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Connecting Band Structure to Sub-picosecond Spectral Photoemission Properties

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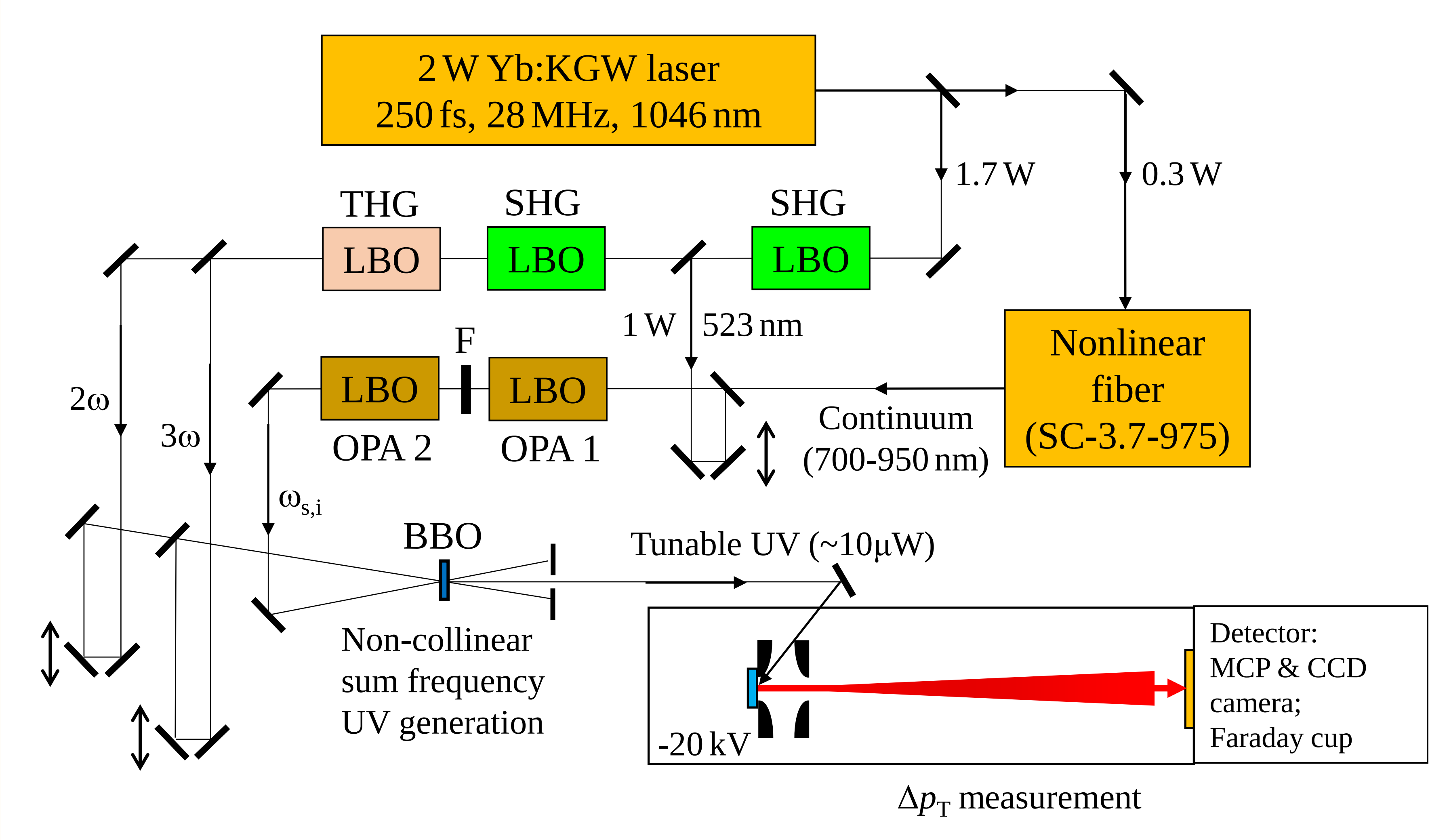
Outline

- GaSb(001)
  - Excited-state thermionic emission (ESTE)
- Cu(111)
  - Sub-threshold (non-surface-state) emission form upper conduction band
- Hf(0001)
  - ‘Sub-Dowell-Schmerge’ spectral *MTE* dependence due to low m^* emission band
- Additional theoretical considerations for (quasi-)instantaneous photoemission
  - Heisenberg Uncertainty
  - Group velocity

Tunable UV radiation source

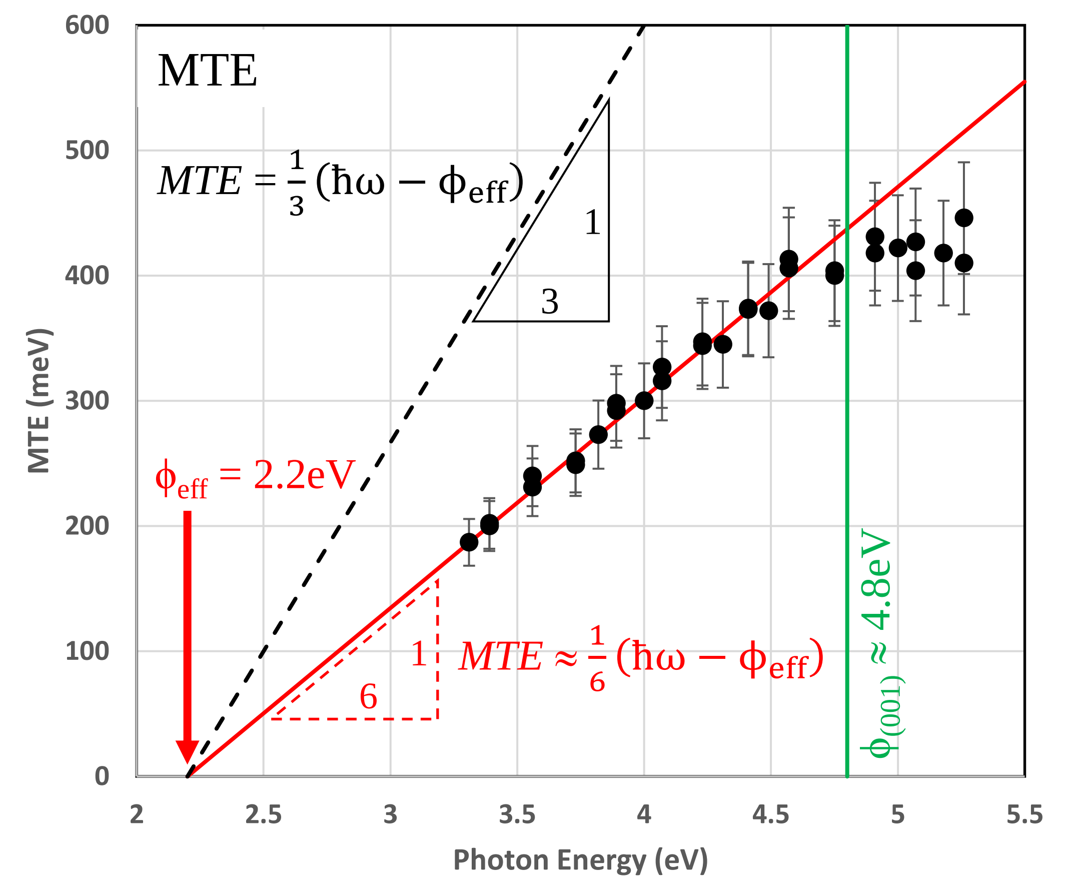
– Laser / NLO based radiation source: 3.0 – 5.3eV (235-410nm)



G. Adhikari et al., *AIP Advances* **9** (2019) 065305

GaSb(001): MTE measurements

– Photoemission data using UV-tunable (235-410nm) sub-picosecond (~0.5ps) laser pulses; GaSb(001) wafer



- Sub-threshold ($\hbar\omega < \phi_{(001)}$) photoemission with $\phi_{eff} = 2.2eV$
- ‘Sub-Dowell-Schmerge’ spectral *MTE* dependence

  $\Rightarrow$ Excited state thermionic emission (ESTE)

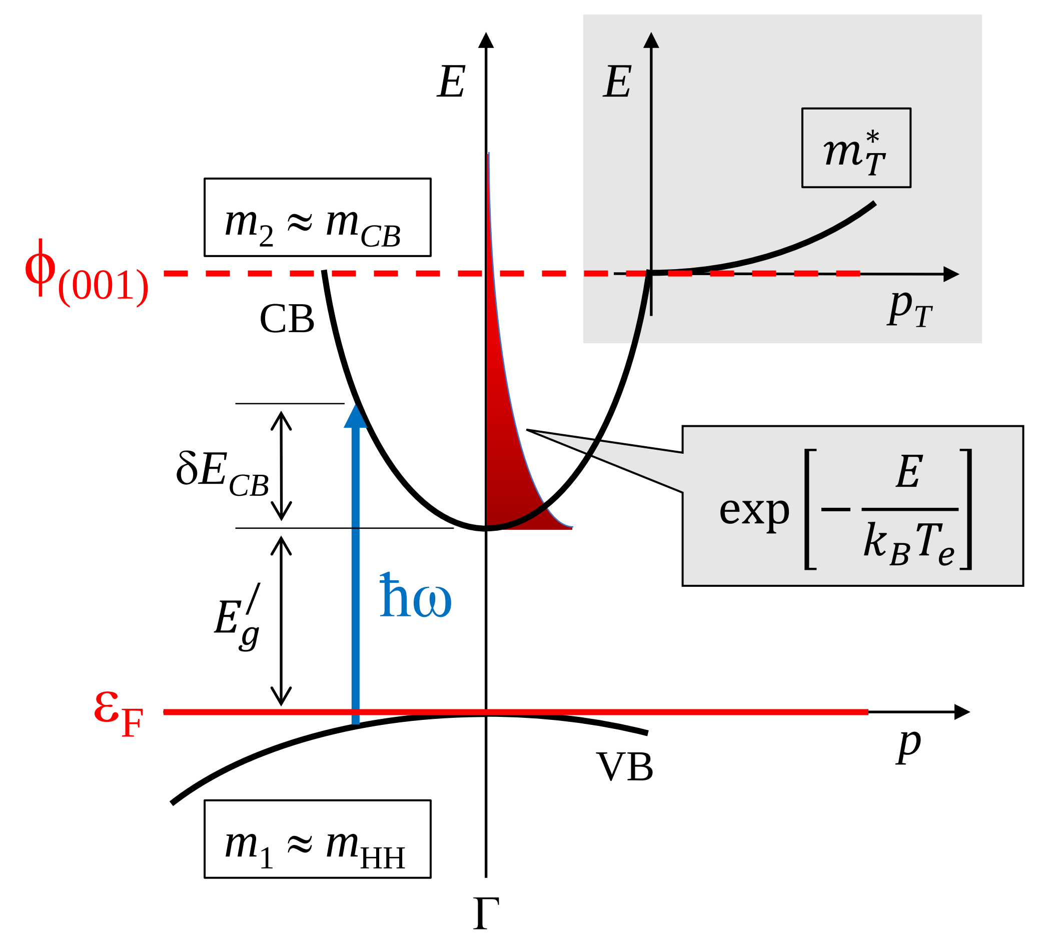
  … Boltzmann tail emission (above vacuum level) from hot thermalized electron distribution photoexcited into upper conduction band with a low effective mass *m**

- Additional contribution from direct one-step photoemission for $\hbar\omega > \phi_{(001)}$

J. A. Berger et al., *Appl. Phys. Lett.* **101** (2012) 194103; G.W. Gobeli & F.G. Allen, *Phys. Rev.* **137** (1965) A245

GaSb(001): ESTE

– Parabolic band approximation



- Photoemission analyses for Boltzmann tail emission:

$$MTE \geq \left|\frac{m_T^*}{m_0}\right| k_B T_e \;\; ; \;\; \left|\frac{m_T^*}{m_0}\right| \rightarrow 1 \text{ for } m_T^* \geq m_0$$

… **no** recipient vacuum density of states

- Thermalized initial photoexcited electron temperature:

$$\frac{3}{2} k_B T_e = \delta E_{CB} = \frac{m_1}{m_1 + m_2}\left(\hbar\omega - E_g^{/}\right)$$

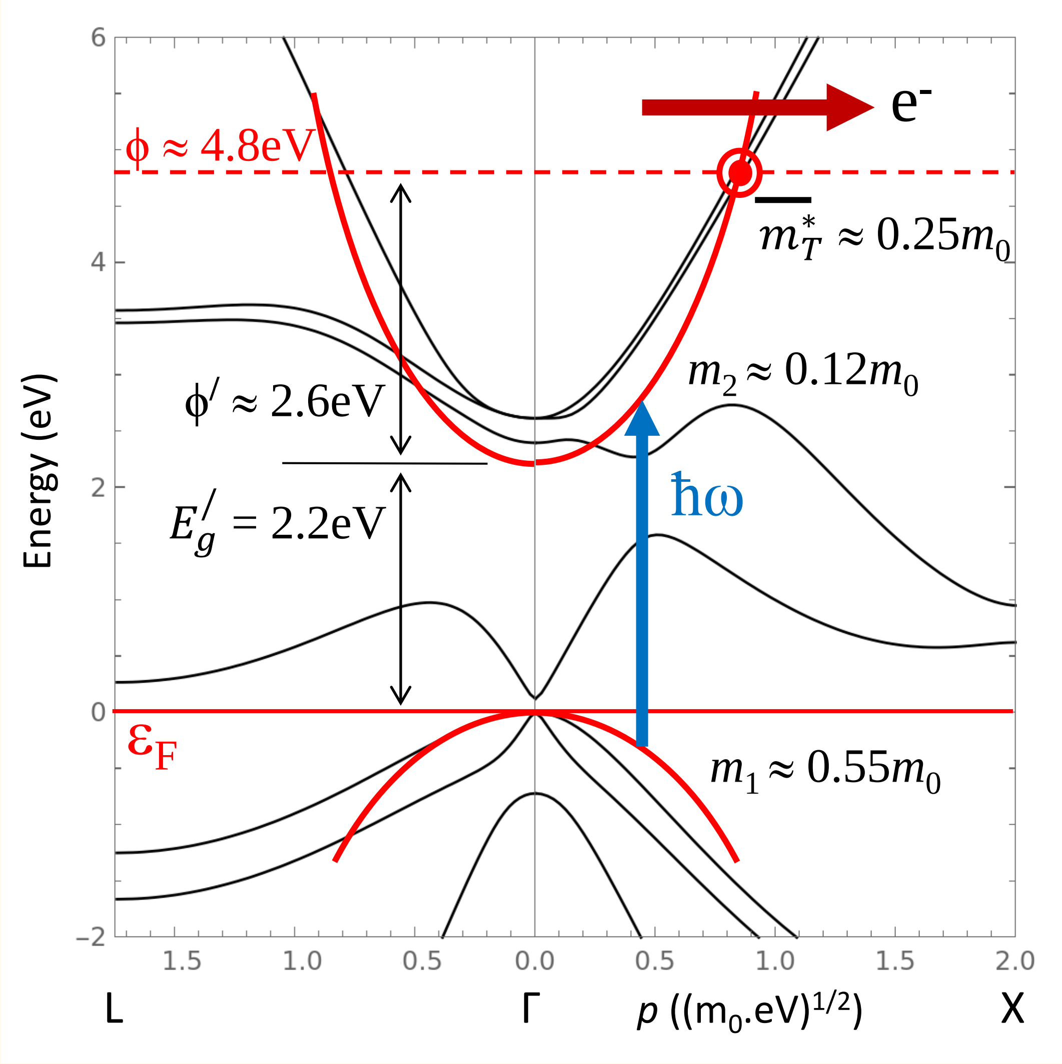
$$\therefore \;\; MTE \geq \frac{2}{3}\left|\frac{m_T^*}{m_0}\right| \frac{m_1}{m_1 + m_2}\left(\hbar\omega - E_g^{/}\right)$$

THUS:

$$E_g^{/} = \phi_{\mathrm{eff}} = 2.2\mathrm{eV} \;\; \text{and} \;\; \left|\frac{m_T^*}{m_0}\right| \frac{m_1}{m_1 + m_2} \approx \frac{1}{4} \quad ??$$

GaSb: Band structure

– Full relativistic calculation with spin-orbit coupling; PAW & PBE functional; **No** ‘scissor’ operator



- Energy gap inconsistencies:

$$\underbrace{\begin{array}{l} E_g^{/}(\text{expt.}) = 2.2\text{eV} \\ E_g(\text{meas.}) = 0.67\text{eV} \end{array}}_{300\text{K}} \qquad \underbrace{\begin{array}{l} E_g^{/}(\text{DFT}) = 2.6\text{eV} \\ E_g(\text{DFT}) = 0.16\text{eV} \end{array}}_{0\text{K}}$$

- Effective masses and predicted *MTE*:

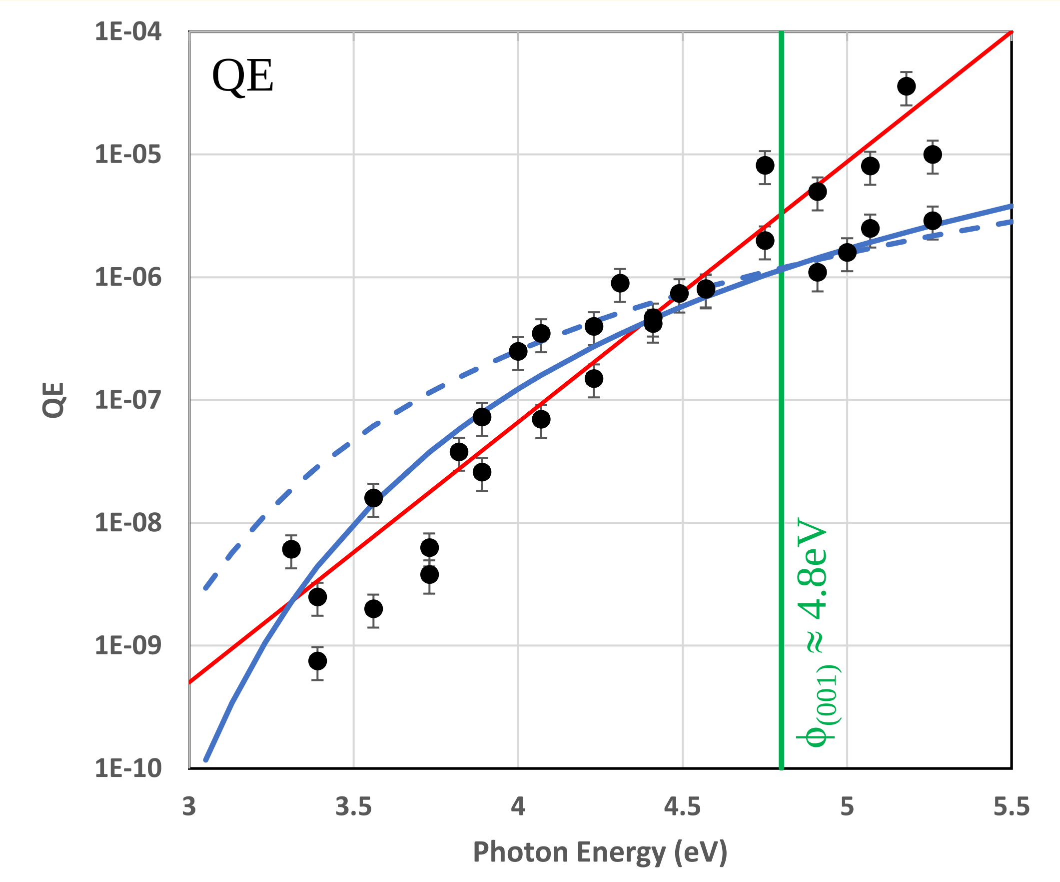
$$\left|\frac{m_T^*}{m_0}\right| \frac{m_1}{m_1+m_2} \approx 0.21$$

$$\therefore \quad MTE \geq \frac{2}{3}\left|\frac{m_T^*}{m_0}\right| \frac{m_1}{m_1+m_2}\left(\hbar\omega - E_g^{/}\right) \approx 0.14\left(\hbar\omega - E_g^{/}\right)$$

… parabolic band approximation

c.f. $MTE_{expt.} \approx \frac{1}{6}\left(\hbar\omega - E_g^{/}\right)$

GaSb(001): Quantum efficiency



- For ħω ≤ $\phi_{(001)}$, *QE* increases by 1,000× as photon energy increases by 1.5eV
  - T_e increases from 7,200K to 17,000K

- *QE*(ħω) difficult to explain by standard thermionic emission
  - ϕ = 4.8eV (—) and ϕ = 2.6eV (- - -)

$$QE = A\,(k_B T_e)^2 \exp\left[-\frac{\phi}{k_B T_e}\right]$$

$$\ldots \text{ with } k_B T_e = \frac{2}{3}\left(\frac{m_1}{m_1+m_2}\right)\left(\hbar\omega - E_g^{/}\right)$$

- Bulk emission band *E*(**p**) and DOS need to be included, as well as vacuum DOS

- Improved *QE* measurements also required
  - More stable tunable UV laser radiation source currently in development

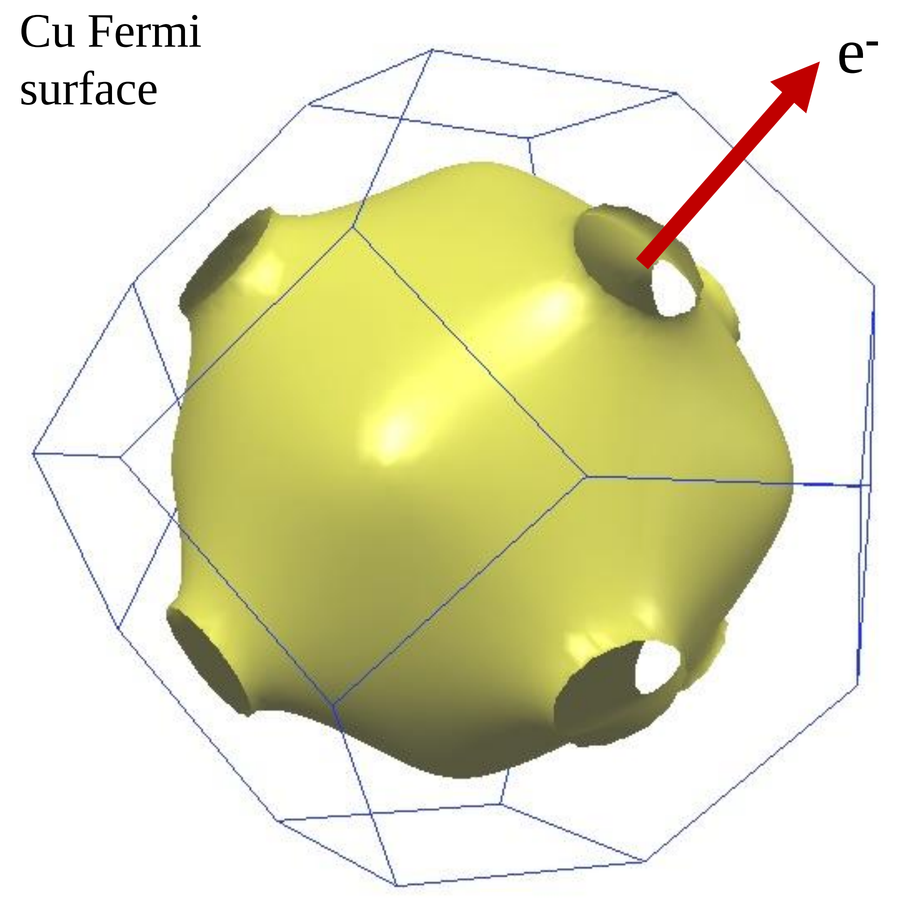
Cu(111) photocathode

- Work function: $\phi_{Cu(111)} = 4.94\text{eV}$
- Photocathode properties:
  – Polished: Surface roughness < 10nm rms
  (**not** atomically flat)
  – Surface **not** clean ($\Delta\phi_{\text{-O-Cu}} \approx -0.4\text{-}0.5\text{eV}$)

  $\Rightarrow$ **No** surface states AND $\phi_{\text{eff.}} \approx 4.5\text{eV}$
- Fermi surface 'hole' in $\Gamma \rightarrow L$ direction

  $\Rightarrow$ Extra $\geq 0.2\text{eV}$ transverse energy required for photoemission from occupied bands

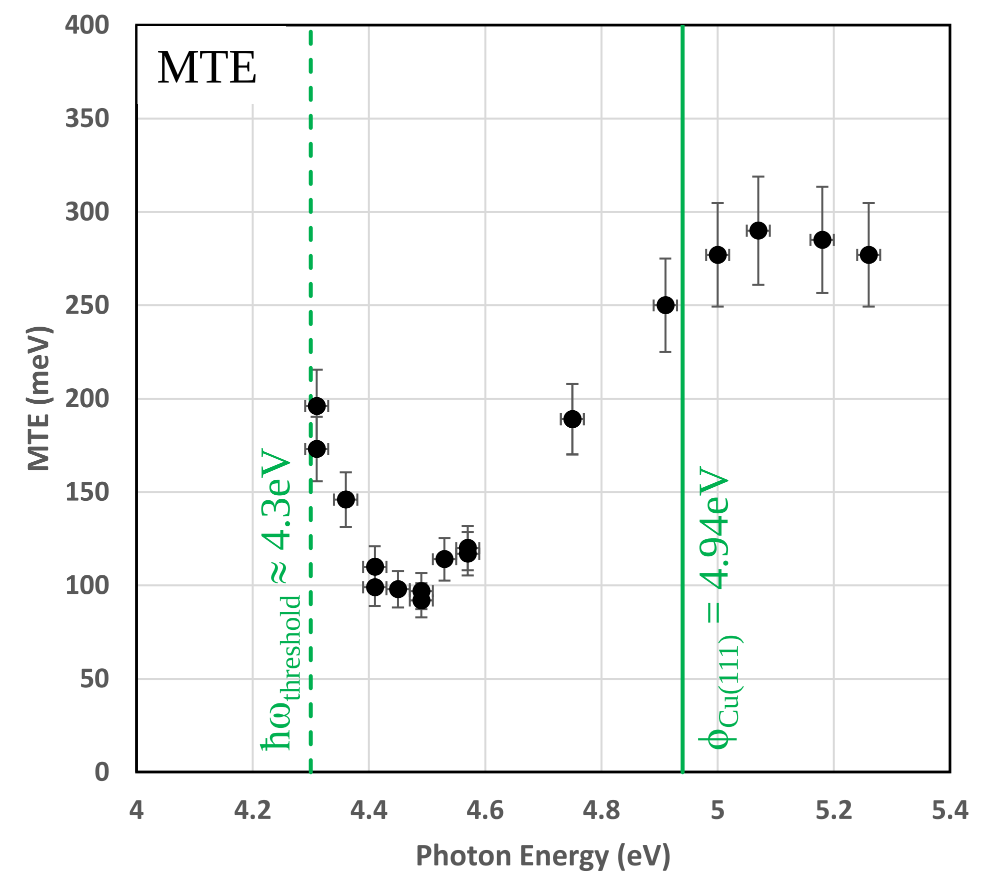
$\therefore$ Expect $\phi_{\text{emission}} \geq 4.7\text{eV}$

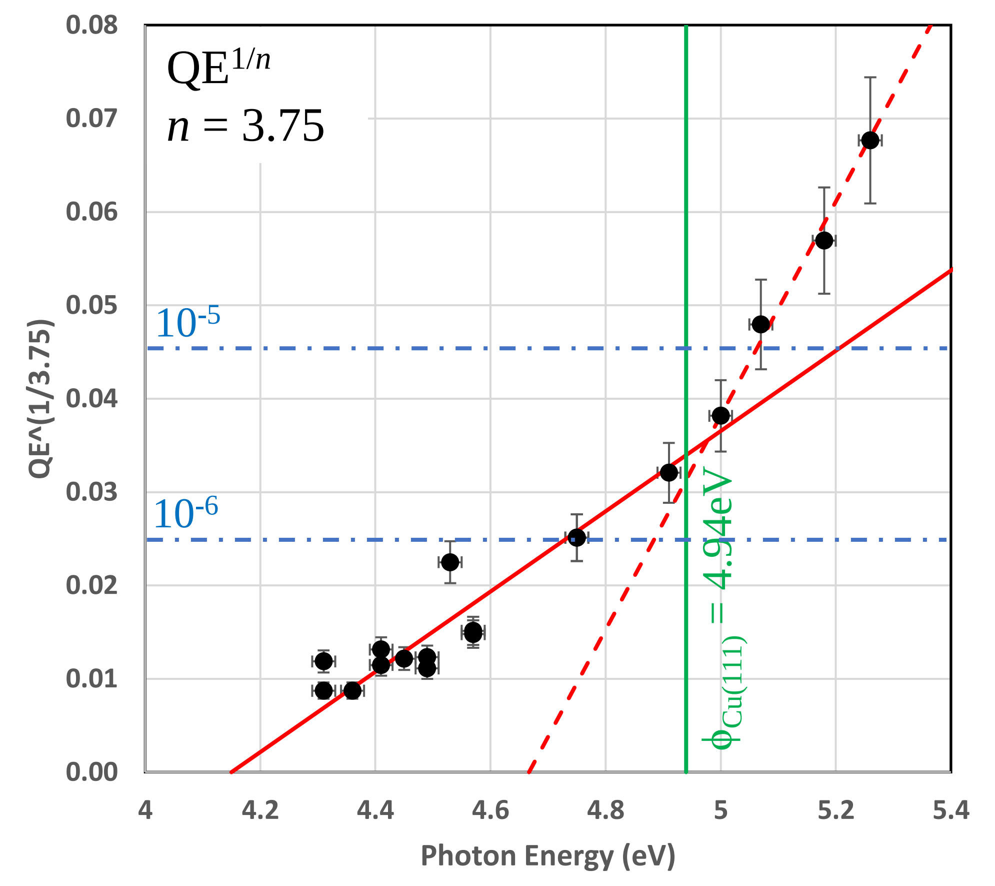


E. Pedersoli et al, *Appl. Phys. Lett.* **93** (2008) 183505; www.phys.ufl.edu/fermisurface

Cu(111): Sub-threshold photoemission

– Photoemission data using UV-tunable (235-410nm) sub-picosecond (~0.5ps) laser pulses



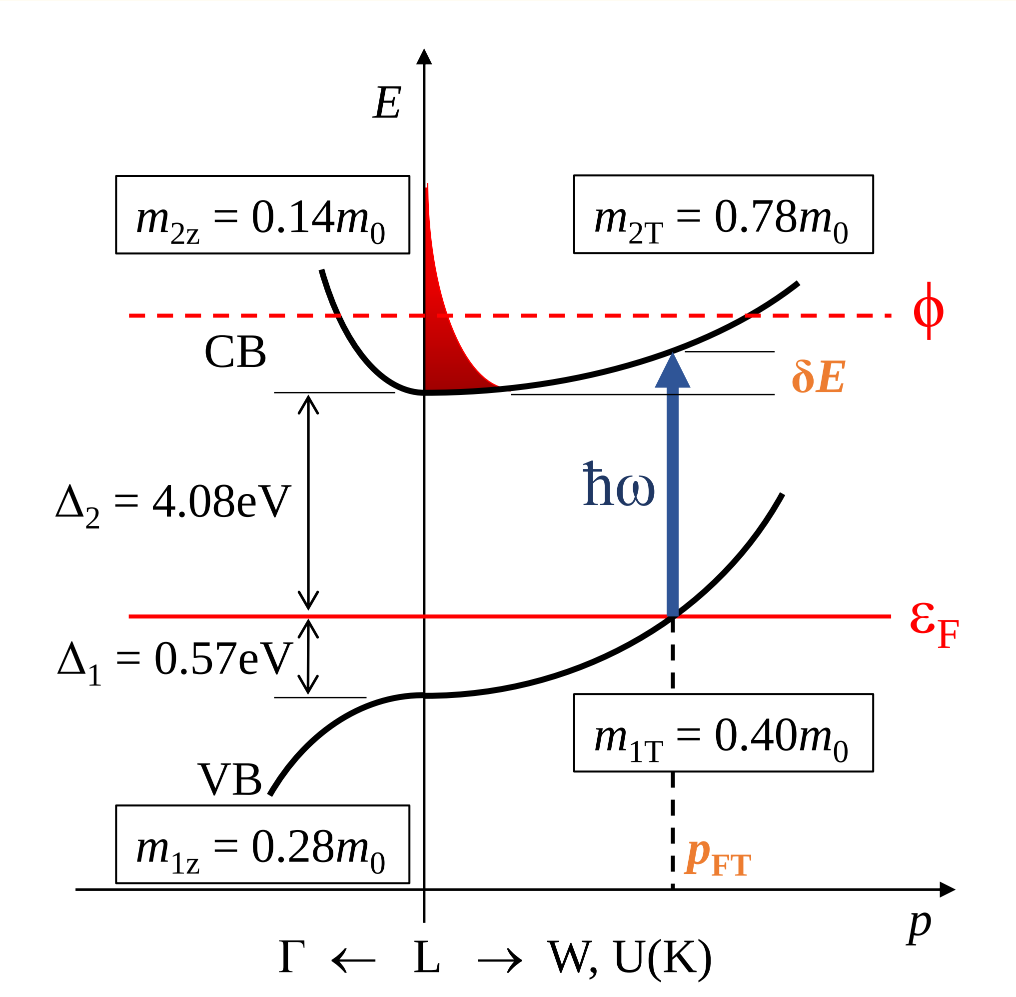


… An ultrafast / band structure effect

G. Adhikari et al., *AIP Advances* **9** (2019) 065305; G.W. Gobeli & F.G. Allen, *Phys. Rev.* **137** (1965) A245

Cu(111): Emission mechanism

– L-point band structure; Parabolic approximation



Emission of the Boltzmann tail (above the vacuum level) of a hot thermalized photo-excited electron distribution:

- At ‘threshold’: ħω ≈ 4.3eV

$$\Rightarrow \delta E = \frac{p_{FT}^2}{2m_{2T}} = \frac{m_{1T}\Delta_1}{m_{2T}} \approx 0.29\text{eV}$$

$$\therefore \ MTE \geq \left|\frac{m_{2T}}{m_0}\right| k_B T_e = \frac{2}{3}\left|\frac{m_{2T}}{m_0}\right| \delta E \approx 150\text{meV}$$

… **no** vacuum states and surface roughness

LEMMA:

$$\hbar\omega = \Delta_2 + \delta E \approx 4.3\text{eV}$$

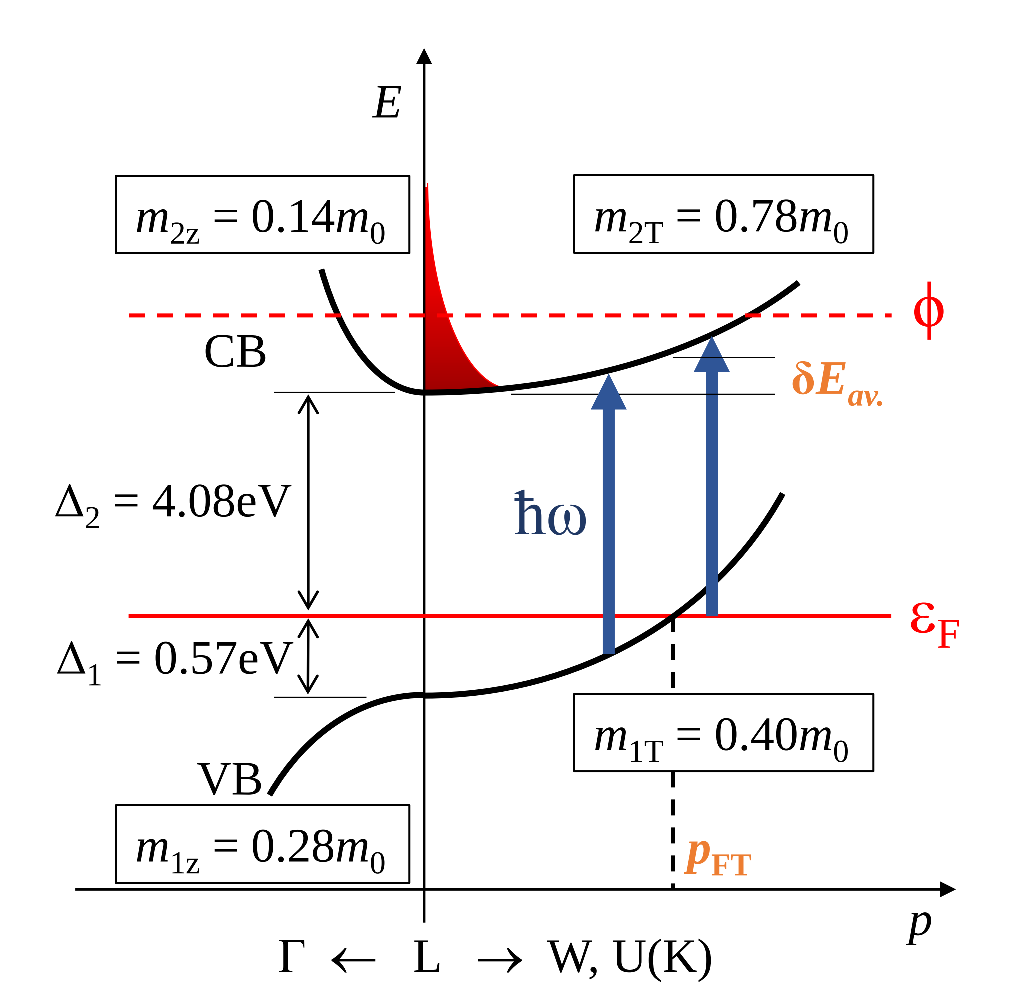
$$\Rightarrow \Delta_2 \approx 4.01\text{eV}$$

… close !

A. Marini et al., *Phys. Rev. Lett.* **88** (2002) 016403

Cu(111): Emission mechanism

– L-point band structure; Parabolic approximation



- At $\hbar\omega \approx 4.5\text{eV} < \Delta_1 + \Delta_2 = 4.65\text{eV}$
  - Hot electron photoexcitation limited by Fermi level
  - More lower energy electrons photoexcited

  $\therefore$ Expect $\delta E_{av.} \leq 0.2\text{eV}$

  $$\Rightarrow MTE \geq \frac{2}{3}\left(\frac{m_{2T}}{m_0}\right)\delta E_{av.} \approx 100\text{meV}$$

- For $\hbar\omega > \Delta_1 + \Delta_2$
  - $\delta E_{av.}$ increases $\Rightarrow$ *MTE* increases again

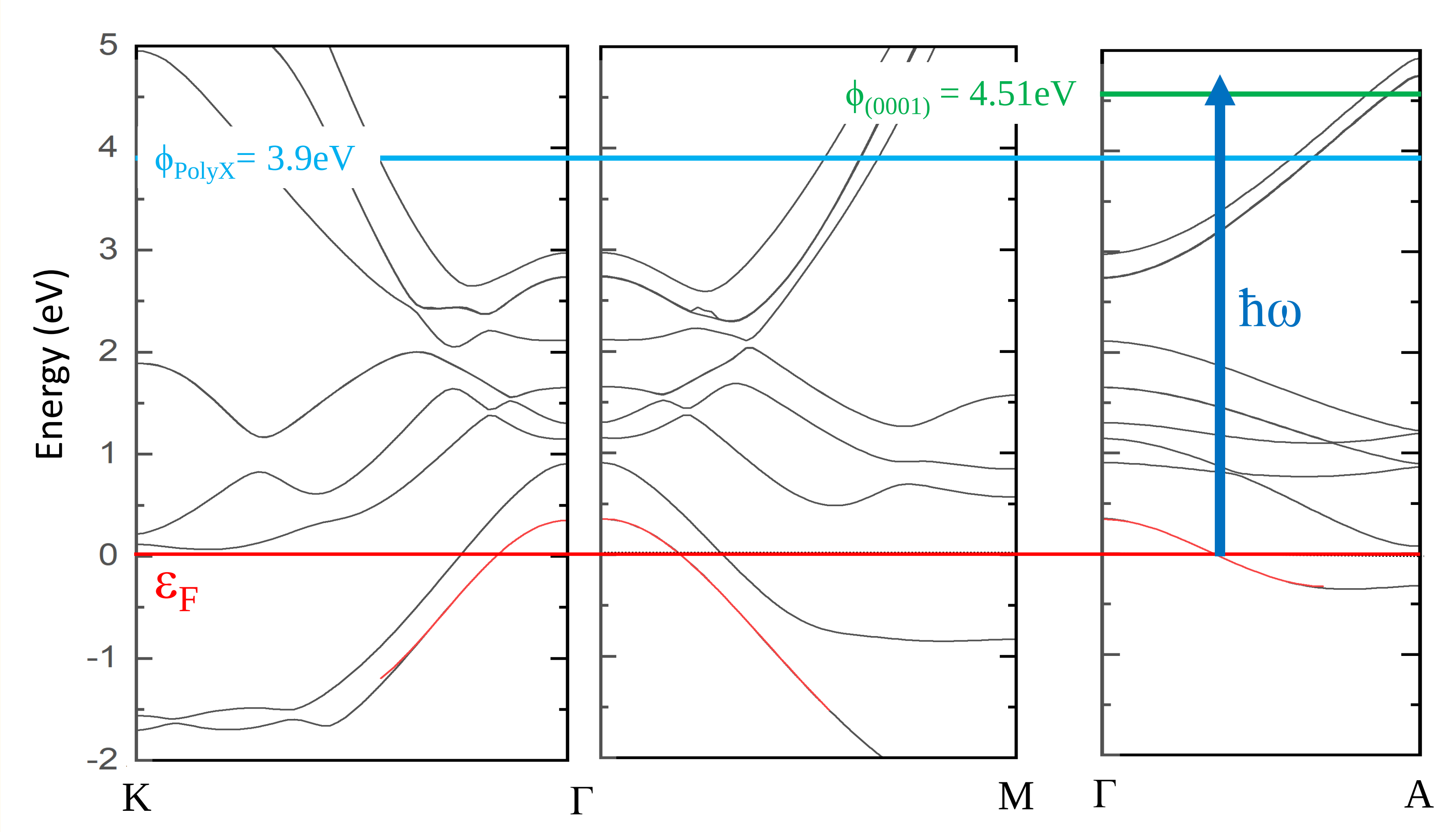
- For $\hbar\omega > \phi - \Delta\phi_{\text{-O-Cu}} + \Delta_1 \approx 5.0\text{eV}$ $(\Rightarrow \Delta\phi_{\text{-O-Cu}} \approx 0.5\text{eV})$
  - Direct near threshold emission from VB with low *MTE*

  $\therefore$ *MTE* reduction (**plus** *QE* increase)

A. Marini et al., *Phys. Rev. Lett.* **88** (2002) 016403

Hf(0001): Band structure

– Full relativistic band structure calculation with spin-orbit coupling



For Γ → A emission:

- No intermediate upper band states

  ⇒ One-step photoemission

- Relatively isotropic ***single*** hole-like emitting band state

$$m_T^* = m_z = 0.47(\pm 0.02)m_0$$

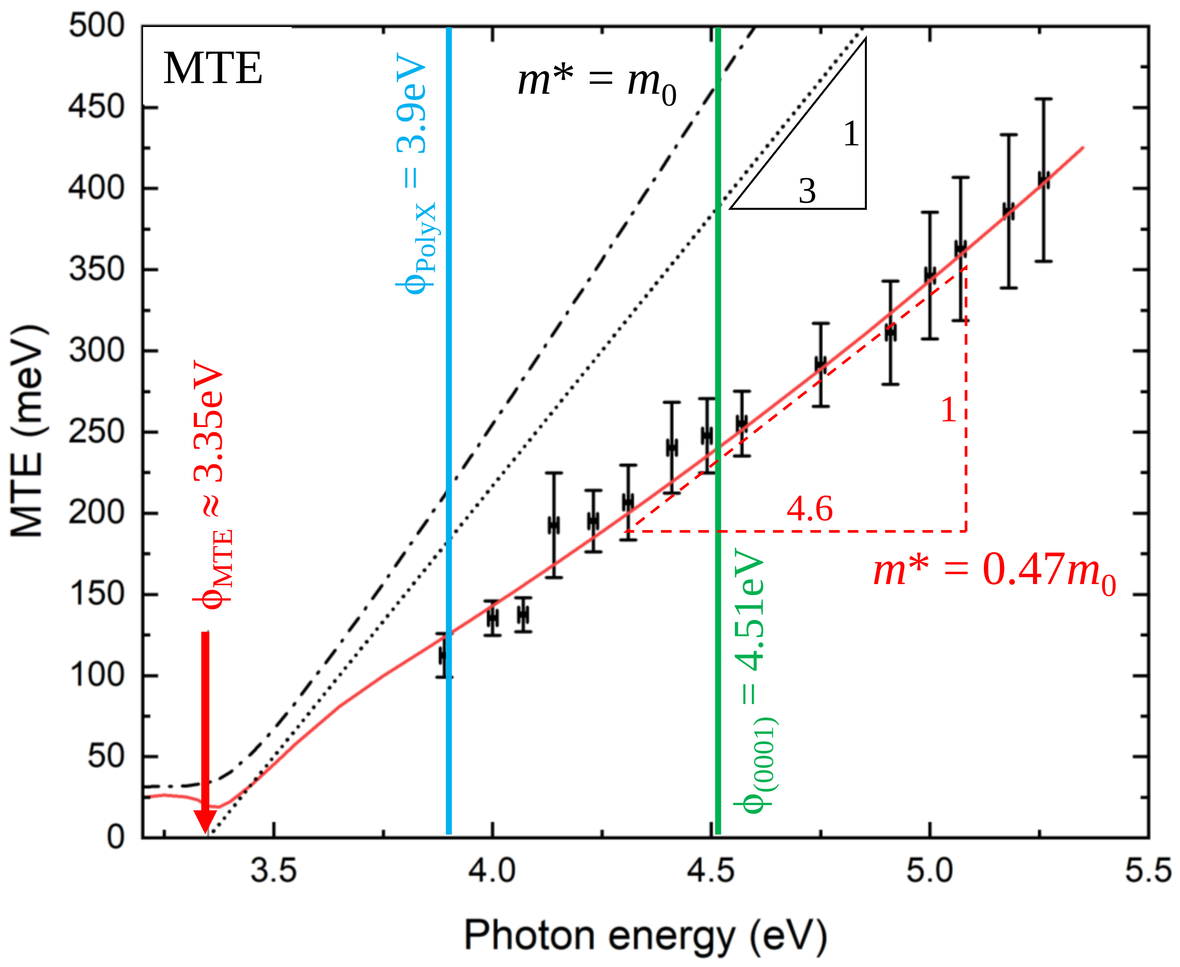
$$\therefore \text{ Expect } MTE < \frac{1}{3}(\hbar\omega - \phi)$$

… dispersion of emitting band state restricts p_T

Tuo Li et al., *Phys. Rev. STAB* **18** (2015) 073401; H.B. Michaelson, *J. Appl. Phys.* **48** (1977) 4729

Hf(0001): MTE measurements

– Photocathode polished to remove HfO_2 layer



- Spectral *MTE* dependence significantly ‘sub-Dowell-Schmerge’ ($m^* = m_0$)

  AND consistent with one-step photoemission theory ($m^* = 0.47m_0$)

$$MTE \geq \left|\frac{m_T^*}{m_0}\right| \frac{\hbar\omega - \phi}{3} \;;\; \left|\frac{m_T^*}{m_0}\right| \rightarrow 1 \text{ for } m_T^* \geq m_0$$

… **no** bulk band or vacuum density of states

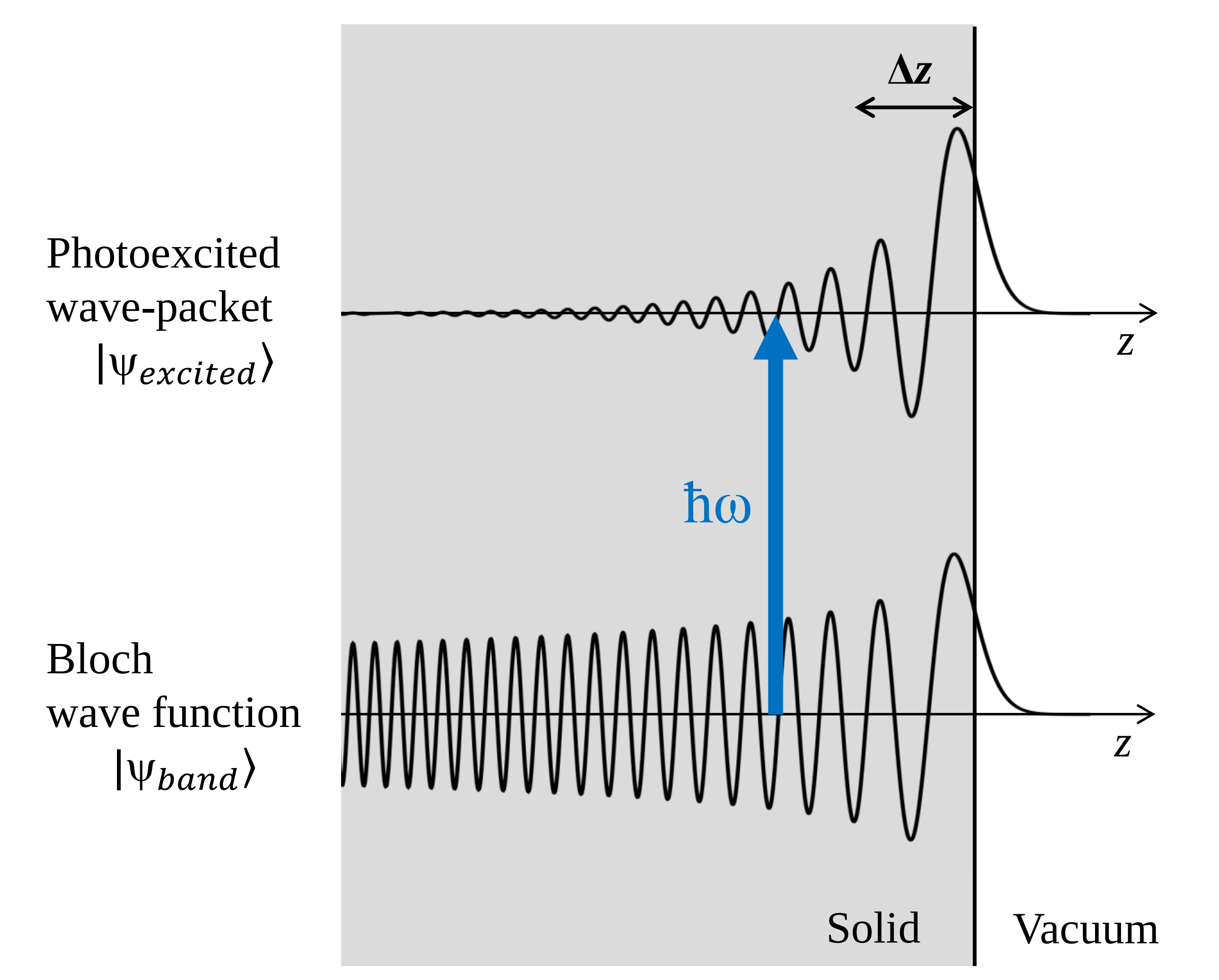
BUT

Inconsistencies in work functions …

⇒ Incomplete theoretical framework

W.A. Schroeder & G. Adhikari, *New J. Phys*. **21**, 033040 (2019); G. Adhikari et al., *AIP Advances* **9** (2019) 065305

Heisenberg Uncertainty and group velocity



- Additional ***required*** theoretical considerations:

(i) Finite spatial extent of $|\psi_{excited}\rangle$ due to absorption depth, electron extraction depth, etc.

$\Rightarrow$ Momentum width $\Delta p_z \geq \frac{\hbar}{2.\Delta z}$

$\therefore$ Convolution in **p**-space !!

… significant analytical and computational issues

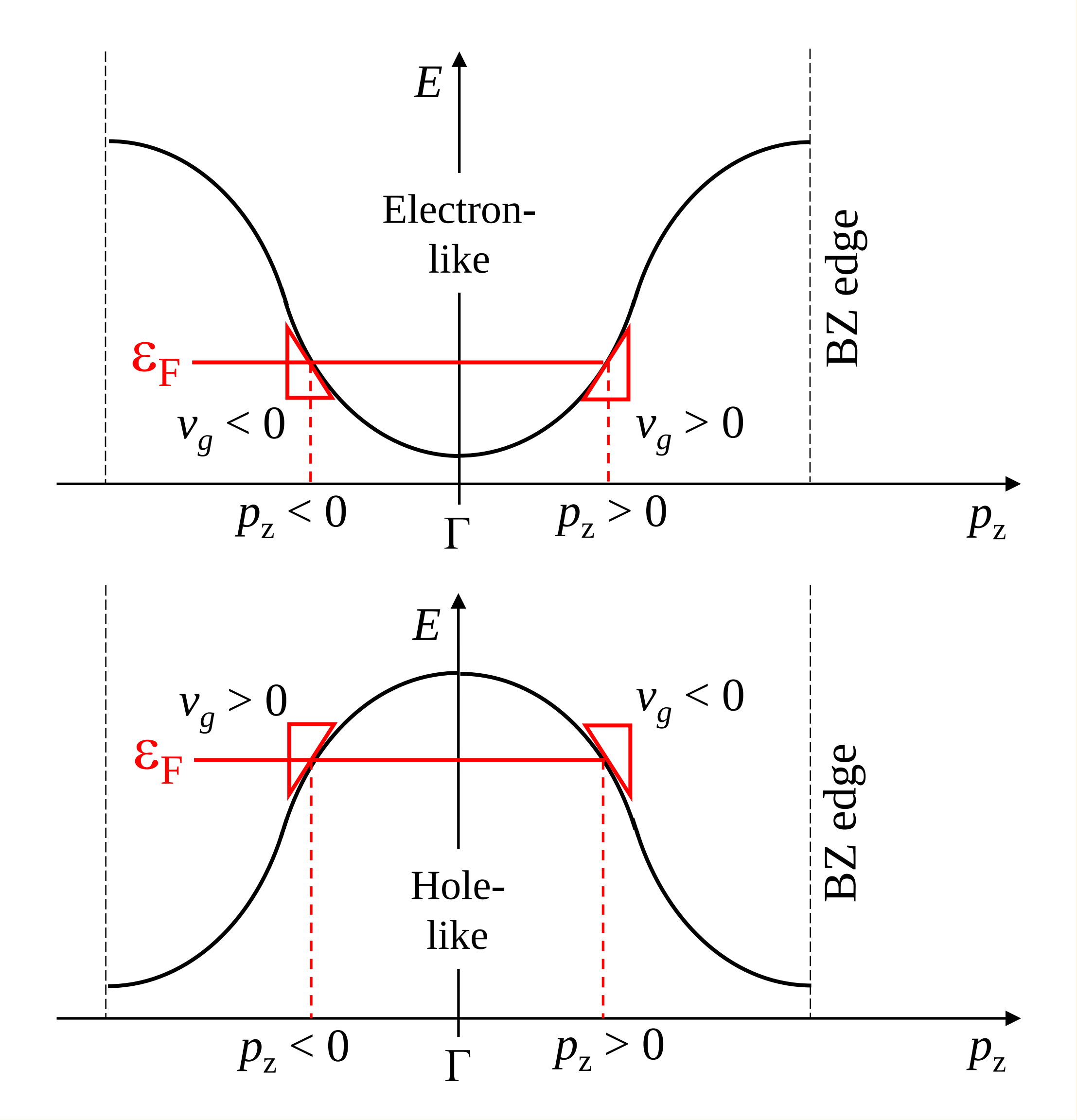
(ii) Wave-packet nature of $|\psi_{excited}\rangle$

$\Rightarrow$ Group velocity effects

$\therefore$ Reduced *QE* for $v_g = \frac{\partial E}{\partial p_z} < 0$

… positive $v_g = \frac{p}{m_0}$ for $|\psi_{vacuum}\rangle$

Group velocity effects



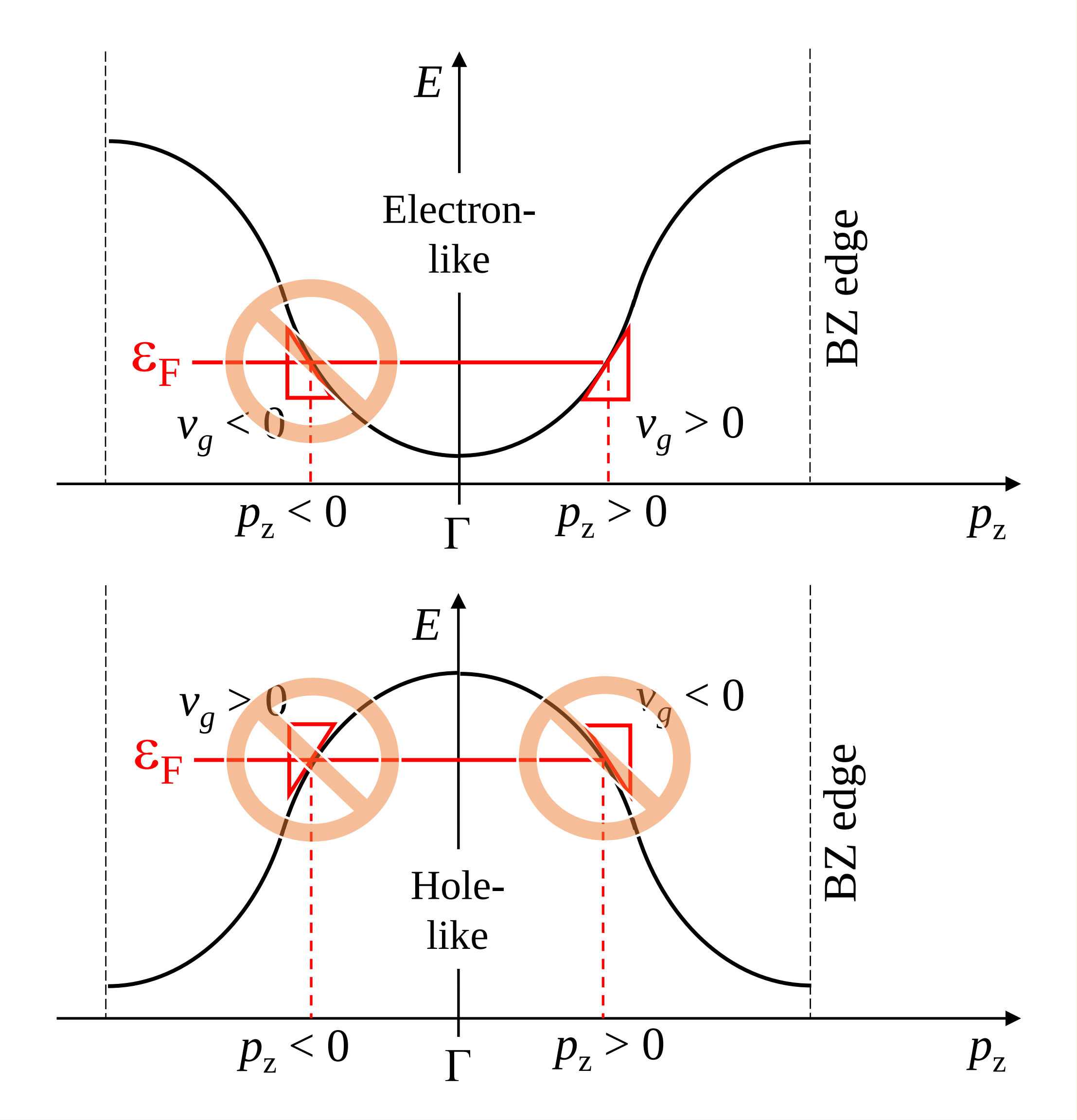
ANSATZ:

Efficient photoemission requires

(i) $p_z > 0$

(ii) $v_g = \frac{\partial E}{\partial p_z} > 0$

Group velocity effects



ANSATZ:

Efficient photoemission requires

(i) $p_z > 0$

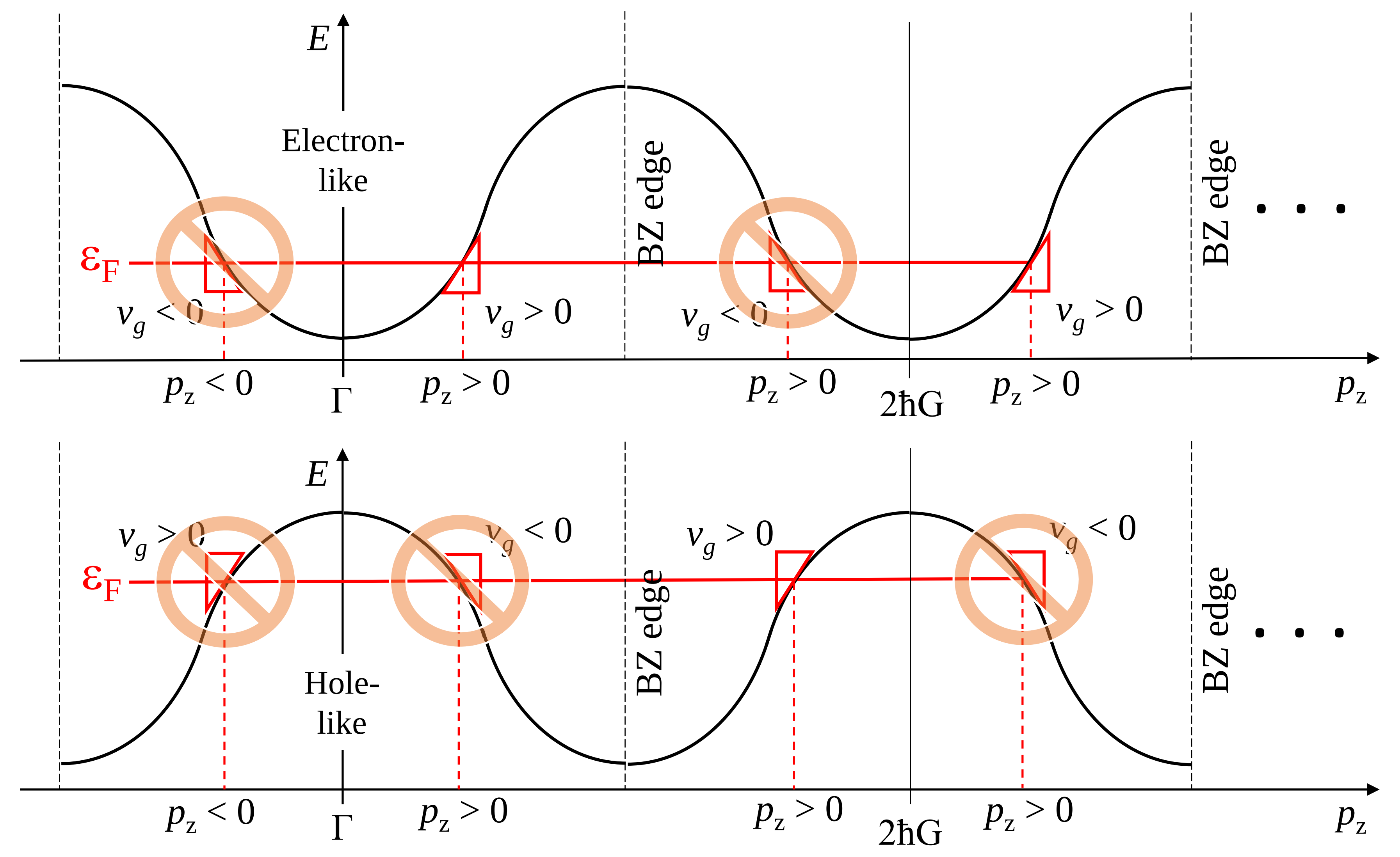
(ii) $v_g = \frac{\partial E}{\partial p_z} > 0$

⇒ Only electron-like band has high *QE* in 1st BZ

BUT

‘Umklappen’ allows emission …

Group velocity effects



- Hole-like band should have higher *QE* in 2nd BZ than in 1st BZ

PLUS

Expect contributions to *QE* (and hence *MTE*) from multiple BZs

Summary

- Direct connection of bulk band structure to spectral photoemission properties:

  (i) GaSb(001): Excited-state thermionic emission (ESTE)

  – Measurements consistent with $MTE \geq \frac{2}{3}\left|\frac{m_T^*}{m_0}\right|\frac{m_1}{m_1+m_2}\left(\hbar\omega - E_g^{/}\right)$

  (ii) Cu(111): Sub-threshold (non-surface-state) emission form upper conduction band

  – $E(\mathbf{p})$ of L-point bands $\Rightarrow$ Observed spectral *MTE* dependence

  (iii) Hf(0001): ‘Sub-Dowell-Schmerge’ spectral *MTE* dependence

  – Low m^* of hole-like emission band restricts p_T

- Further theoretical considerations:

  (i) Heisenberg Uncertainty …

  (ii) Group velocity: $p_\mathrm{z} > 0$ ***and*** $v_g = \frac{\partial E}{\partial p_z} > 0$ for efficient photoemission