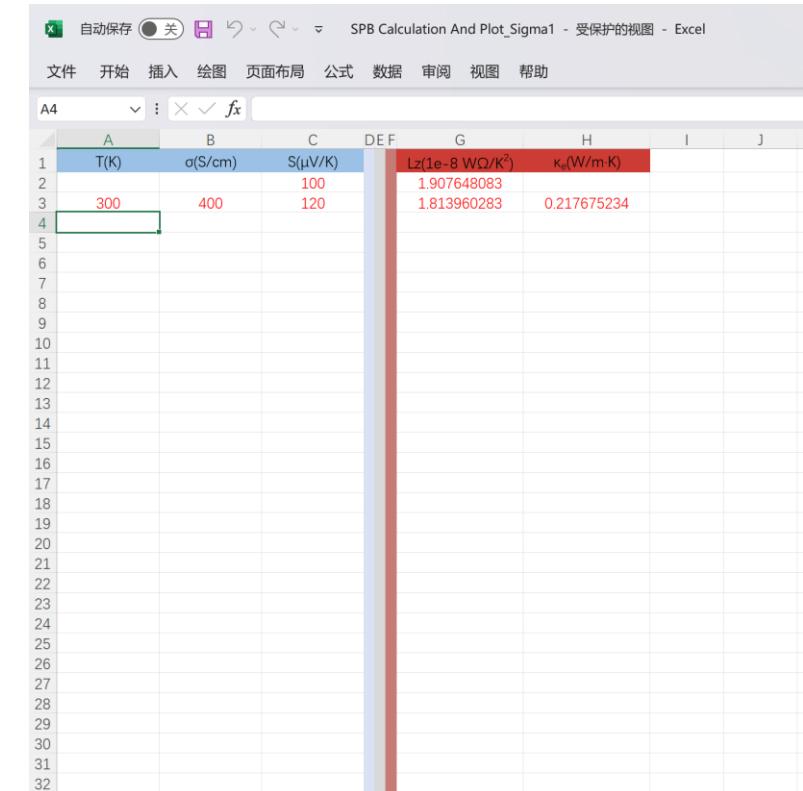
A	B	C	D	E	F	G	H	I	J	K	L	M	N	P	Q
Temperature(K)	$n(10^19 \text{ cm}^{-3})$	$\mu(\text{cm}^2/\text{V}\cdot\text{s})$	$S(\mu\text{V/K})$												
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300.00	0.26	78.50	340.00	32.70	3.78	0.80	80.36	57.05	57.05	6.9102					
300.00	0.29														

#### 3. Plot



Input

Output



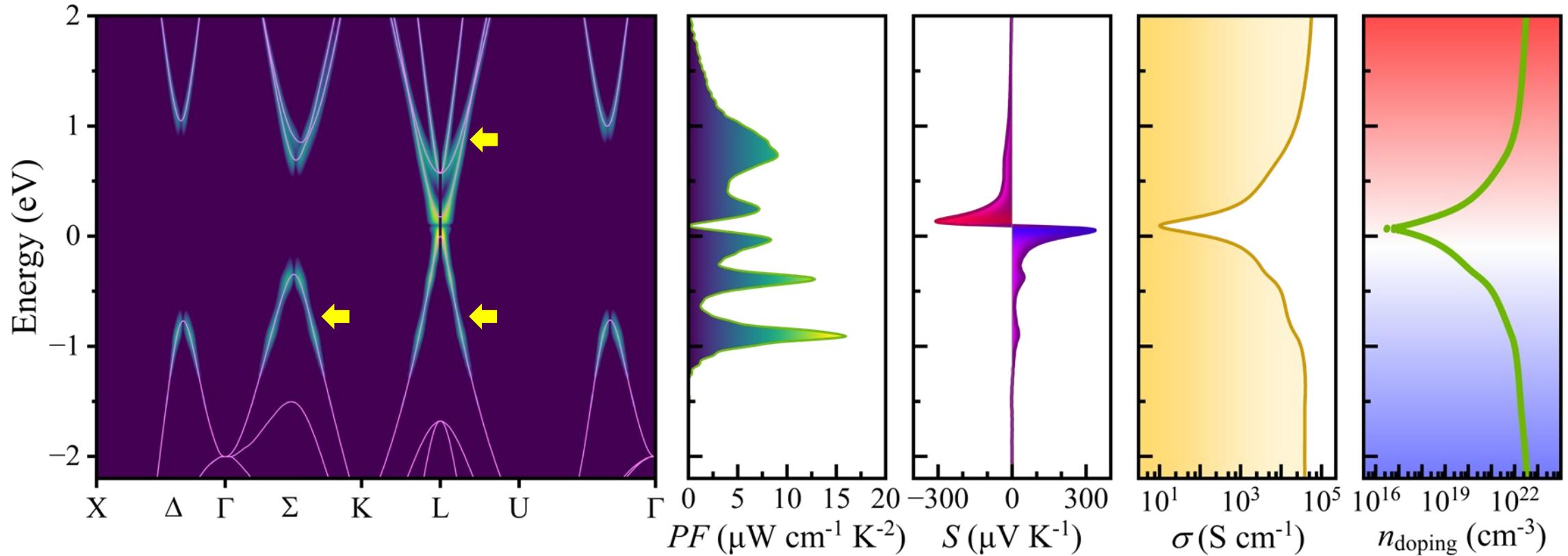
◆ 抛物带模型的易用性使其能够高效的被用于实验数据处理和分析，并指导材料性能优化

# 抛物带模型的局限性

- 功率因子分布函数  $PF_s(\varepsilon, k; T)$

◆  $PF_s(E, k; T) = \sigma_s(E, k; T) \cdot S^2(E; T)$

$$PF(E_F; T) = \sum_{\Omega_k} \int_{-\infty}^{+\infty} PF_s(E, k; T) \cdot \left( -\frac{\partial f_0}{\partial E} \right) dE$$



◆ 价带/导带深处的线性区域部分对  $PF$  的贡献同样不容忽视，对其它电输运参数也有重要影响

# 抛物带模型的局限性

## ● Modified Pisarenko Plots ( $S - n_r$ )

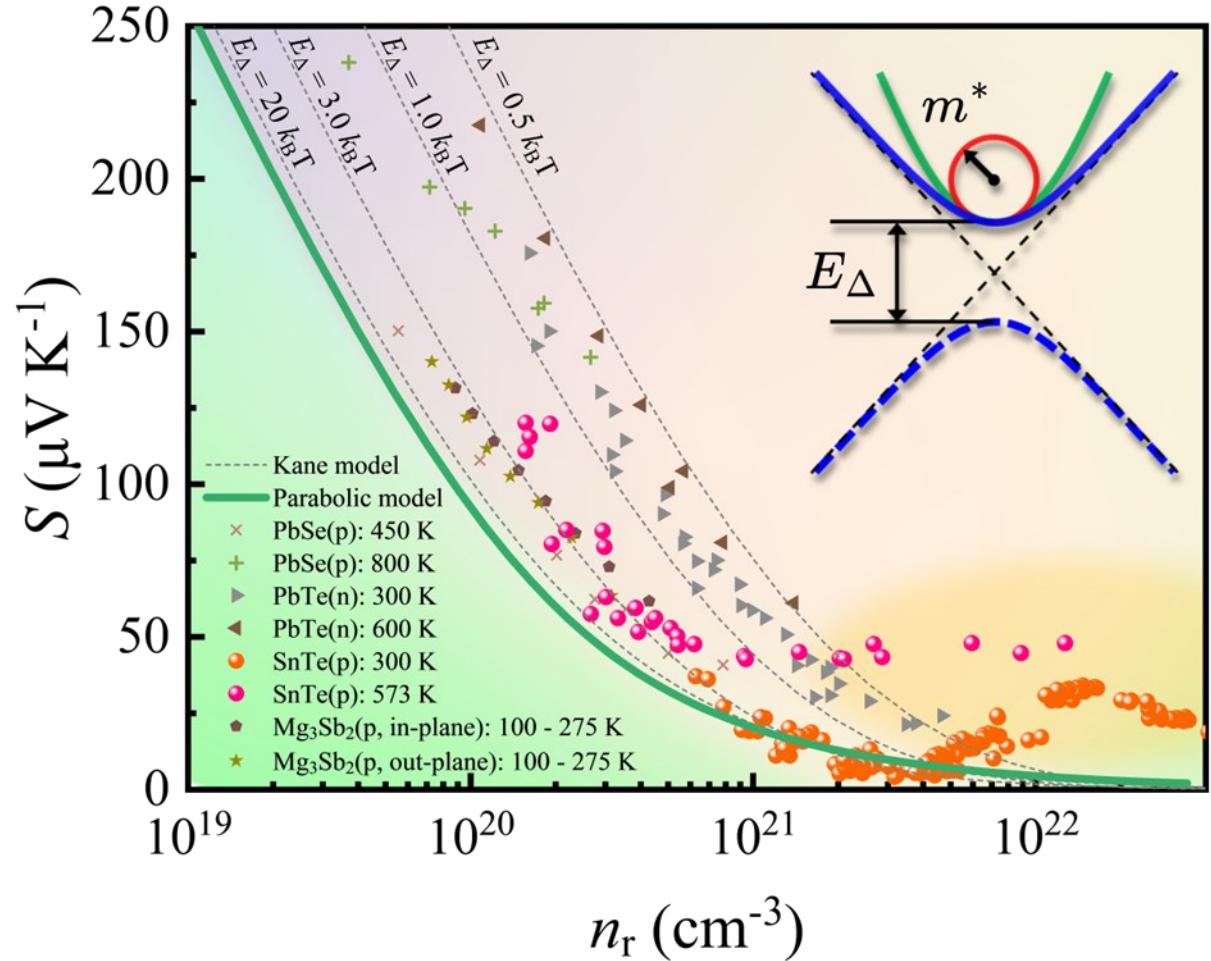
❖ 抛物带模型:  $E = \frac{\hbar^2 k^2}{2 m^*}$

- $E$  随着  $k$  增加始终平方关系增长
- $S - n_r$  与材料无关

❖ Kane模型:  $E \left(1 + \frac{E}{E_\Delta}\right) = \frac{\hbar^2 k^2}{2 m^*}$

- $E$  随着  $k$  增加由平方关系渐变到线性关系
- $S - n_r$  依赖于  $E_\Delta/k_B T$  值
- $E_\Delta \rightarrow \infty$  时退化到抛物带模型

❖ 约化载流子浓度:  $n_r = n / \left( \frac{m^*}{m_e} \frac{T}{T_r} \right)^{3/2}$

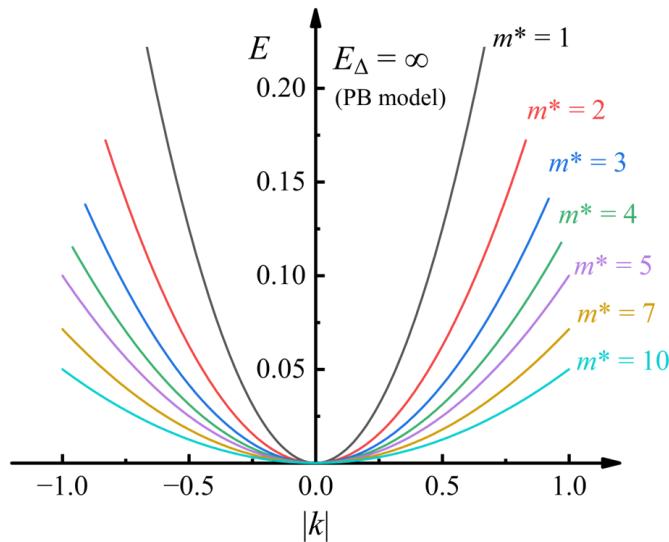


◆ 考虑线性能带区域影响的 Kane 模型能更好解释试验结果

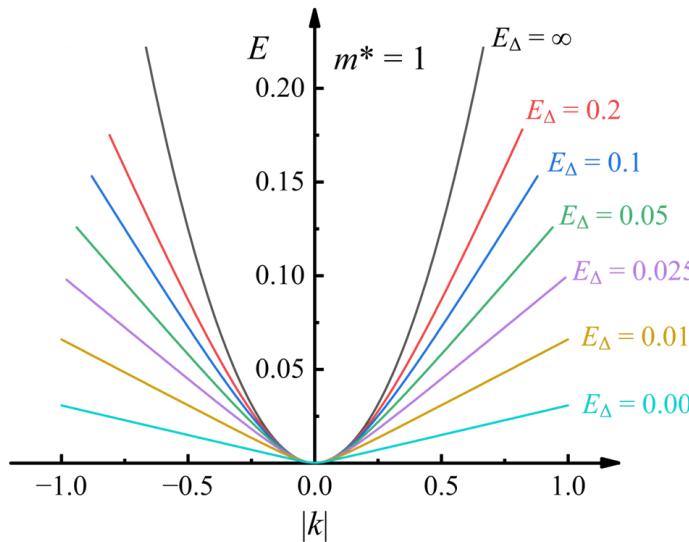
# 抛物带模型的局限性

## ● Kane 模型 vs. 抛物带模型

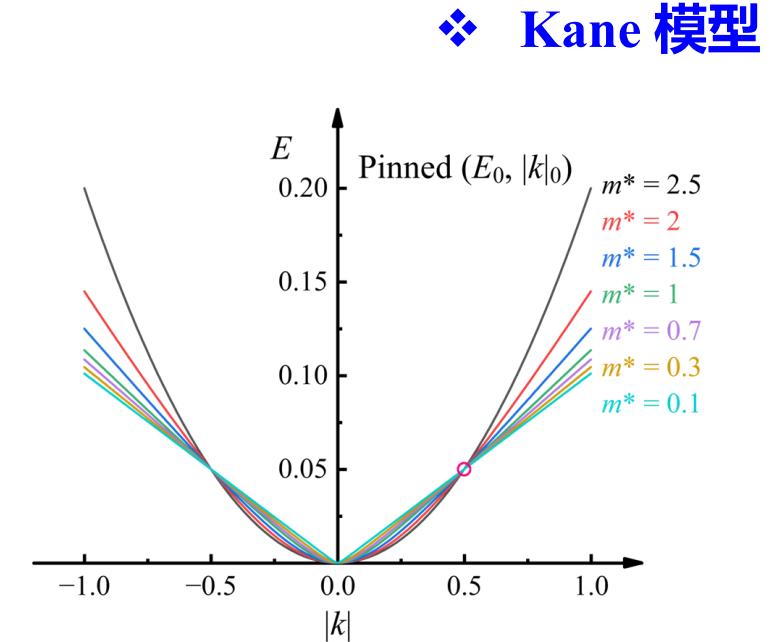
### ❖ 抛物带模型



有效质量  $m^*$  对能带的影响  
( $E_{\Delta}$  固定在  $\infty$ )



参数  $E_{\Delta}$  对能带的影响  
(固定  $m^*$ )

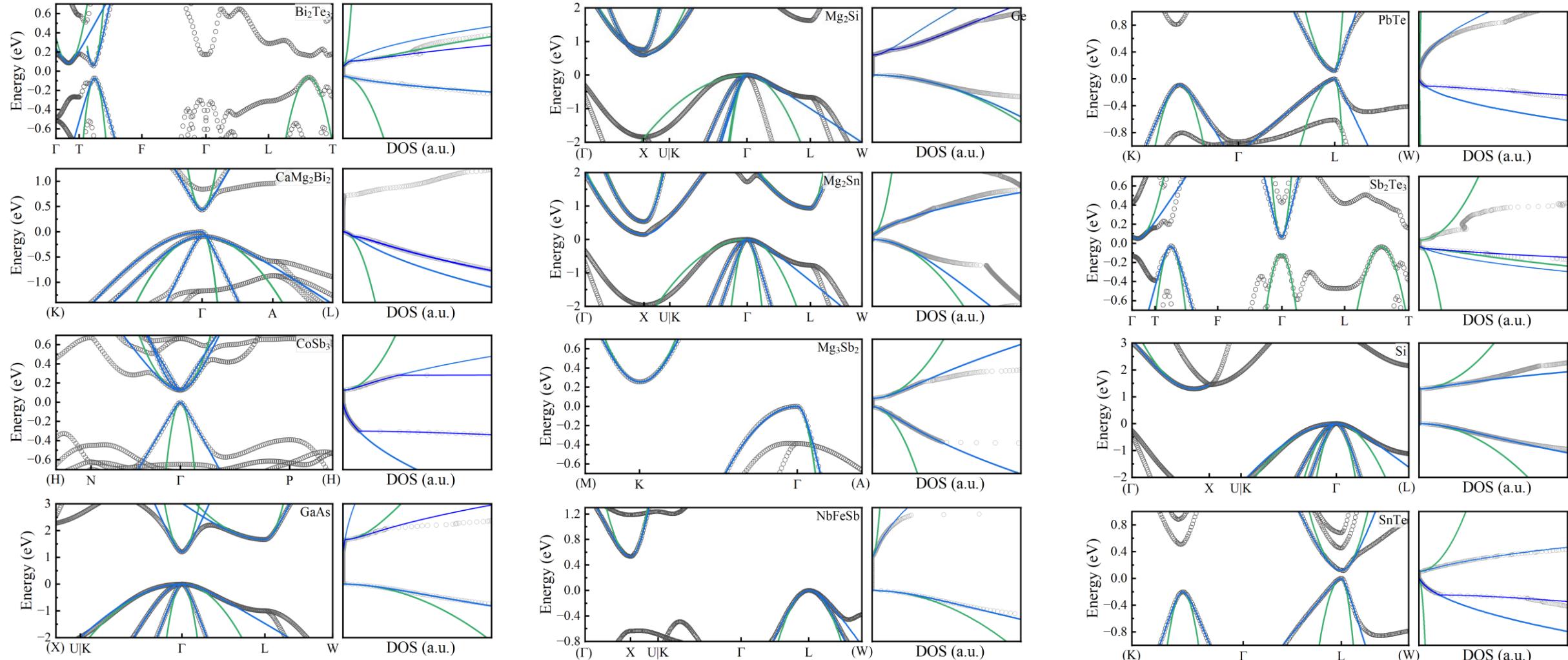


协同调整  $(m^*, E_{\Delta})$  对能带的影响  
(固定经过  $(E_0, |k|_0)$  点)

◆ Kane 模型引入了新的参数  $E_{\Delta}$  与  $m^*$  共同描述能带结构，能够更好拟合能带中的线性区域

# 抛物带模型的局限性

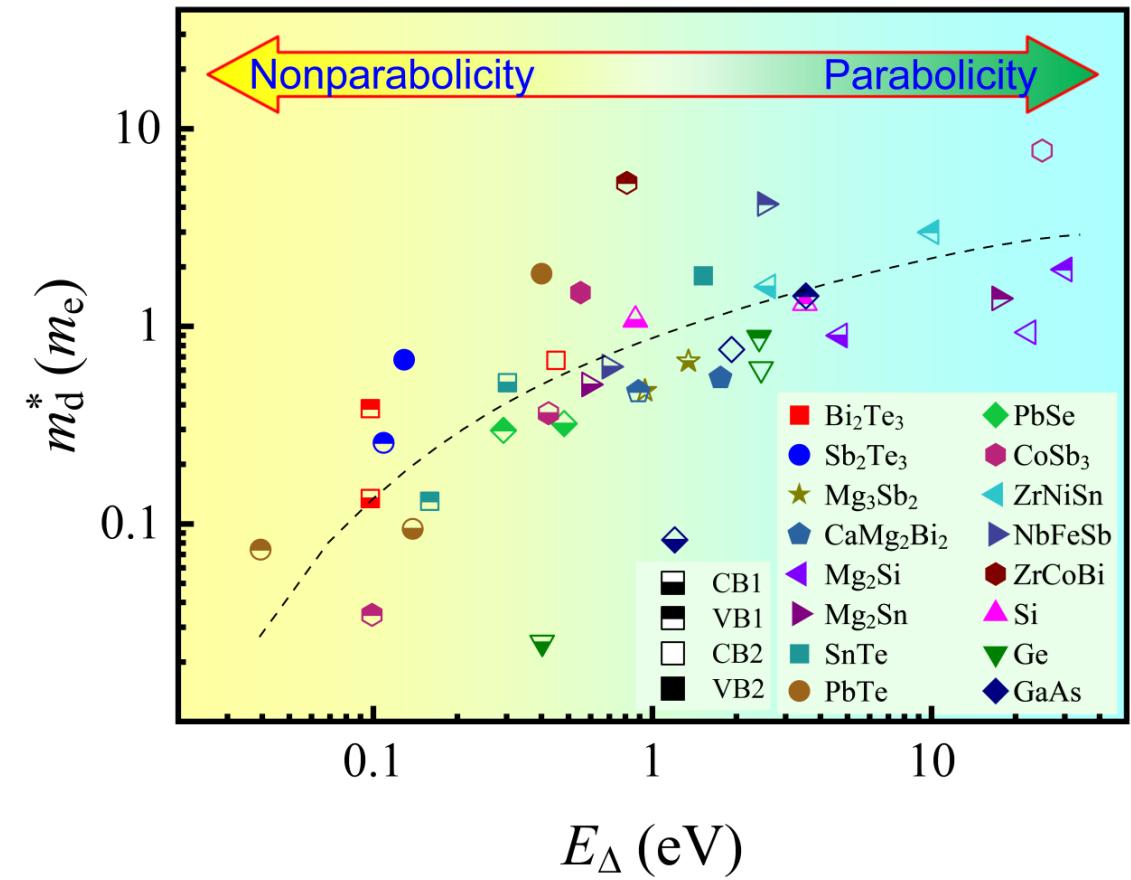
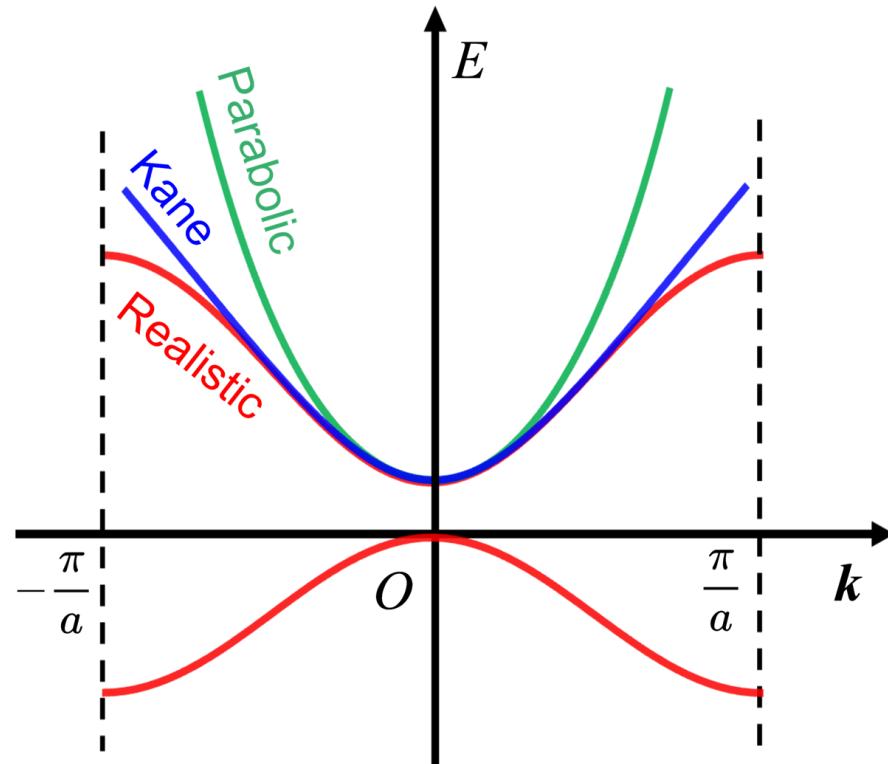
## ● Kane 模型 vs. 抛物带模型



◆ Kane 模型引入了新的参数  $E_\Delta$  与  $m^*$  共同描述能带结构，能够更好拟合能带中的线性区域

# 抛物带模型的局限性

## ● Kane 模型 vs. 抛物带模型

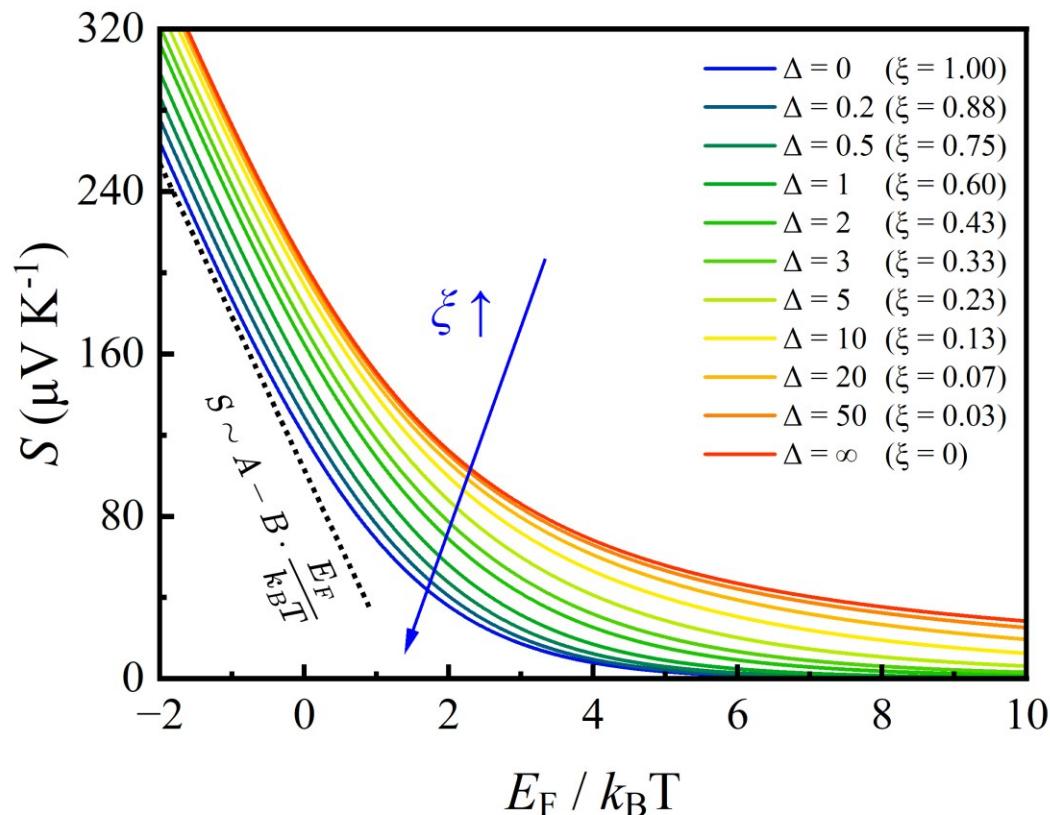


◆ Kane 模型作为抛物带模型的“超集”，能够更加精准的拟合常规半导体材料的能带极值点

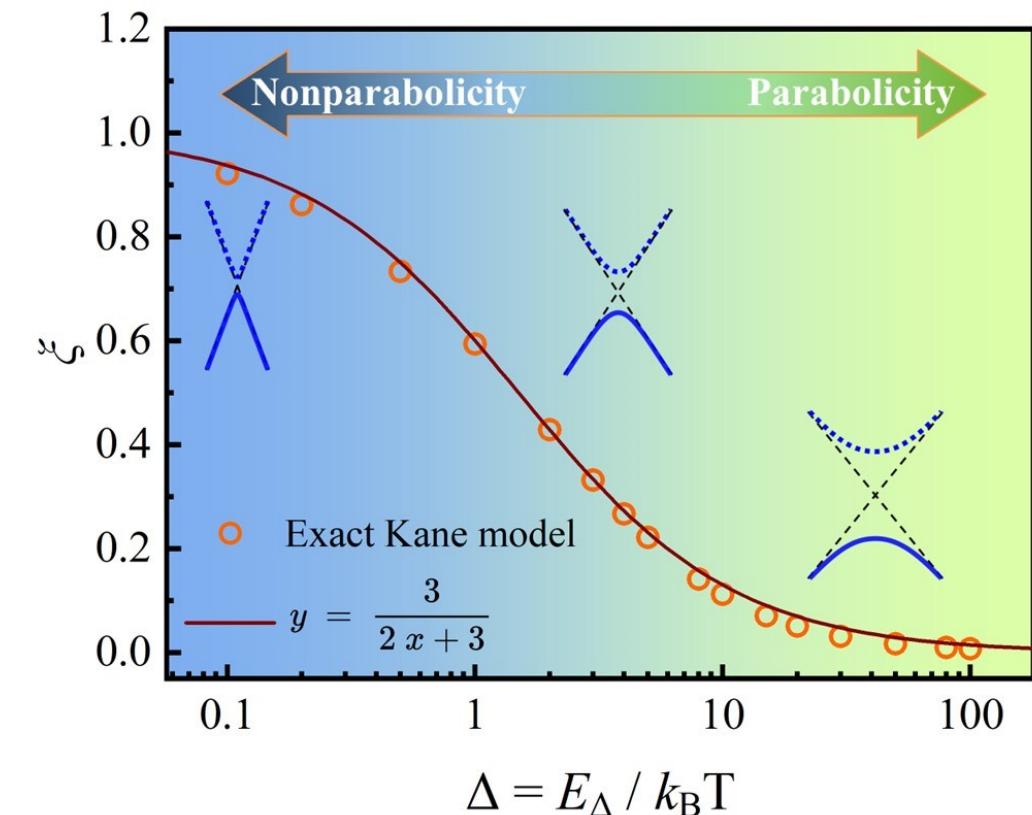
- Kane模型的非抛物性:  $\xi \approx 3/(2\Delta + 3)$

❖ 定义: 能带非抛物性因子  $\xi$

$$\xi \stackrel{\text{def}}{=} \lim_{E_F \rightarrow -\infty} \frac{S^{PB}(E_F; T) - S(E_F; T)}{k_B/q}$$

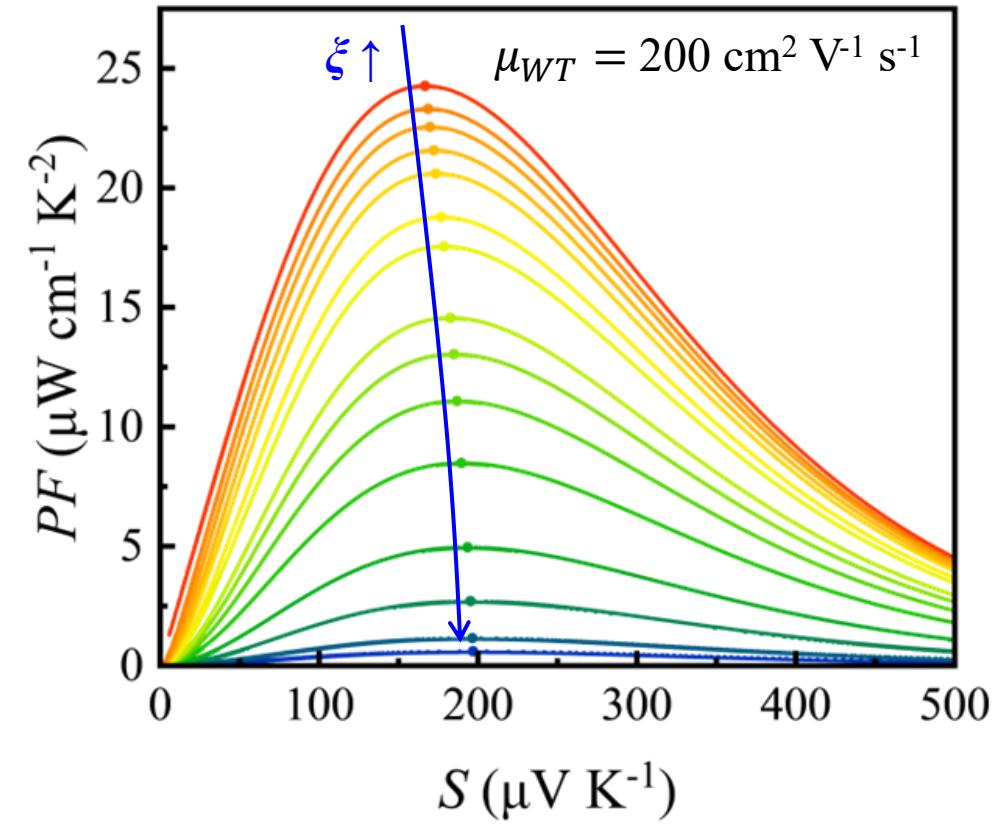
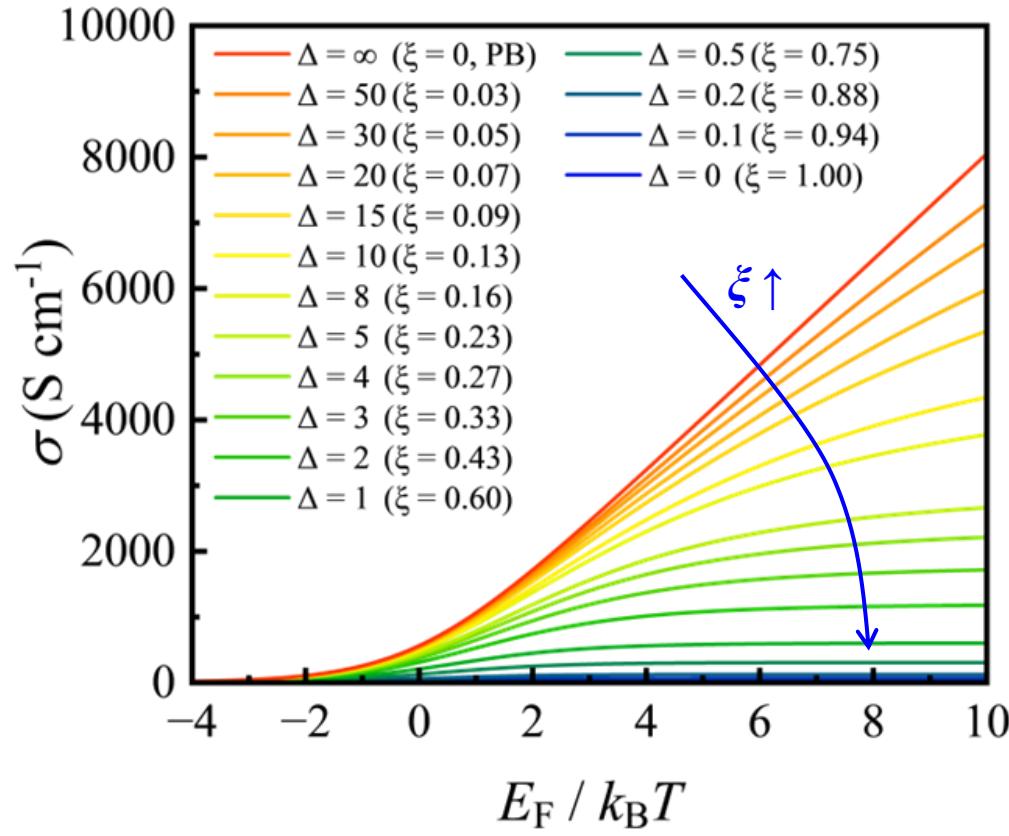


$\Delta \rightarrow \infty \rightarrow \xi = 0$ : 理想化的抛物线型能带 (经典SPB模型) ;  
 $0 < \xi < 1$ : 能带介于线性和抛物线形之间;  
 $\Delta \rightarrow 0 \rightarrow \xi = 1$ : 能带完全退化为线性关系。



- 对电导率和功率因子的影响

$$\diamond \quad \beta^* = \frac{PF_{max}}{PF_{max}^{PB}} \approx (1 - \xi)^2$$



◆ 当固定  $m^*$  时，电导率和峰值功率因子随着能带非抛物性因子  $\xi$  的增加而降低，损伤热电性能

- 对  $L$  -  $S$  关系的影响（通用模型构建  $\Rightarrow$ ）

$$L_0 = 2 - 2\xi + 2\xi^2$$

$$p_\xi = -0.33 + 6.90\xi - 7.78\xi^2 + 2.75\xi^3$$

$$q_\xi = -0.14 + 4.08\xi - 2.13\xi^2$$

❖ 重掺杂半导体： $S \rightarrow 0$

➤  $L \equiv \frac{\pi^2}{3} \left( \frac{k_B}{q} \right)^2$

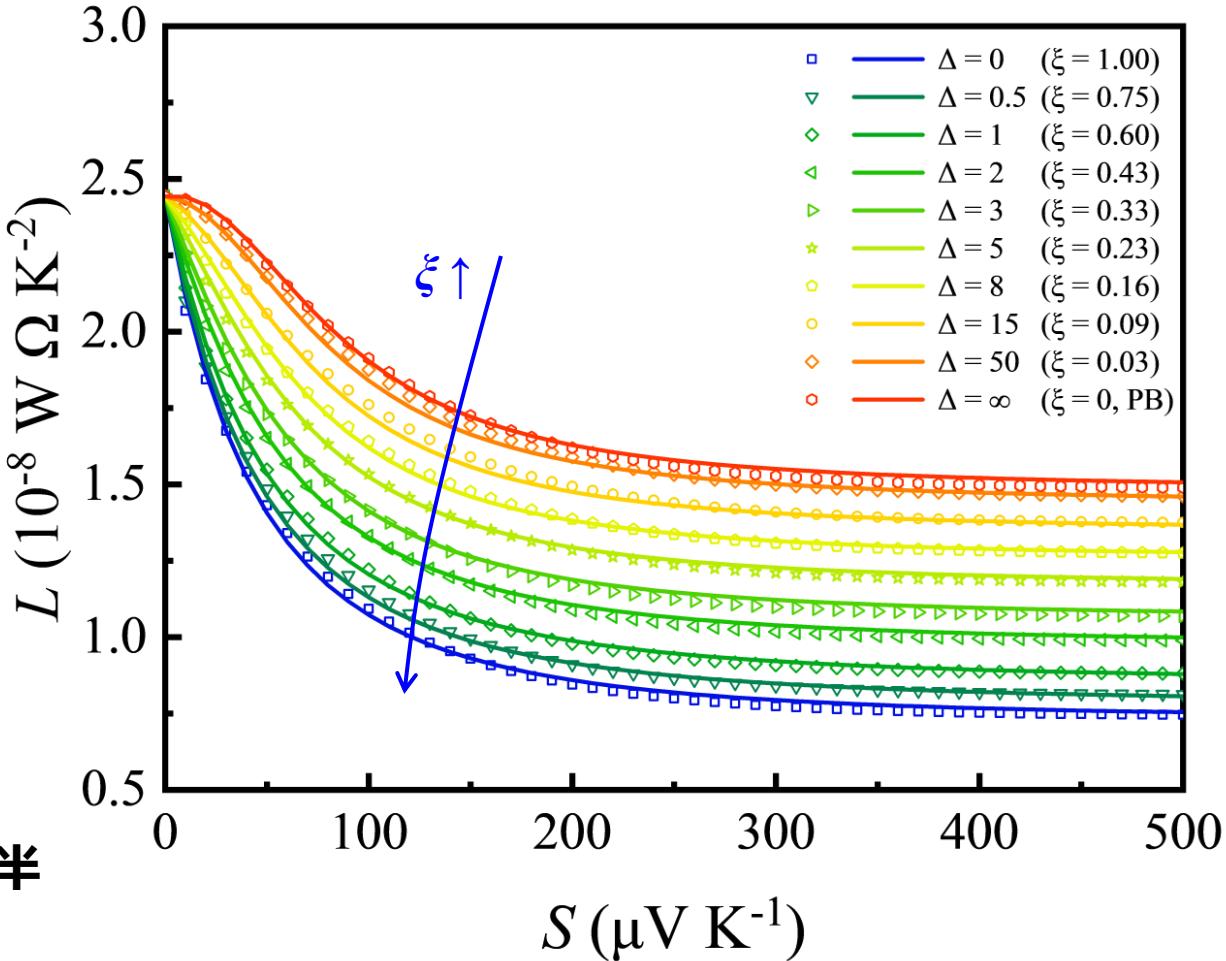
➤  $L$  不受  $\xi$  影响，与金属材料一样

❖ 本征半导体： $S \rightarrow \infty$

➤  $L = L_0 \left( \frac{k_B}{q} \right)^2 \approx (2 - 2\xi + \xi^2) \left( \frac{k_B}{q} \right)^2$

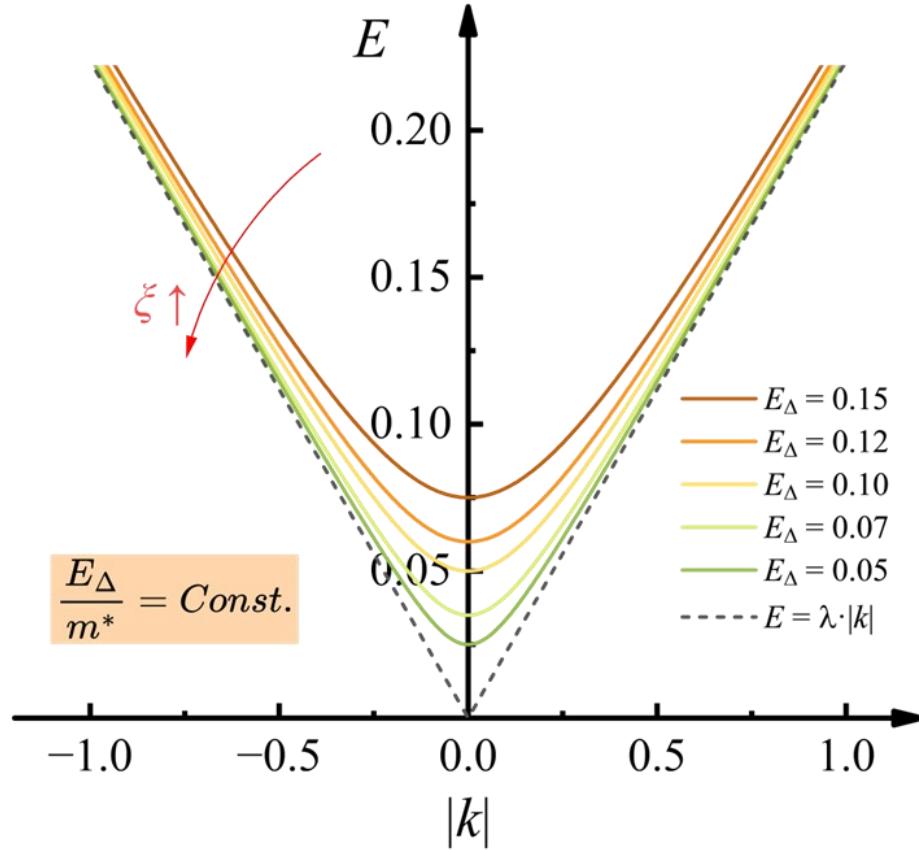
➤  $L$  随着  $\xi$  增加而减小，最低仅为抛物带模型的一半

❖  $L = \frac{\pi^2/3 + p_\xi S_r + L_0 S_r^2}{1 + q_\xi S_r + S_r^2} \left( \frac{k_B}{q} \right)^2$ , where  $S_r = \frac{S}{k_B/q}$



◆ 洛伦兹常数  $L$  随着  $\xi$  的增加而降低，在低掺杂的本征半导体材料中  $L$  可降低 50%

## ● 能带尖锐化设计



$$PF_{max} = C \cdot (1 - \xi)^2 \mu_{WT}$$



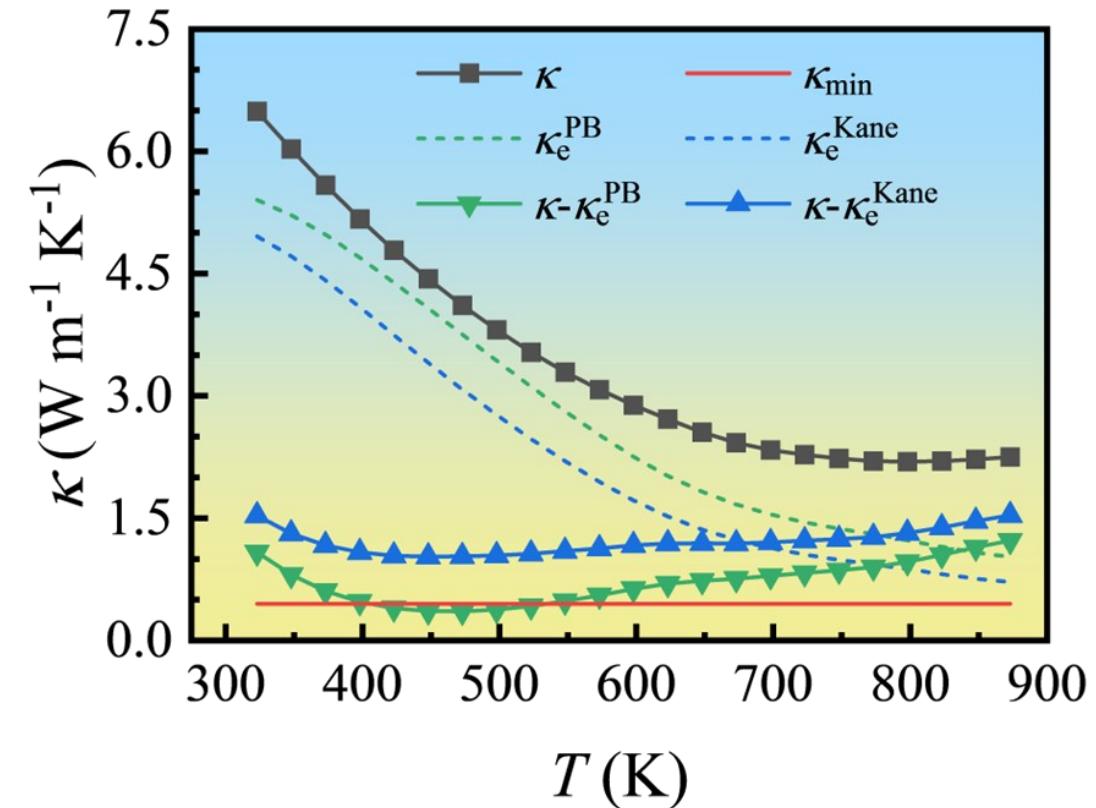
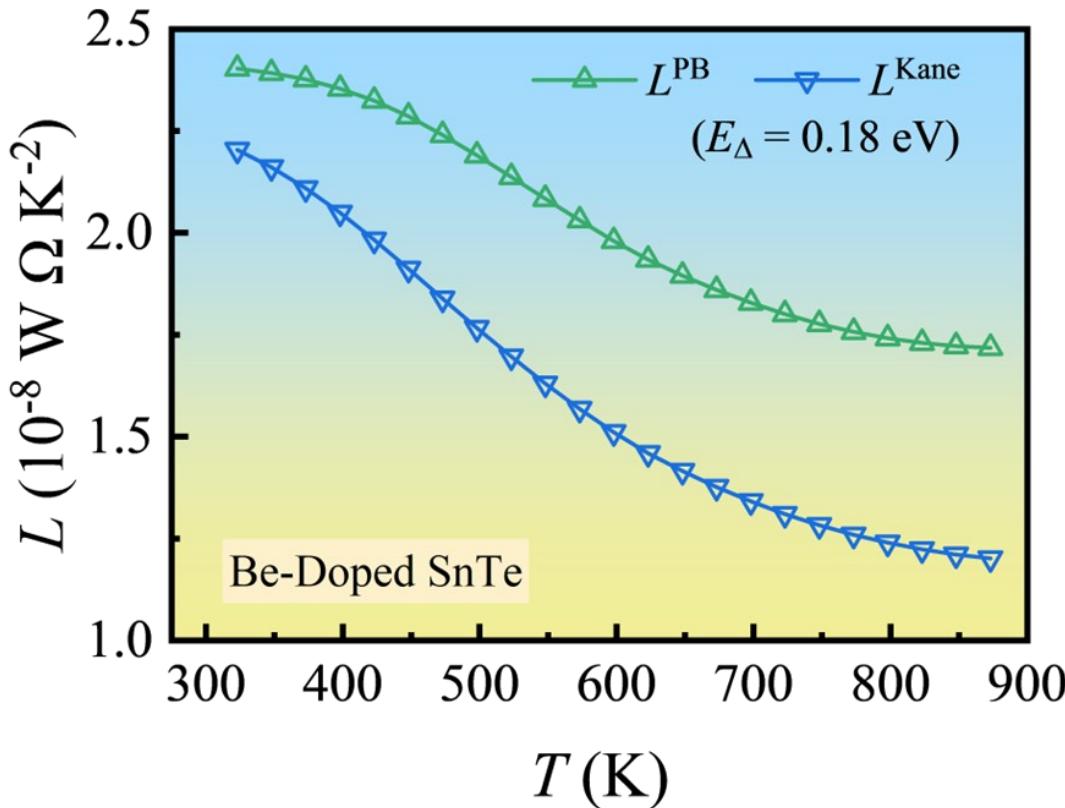
$$\mu_{WT} \propto \frac{1}{m^*} \propto \frac{1}{E_\Delta} \propto \frac{\xi}{1 - \xi}$$



$$PF_{max} \propto \xi \cdot (1 - \xi)$$

◆ 在进行能带尖锐化调控（固定  $E_\Delta/m^*$ ）时，峰值功率因子随  $\xi$  先上升后下降，在  $\xi = 0.5$  取得最大值

## ● Be掺杂SnTe的晶格热导率估计



◆ 抛物带模型下，Be掺杂SnTe 的晶格热导率估计值低于  $\kappa_{\min}$ ，可通过 Kane 模型克服

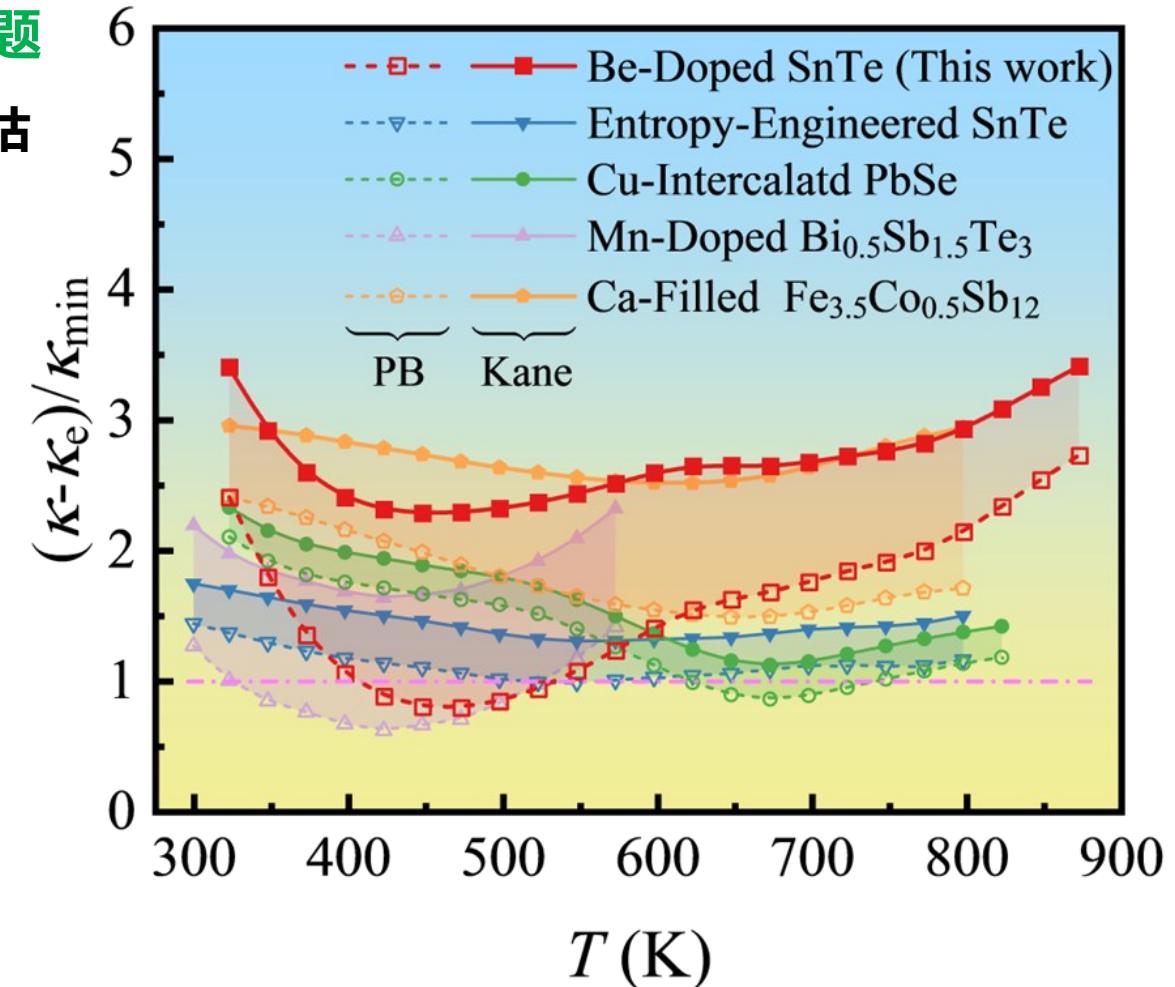
## ● 其它热电材料的晶格热导率估计

### ❖ 克服 Be 掺杂 SnTe 晶格热导率估计过低问题

- 载流子浓度低，非抛物性效应显著， $L$  被高估
- 修正后晶格热导率低于高熵样品，更加合理

### ❖ 解决晶格热导率估计值小于 $\kappa_{\min}$ 的问题

- Be 掺杂 SnTe
- Cu 掺杂 PbSe
- Mn 掺杂  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$



◆  $\xi$  修正的  $L-S$  关系能够获得更加合理晶格热导率估计值

## ■ SPB Calculation And Plot\_Nonparabolicity.xlsx

- Gitee仓库 <https://gitee.com/joulehit/rSPB> ➔ 国内访问更流畅
- Github仓库 <https://github.com/JianboHIT/rSPB> ➔ 更新/纠错更及时



**Ref:** J. Zhu, M. Liu, X. Dong, J. Li, P. Liu, X. Chen, Z. Liu, Y. Zhang, F. Guo, J. Sui, Revisiting thermoelectric transport properties through a band nonparabolicity factor, *National Science Review*, 2025:nwaf216,

SPB Calculation And Plot\_Nonparabolicity1 - Excel

The screenshot shows an Excel spreadsheet titled "SPB Calculation And Plot\_Nonparabolicity1". The data is organized into columns A through J. Row 1 contains headers: T(K), σ(S/cm), S(μV/K), EΔ(eV), Nonparabolicity\_Factor\_ξ, Lz(1e-8 WΩ/K²), and κe(W/m·K). Rows 2 through 5 provide data points. Row 2 has values 300, 400, 100, 0.15, 0, 1.907648083, and 0.22891777. Row 3 has values 300, 400, 100, 0.15, 0, 1.907648083, and 0.22891777. Row 4 has values 300, 400, 100, 0.15, 0.205415884, 1.555840928, and 0.186700911. Row 5 has values 300, 400, 100, 0.15, 0.205415884, 1.555840928, and 0.186700911. The Nonparabolicity\_Factor\_ξ column is highlighted in red.

A	B	C	D	E	F	G	H	I	J
1	T(K)	σ(S/cm)	S(μV/K)	E <sub>Δ</sub> (eV)	Nonparabolicity_Factor_ξ		Lz(1e-8 WΩ/K <sup>2</sup> )	κ <sub>e</sub> (W/m·K)	
2	300	400	100		0		1.907648083		
3	300	400	100	0.15		0	1.907648083	0.22891777	
4	300	400	100	0.15	0.205415884		1.555840928		
5	300	400	100	0.15	0.205415884		1.555840928	0.186700911	

gitee.com

The screenshot shows a Gitee repository page for "joulehit/rSPB". The "Code" tab is selected. The main branch is "main". There are 48 commits. The repository contains files like "How\_to\_Use.png", "LICENSE", "README.md", "SPB Calculation And Plot.xlsx", "SPB Calculation And Plot\_Nonparabolicity.xlsx" (which is highlighted with a red box), and "SPB Calculation And Plot\_Sigma.xlsx". The last commit, "SPB Calculation And Plot\_Nonparabolicity.xlsx", was made 43 minutes ago.

概览 代码 Issues Pull Requests

main 48 次提交

SPB Calculation And Plot\_Nonparabolicity.xlsx

## 总结与展望

1. 提出了能带非抛物性因子  $\zeta$  参数，量化描述能带偏离抛物线的程度
2. 系统性研究了  $\zeta$  对电输运参数的影响，并构建定量解析关系式
3. 强调了  $\zeta$  对  $L-S$  关系的影响，成功解释部分材料晶格热导率被高估的问题
4. 开发了 Excel 计算模板，降低模型使用难度，提升工作效率
5. 拓展了描述能带结构的新参数，为功能半导体能带设计提供新维度

感谢各位老师！  
敬请指正

哈尔滨工业大学 · 隋解和教授课题组

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汇报人：朱建博