Electron-phonon interactions

Fabio Caruso

August 22nd, 2023

Selb
Summer School
of the CRC 1242

C | A | U
Christian-Albrechts-Universität zu Kiel

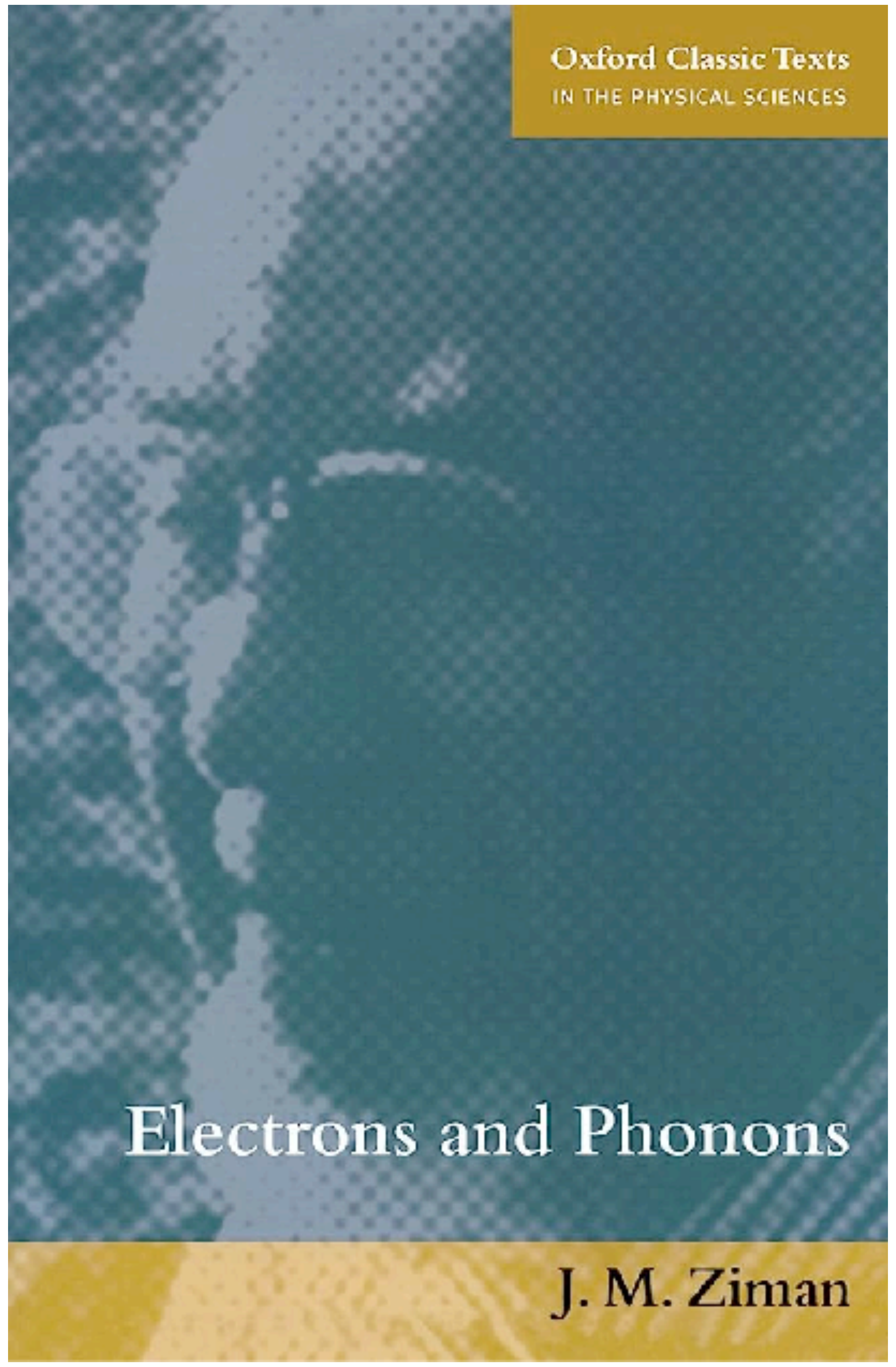
https://cs2t.de
C | S² | T Computational Solid-State Theory group

PRACE

Funded by DFG Deutsche Forschungsgemeinschaft German Research Foundation

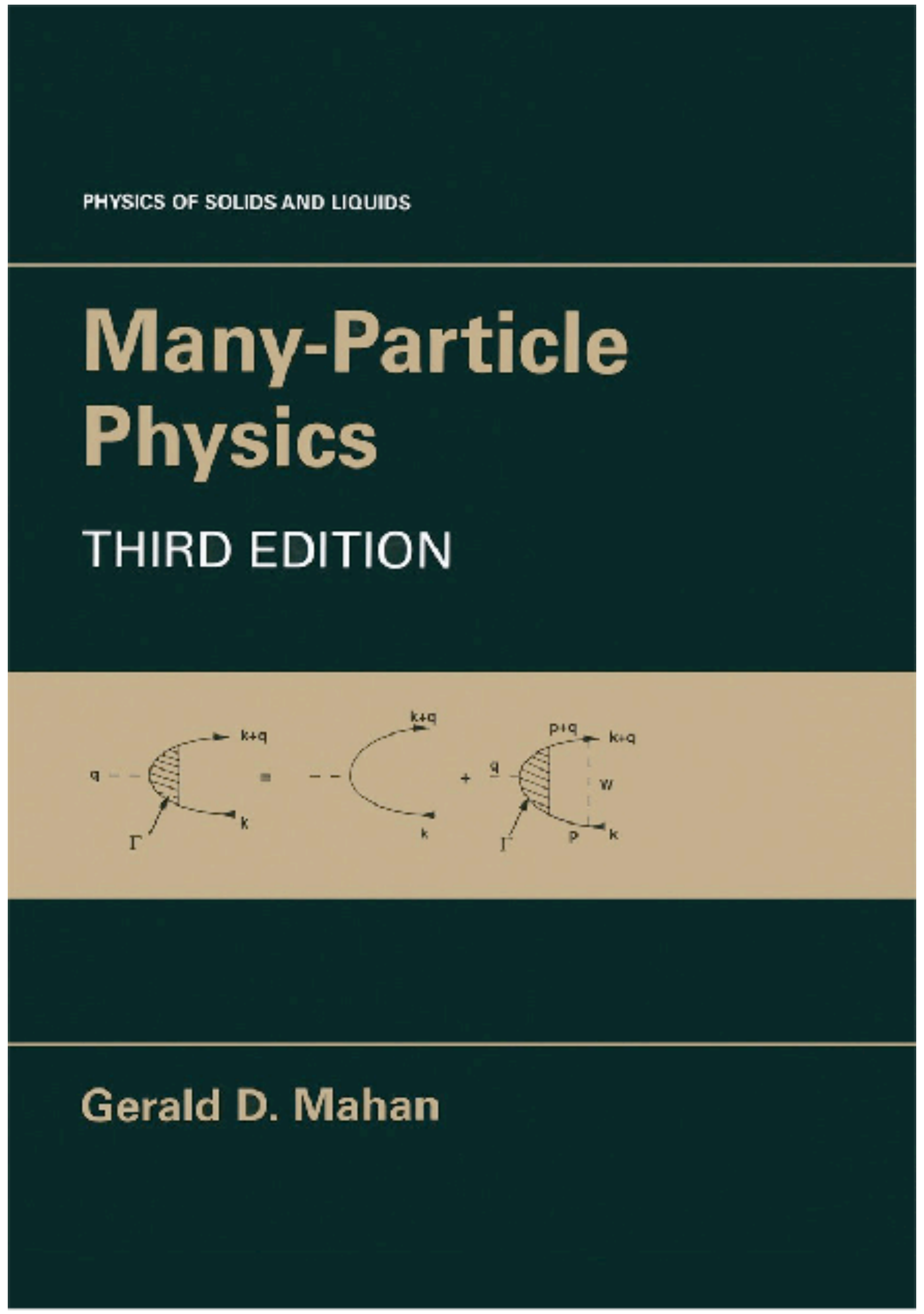
Further readings

Fundamentals



J. M. Ziman,
Electrons and Phonons,
Oxford University Press (1960)

Many-body formalism



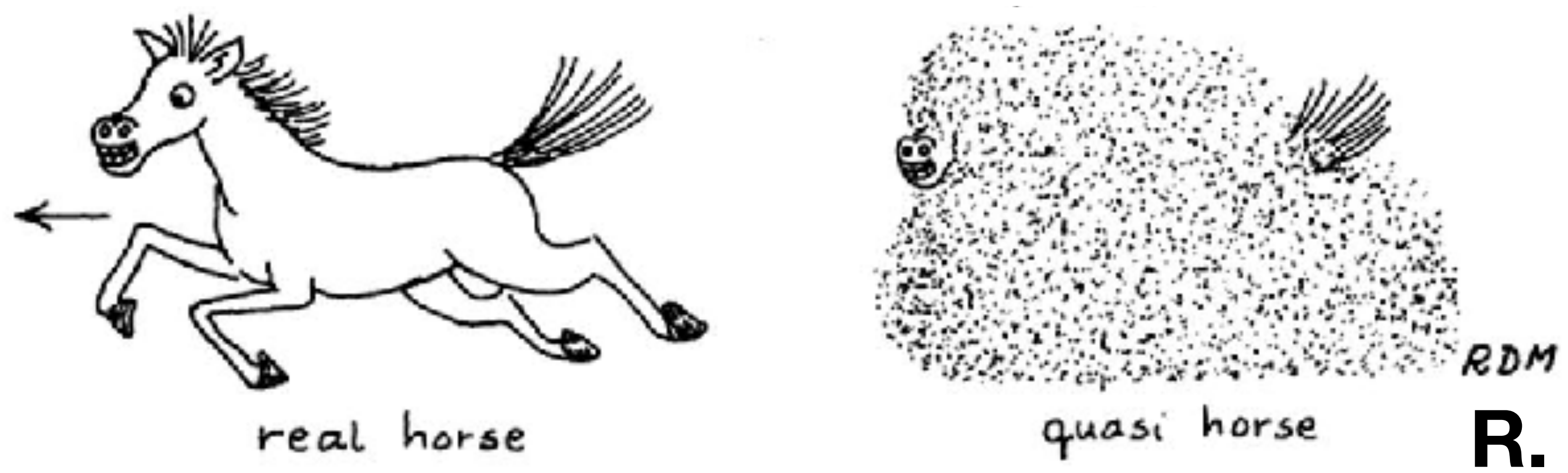
G. D. Mahan,
Many-Particle Physics,
Springer (2000)

Latest developments: Reviews

F. Giustino,
Electron-phonon interactions from first principles
Rev. Mod. Phys. **89**, 015003 (2017)

C. Franchini et al.,
Polarons in Materials,
Nat. Rev. Mater. **6**, 560 (2021)

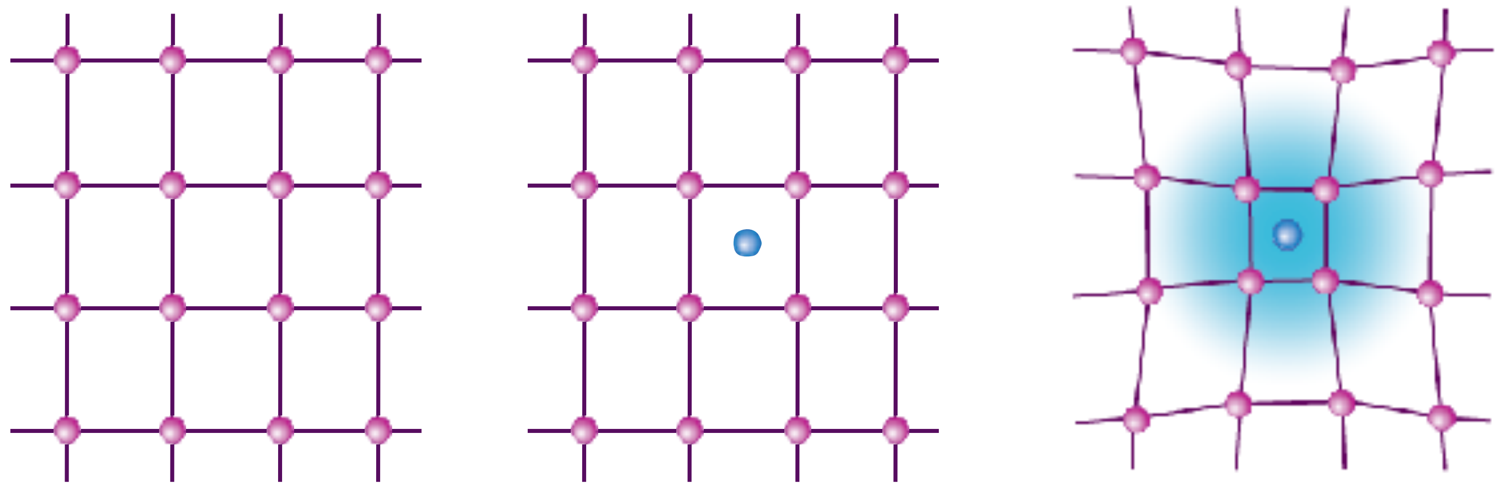
Quasiparticles and phonons



R. Mattuck

L. Landau, Electron motion in crystal lattices,
Phys. Z. Sowjetunion **3**, 664 (1933)

Phonon assisted quasiparticles

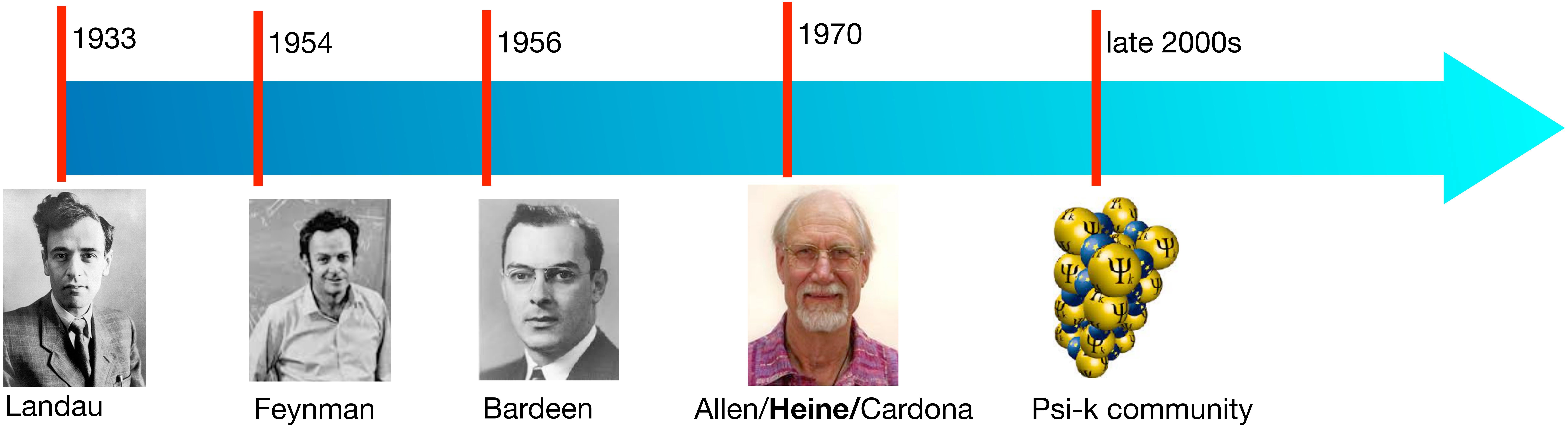


lattice   external particle   quasi-particle

example:

electron (hole) +
lattice distortion
= **polarons**

The timeline of the electron-phonon interaction



(1933) Landau: The polaron problem

(1954) Feynman: Exact solution of the polaron problem via a variational principle

(1956) Bardeen-Cooper-Schrieffer: BCS Theory of superconductivity

(1970) Allen-Heine-Cardona: Theory of the temperature dependence of the band structure

(~2005) Psi-k community: Ab-initio calculation of the electron-phonon interaction

and many more

Year	Theoretical and computational models	Polaron properties
1933 (REF.[6])	Dielectric theory: charge moving in a dielectric crystal	Auto-localization due to lattice deformation
1946–1948 (REFS[4,306–308])	Self-consistent theory of a large polaron	Enhancement of effective mass
	Landau–Pekar model	Localization of the wavefunction
1950s[7,8,85,86]	Quantum-mechanical variational theory of large polarons	Effective mass, energy, mobility
	Fröhlich large polaron Hamiltonian (continuum approximation)	Intermediate electron–phonon interaction
1955–2017 (REFS[11,12,93,161,162])	All-coupling continuum polaron theory	Energy, effective mass, mobility (large polaron)
	Feynman variational path-integral formalism	
1956 (REF.[95]), 1980s[94,96]	Monte Carlo calculations	Large polaron ground-state energy
1958 (REFS[309,310]), 1959 (REFS[9,10])	Holstein small polaron theory	Small polaron conduction mechanism
	Holstein small polaron Hamiltonian (lattice approximation)	Effective mass, energy
1963–2000s[87–89,311]	Exact solution of the two-site Holstein polaron	Dynamical characteristics
1969 (REF.[148]), 2000 (REFS[149,150])	Emin–Holstein–Austin–Mott theory	Small polaron hopping
1980 (REF.[146]), 1985 (REFS[119,147])	Marcus theory	Polaron hopping
1994 (REF.[101])	Exact diagonalization	Small polaron frequencies
1997 (REF.[312])	Hartree–Fock	Small polaron density of states
1998–2000 (REFS[58,59])	Diagrammatic Monte Carlo	Energy, effective mass, phonon distribution, spectral density
1999 (REF.[157])	Random walk Monte Carlo	Dispersive transport and recombination
2001 (REF.[104]), 2010 (REF.[56])	Analytical variational approach (variational LDB many-polaron wavefunction)[103]	Many-polaron (large) optical conductivity
2001 (REF.[60])	Path-integral Monte Carlo	Large polaron energy (2D and 3D)
1995 (REF.[65]), 1997 (REF.[66]), 2003 (REF.[67])	Dynamical mean-field theory	Small polaron energy, mass, spectral and transport properties
2010 (REF.[154]), 2018 (REF.[155])	First-principles molecular dynamics of small polarons	Polaron configurations
2002 (REF.[61]), 2006 (REF.[166])	Hybrid functionals	Small polaron spin density
2006 (REF.[92])	Analytical approximation for the Green's function	Energy, mass, dispersion, spectral weight
2006 (REFS[117,118]), 2009 (REF.[313])	DFT+*U*	Small polaron migration, DOS, bipolaron
2007–2010 (REFS[68,69])	Multiscale modelling and kinetic Monte Carlo	Charge transport
2014 (REF.[151])	Random phase approximation	Small energy and hopping
2009 (REF.[62]), 2011 (REF.[132])	Generalized Koopmans' density functional	Small polarons states
2015 (REF.[64])	Density-functional perturbation theory	Fröhlich electron–phonon vertex
2016 (REF.[102])	Renormalization group (large polaron)	Energy, effective mass
2019 (REFS[13,70])	Ab initio theory of polarons	Formation and excitation energies wavefunction (small and large polarons)

Compendium of theoretical works in the study of polarons

Electron-phonon coupling in condensed matter: a very active (and rapidly evolving) field of research

from C. Franchini et al.,Nat. Rev. Mater. 6, 560 (2021)

The electron-phonon coupling (EPC) Hamiltonian: the basics

Electron in a solid: $\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{qr}}$ (Bloch theorem)

Single particle Hamiltonian : $\hat{h} = -\dfrac{\nabla^2}{2} + \boxed{\hat{v}_{\text{eff}}(\{R\})}$ effective single-particle potential (e.g., the Kohn-Sham potential)

$\hat{v}_{\text{eff}}(\{R_I\})$ a function of all the nuclear coordinates

In presence of a phonon $\{\mathbf{R}_I\} \to \{\mathbf{R}_I + \mathbf{u}_I\}$ Tailor expansion for small displacements:

$$v_{\text{eff}}(\{R_I + u_I\}) = v_{\text{eff}}(\{R_I\}) + \Delta^{(1)}v_{\text{eff}} + \Delta^{(2)}v_{\text{eff}} + \dots$$

$$\Delta v_{\text{eff}} = \sum_I \left.\frac{\partial v_{\text{eff}}}{u_I}\right|_{u=0} u_I$$

some algebra

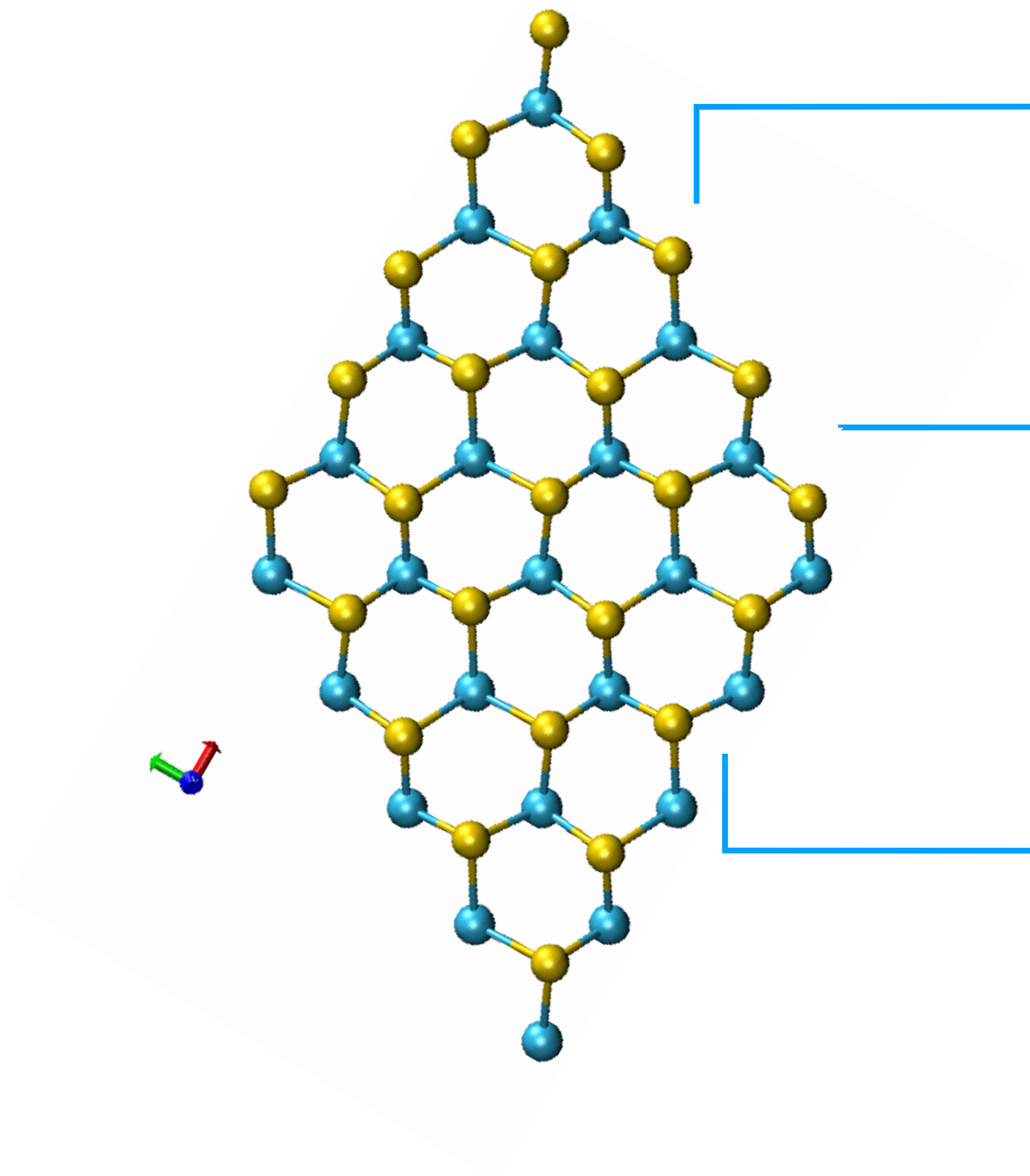
The electron-phonon interaction Hamiltonian

$$\hat{H}_{e-ph} = N_p^{-\frac{1}{2}} \sum_{mn\nu} \sum_{\mathbf{kq}} g^{\nu}_{mn}(\mathbf{k},\mathbf{q})\hat{c}^{\dagger}_{m\mathbf{k}+\mathbf{q}}\hat{c}_{n\mathbf{k}}[\hat{a}_{\mathbf{q}\nu} + \hat{a}^{\dagger}_{-\mathbf{q}\nu}]$$

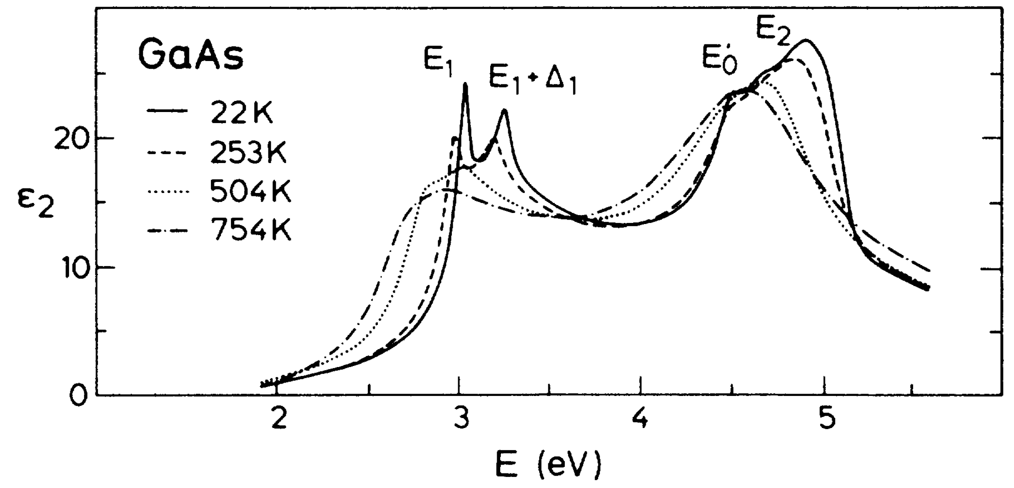
Linear change of the electronic Hamiltonian due to a phonon perturbation

- EPC matrix element. $g^{\nu}_{mn}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta v_{\text{eff}} | \psi_{n\mathbf{k}} \rangle$
- Phonon creation/annihilation operators $\hat{a}^{\dagger}_{\mathbf{q}\nu}, \hat{a}_{\mathbf{q}\nu}$
- Electron creation/annihilation operators $\hat{c}^{\dagger}_{n\mathbf{k}}, \hat{c}_{n\mathbf{k}}$

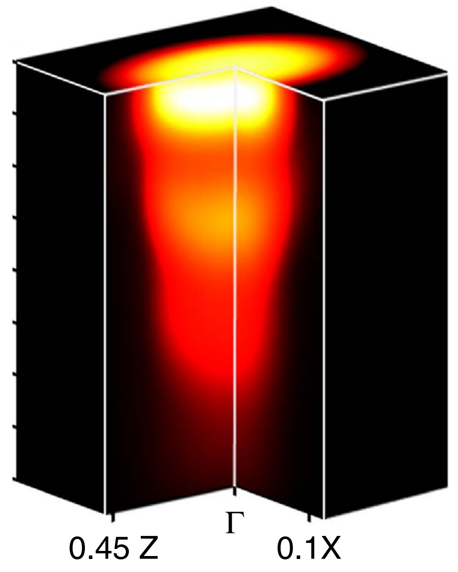
Derivation:
F. Giustino, Rev. Mod. Phys. **89**, 015003 (2017)



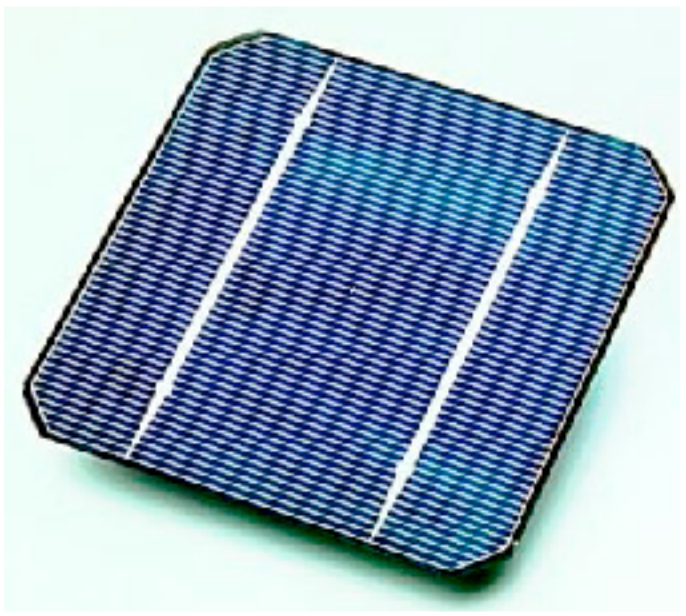
The temperature dependence of the band structure



Polaronic satellites in angle-resolved photoemission spectroscopy (ARPES)



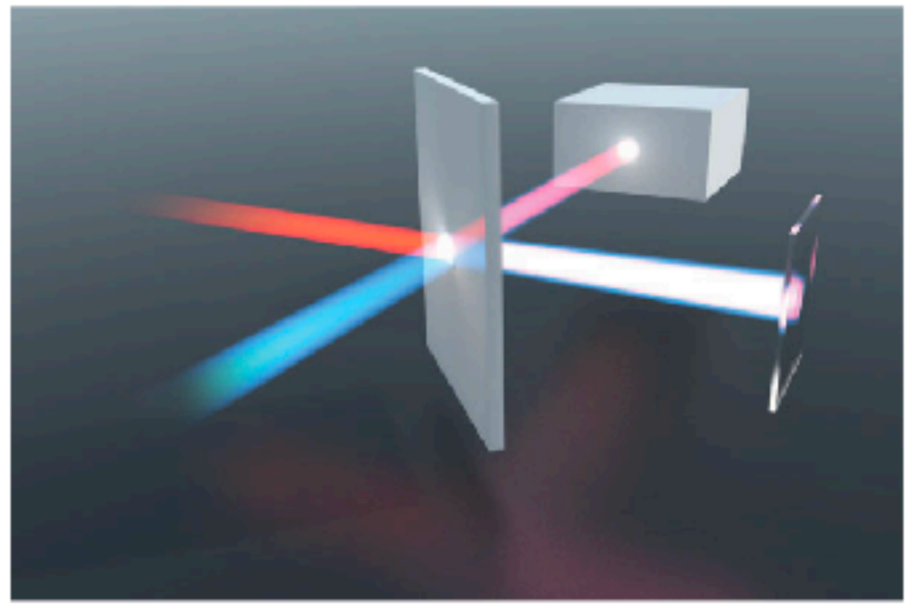
Phonon-assisted optical absorption in semiconductors



Part 1

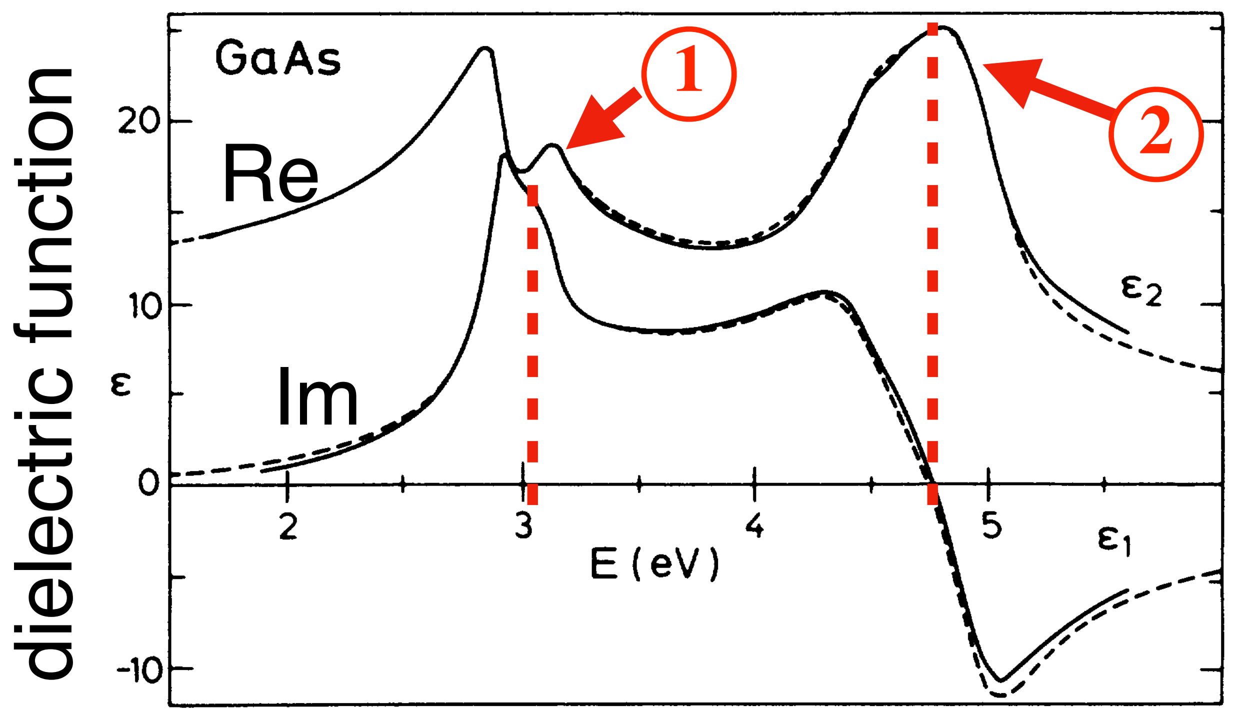
The temperature dependence of the band structure

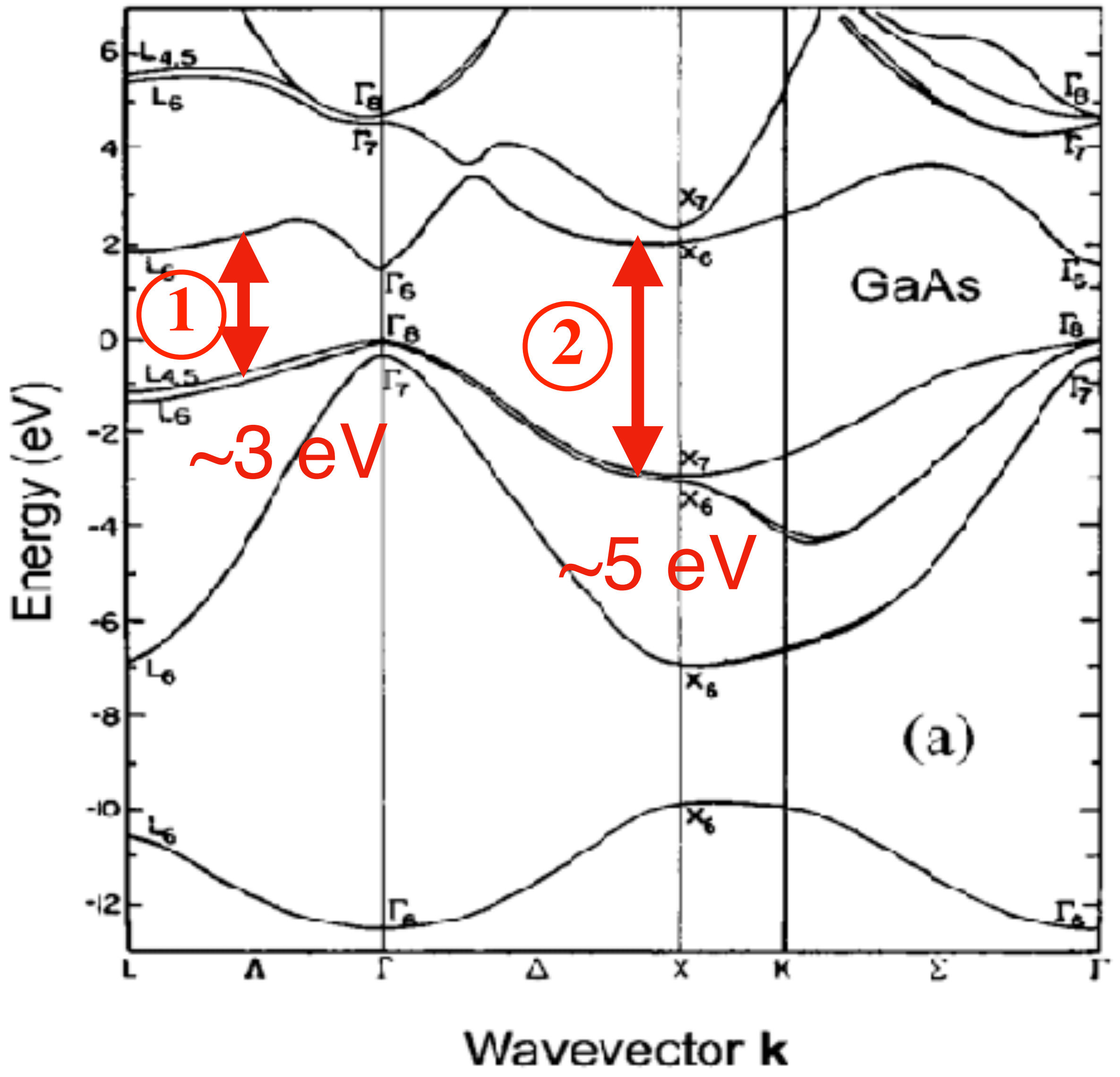
Temperature-depedent of optical measurements of semiconductors



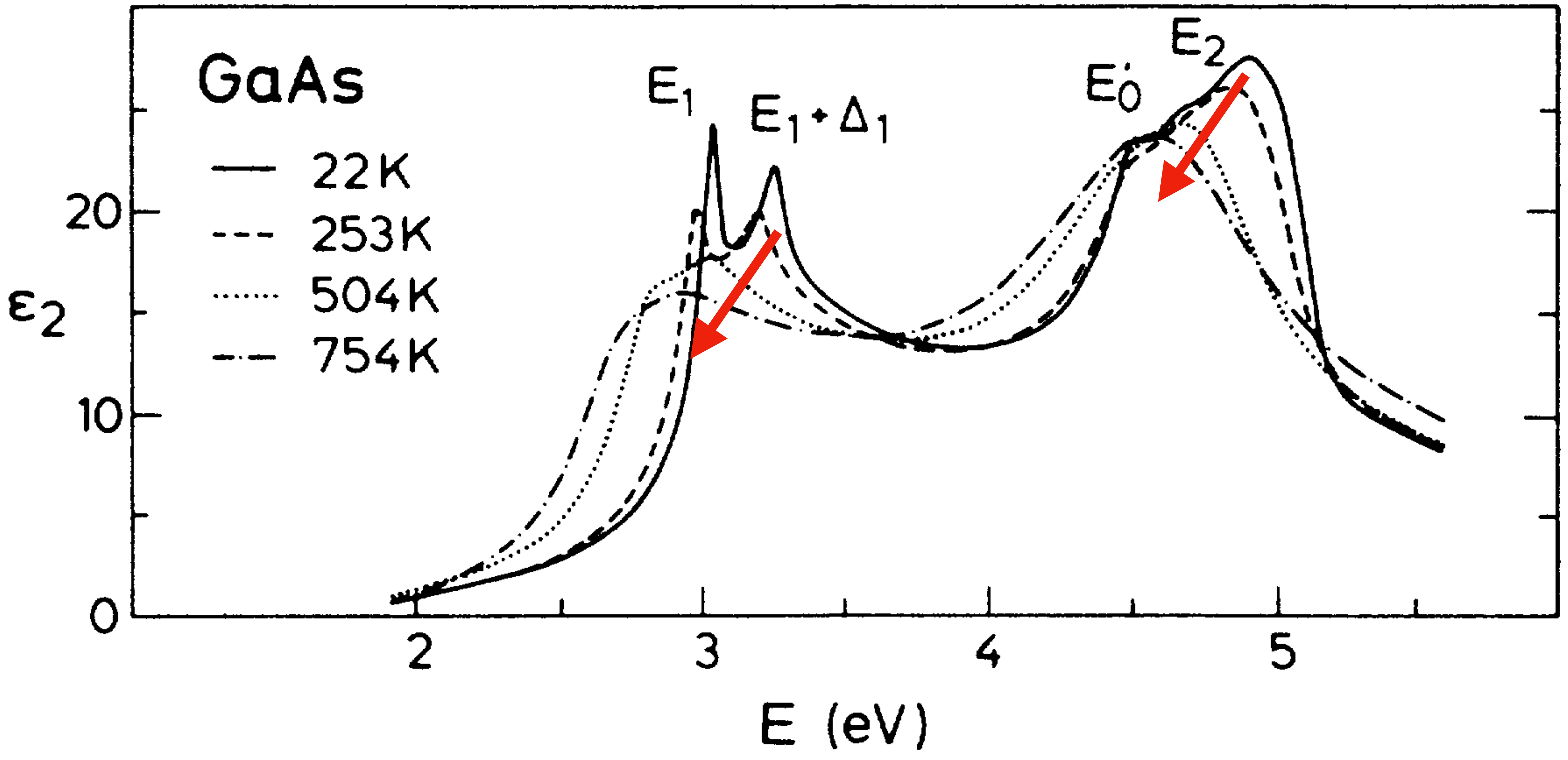
Signatures of electron-phonon coupling in optical measurements

Dielectric function of GaAs
(from ellipsometry measurement





Temperature dependence of the dielectric function



$$\mathrm{Im}\,\epsilon(\omega) \sim \mathrm{JDOS}(\omega) = N_k^{-1} \sum_{nm\mathbf{k}} \delta(\omega - (\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}}))$$

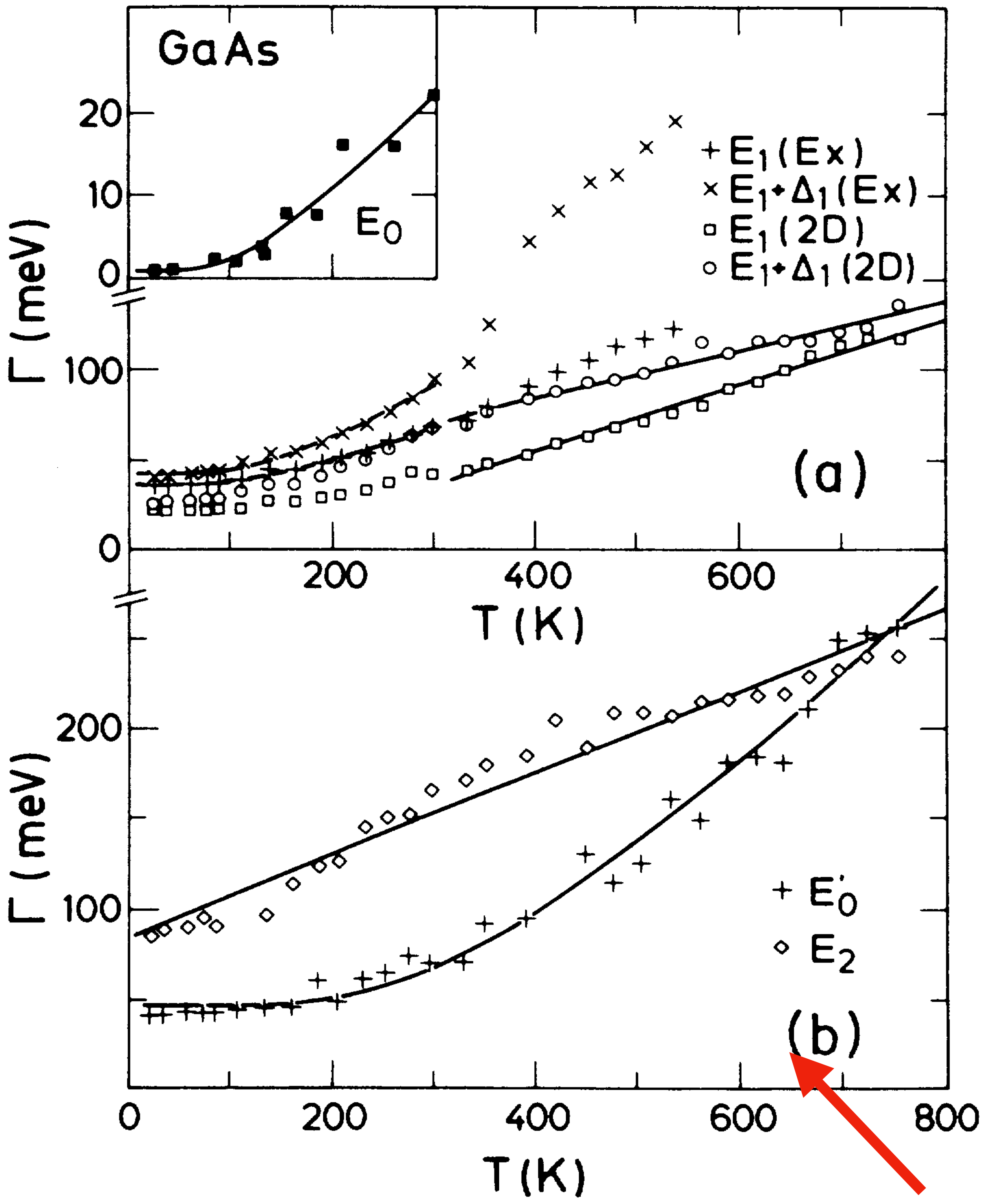
peaks in $\mathrm{Im}\,\epsilon$ → transitions from occupied to empty states

Temperature dependence of the band structure

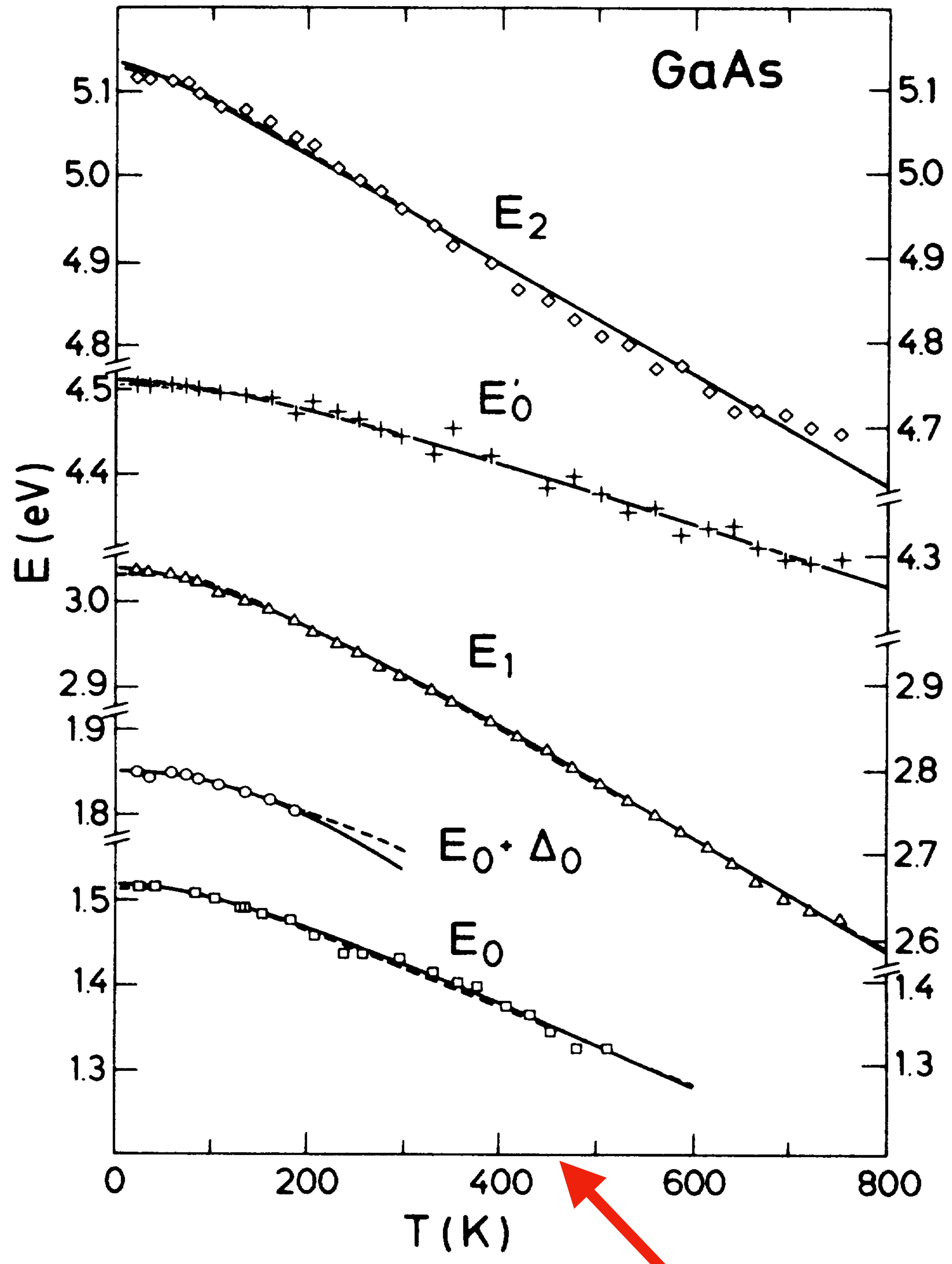
Lautenschlager et al., Phys. Rev. B **35**, 9173 (1987)

Temperature-depedent of optical measurements of semiconductors

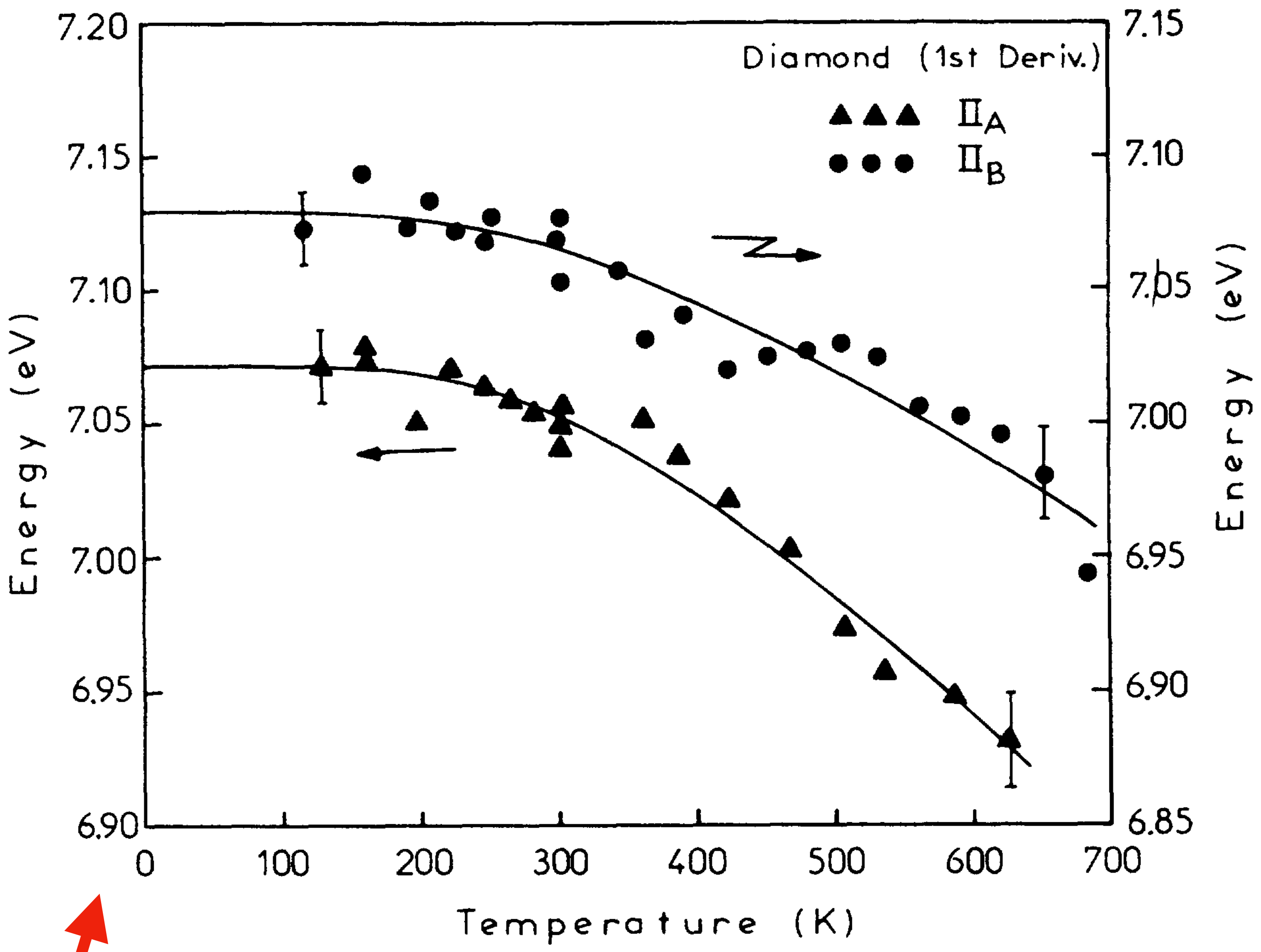
Peak broadening
(lifetime)



Critical points
(peaks in the Joint DOS)



Fundamental gap



Strong temperature dependent renormalization of the band structure

- **Not explained by the thermal expansion (TE):**
  Measured shifts **~0.2 meV / K**
  Expected shifts (from TE) **~0.004 meV / K**
- **Depends on T as the Bose Einstein distribution**

Electron-phonon interaction

Temperature dependence

$$\Gamma(T)=\Gamma_1+\frac{\Gamma_0}{e^{\Theta/T}-1}$$

$$E(T)=E_B-a_B\left[1+\frac{2}{e^{\Theta/T}-1}\right]$$

Lautenschlager et al., Phys. Rev. B **35**, 9173 (1987)
Logothetidis et al., Phys. Rev. B **46**, 4483 (1992)

Perturbative treatment of the electron-phonon interaction: the Fan-Migdal term

$$\hat{H}_{e-ph} = \sum_I \boxed{\left.\frac{\partial v_{\mathrm{eff}}}{u_I}\right|_{u=0}} \boxed{u_I}$$

electrons **phonons**

Hamiltonian: $\hat{H} = \hat{H}_0 + \Delta\hat{H}$
Perturbation: $\Delta\hat{H} \equiv \hat{H}_{e-ph}$

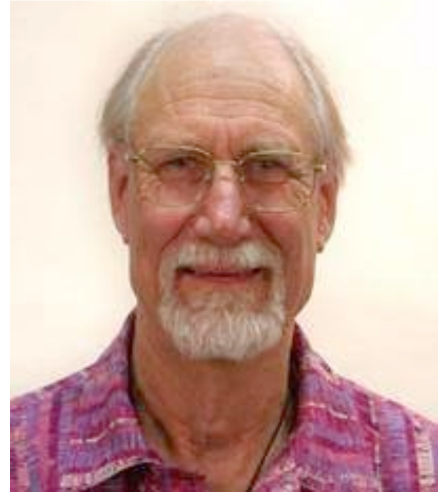
Rayleight-Schrödinger perturbation theory

Perturbative expansion

$$\varepsilon_{n\mathbf{k}} = \varepsilon^{(0)}_{n\mathbf{k}} + \varepsilon^{(1)}_{n\mathbf{k}} + \varepsilon^{(2)}_{n\mathbf{k}} + \ldots$$

$$\psi_{n\mathbf{k}} = \psi^{(0)}_{n\mathbf{k}} + \psi^{(1)}_{n\mathbf{k}} + \psi^{(2)}_{n\mathbf{k}} + \ldots$$


Phil Allen


Volker Heine


Manuel Cardona

Allen-Heine-Cardona theory

- Apply second-order perturbation-theory to the electrons
- Treat the phonons via a thermal average

First-order perturbation theory

$$\varepsilon^{(1)}_{n\mathbf{k}} = \langle \psi^{(0)}_{n\mathbf{k}} | \hat{H}_{e-ph} | \psi^{(0)}_{n\mathbf{k}} \rangle = 0 \quad \leftarrow \langle u_I \rangle_T = 0$$

$\langle u_I \rangle_T$ average displacement at temperature T

Second-order perturbation theory

$$\varepsilon^{(2)}_{n\mathbf{k}} = \sum_{m \neq n} \sum_{\mathbf{q}} \frac{|\langle \psi^{(0)}_{m\mathbf{k}+\mathbf{q}} | \hat{H}_{e-ph} | \psi^{(0)}_{n\mathbf{k}} \rangle|^2}{\varepsilon^{(0)}_{n\mathbf{k}} - \varepsilon^{(0)}_{m\mathbf{k}+\mathbf{q}}} \quad \leftarrow \langle u_I^2 \rangle_T \neq 0$$

$\langle u_I^2 \rangle_T$ mean squared displacement

... some algebra:

$$\varepsilon^{\mathrm{FM}}_{n\mathbf{k}} = \frac{1}{N_p} \sum_{\mathbf{q}\nu} \sum_{m \neq n} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 \frac{2n_{\mathbf{q}\nu}(T) + 1}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}}$$

Fan-Migdal term
Phonon-assisted renormalization of the electron energy levels

Perturbative treatment of the electron-phonon interaction: the Debye-Waller term

$$v_{\text{eff}}(\{R_I + u_I\}) = v_{\text{eff}}(\{R_I\}) + \Delta^{(1)} v_{\text{eff}} + \Delta^{(2)} v_{\text{eff}} + \ldots$$

Debye-Waller term

quadratic change of v_{eff} treated at 1st order in perturbation theory ... **also quadratic in the perturbation**

linear change of v_{eff} treated at 2nd order in perturbation theory **quadratic dependence on the phonon displacement (the perturbation)**

Fan-Migdal term

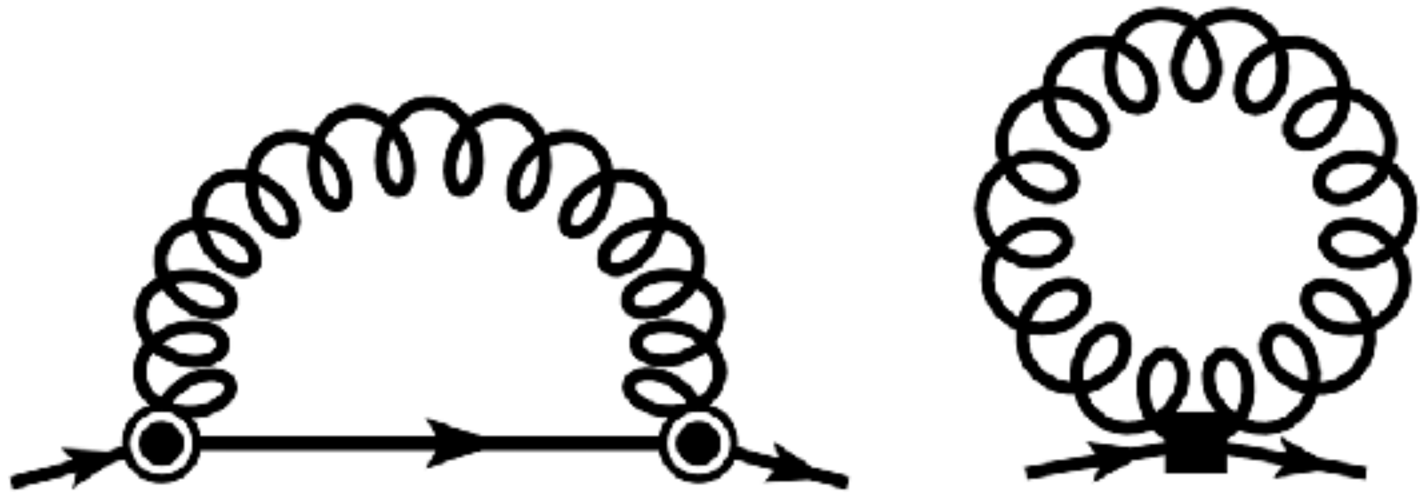
Debye-Waller term

$$\varepsilon_{n\mathbf{k}}^{\text{DW}} = \langle \psi_{n\mathbf{k}}^{(0)} | \Delta^{(2)} v_{\text{eff}} | \psi_{n\mathbf{k}}^{(0)} \rangle \xrightarrow{\text{some algebra}} \Delta\varepsilon_{n\mathbf{k}}^{(2),\text{DW}} = \frac{1}{N_p} \sum_{\mathbf{q}\nu} \tilde{g}_{nn}^{\nu\nu}(\mathbf{k}, \mathbf{q}, -\mathbf{q})(2n_{\mathbf{q}\nu} + 1)$$

second-order

Temperature dependence of the band structure in Allen-Heine-Cardona theory

$$\Delta\varepsilon_{n\mathbf{k}}^{\text{AHC}} = \Delta\varepsilon_{n\mathbf{k}}^{\text{FM}}(T) + \Delta\varepsilon_{n\mathbf{k}}^{\text{DW}}(T)$$



Review: X. Gonze et al., Ann. Phys. (Berlin) 523, 168 (2011)

Temperature-dependence of the AHC correction to the bands and zero-point motion renormalization

$$\Delta\varepsilon^{\mathrm{AHC}}_{n\mathbf{k}} = \Delta\varepsilon^{\mathrm{FM}}_{n\mathbf{k}}(T) + \Delta\varepsilon^{\mathrm{DW}}_{n\mathbf{k}}(T)$$

$$\varepsilon^{\mathrm{FM}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu}\sum_{m\neq n} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 \frac{2n_{\mathbf{q}\nu}(T)+1}{\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}}$$

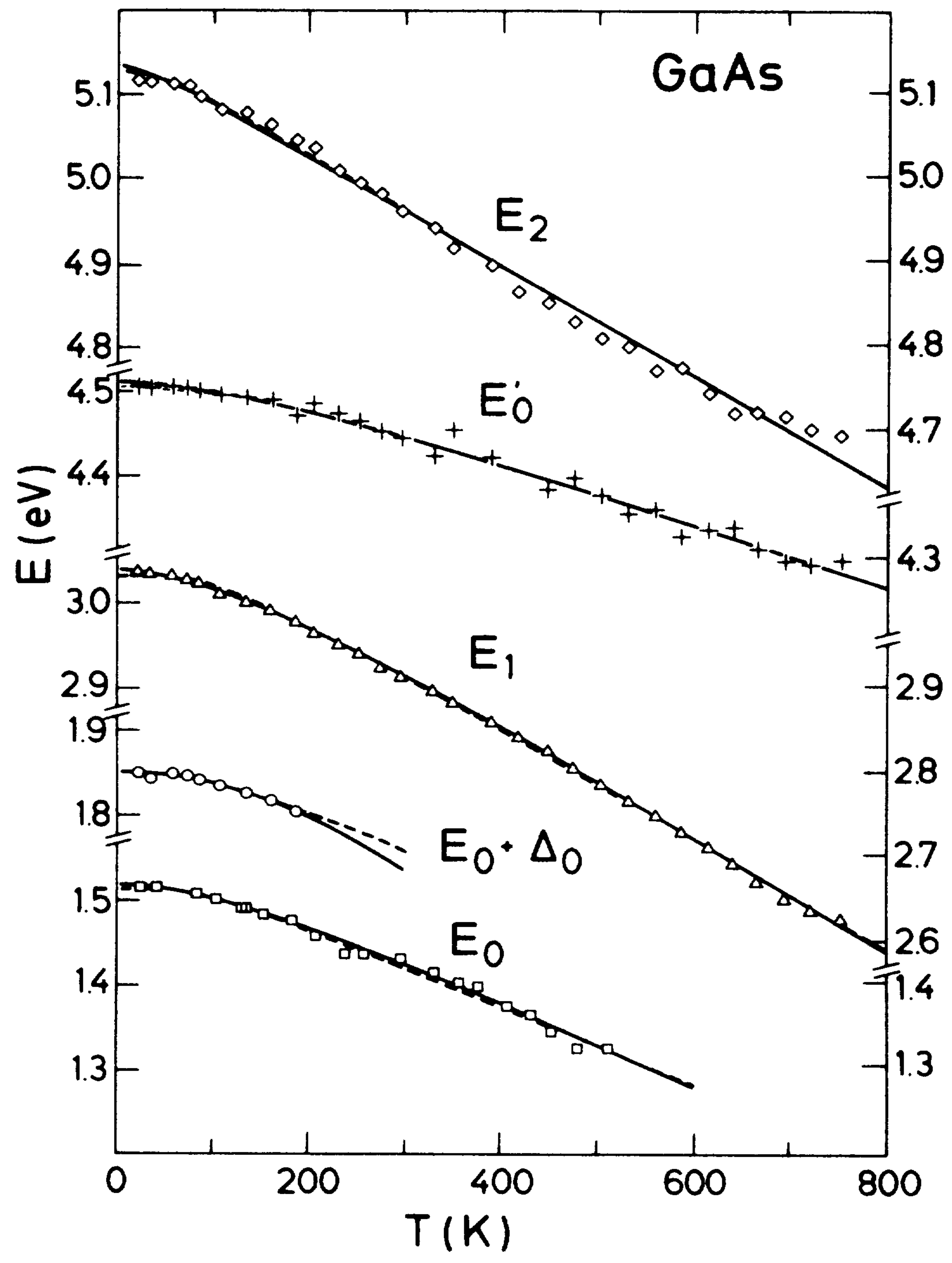
$$\varepsilon^{\mathrm{DW}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu} \tilde{g}^{\nu\nu}_{nn}(\mathbf{k},\mathbf{q},-\mathbf{q})(2n_{\mathbf{q}\nu}+1)$$

Consider a materials with only one vibrational frequency ($n_{\mathbf{q}\nu}(T) \simeq n(T)$):

number of phonons at temperature T

$$\varepsilon^{\mathrm{FM}}_{n\mathbf{k}} = [2n(T)+1]\frac{1}{N_p}\sum_{m\neq n}|g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2\frac{1}{\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}} = \alpha[2n(T)+1]$$

$$E(T) = E_B - a_B\left[1+\frac{2}{e^{\Theta/T}-1}\right]$$



1. Fully captures the temperature-dependence of bands determined in experiments.

2. At T=0, $n(T)=0$ however $\varepsilon^{\mathrm{AHC}}_{n\mathbf{k}} \neq 0$
   Renormalization of the bands even in absence of phonons
   Zero-point motion effect (purely quantum)

The Allen-Heine-Cardona theory in ab-initio calculations

$$\boxed{\Delta\varepsilon^{\mathrm{AHC}}_{n\mathbf{k}} = \Delta\varepsilon^{\mathrm{FM}}_{n\mathbf{k}}(T) + \Delta\varepsilon^{\mathrm{DW}}_{n\mathbf{k}}(T)}$$

$$\varepsilon^{\mathrm{FM}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu}\sum_{m\neq n} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 \frac{2n_{\mathbf{q}\nu}(T)+1}{\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}} \qquad \varepsilon^{\mathrm{DW}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu} \tilde{g}^{\nu\nu}_{nn}(\mathbf{k},\mathbf{q},-\mathbf{q})(2n_{\mathbf{q}\nu}+1)$$

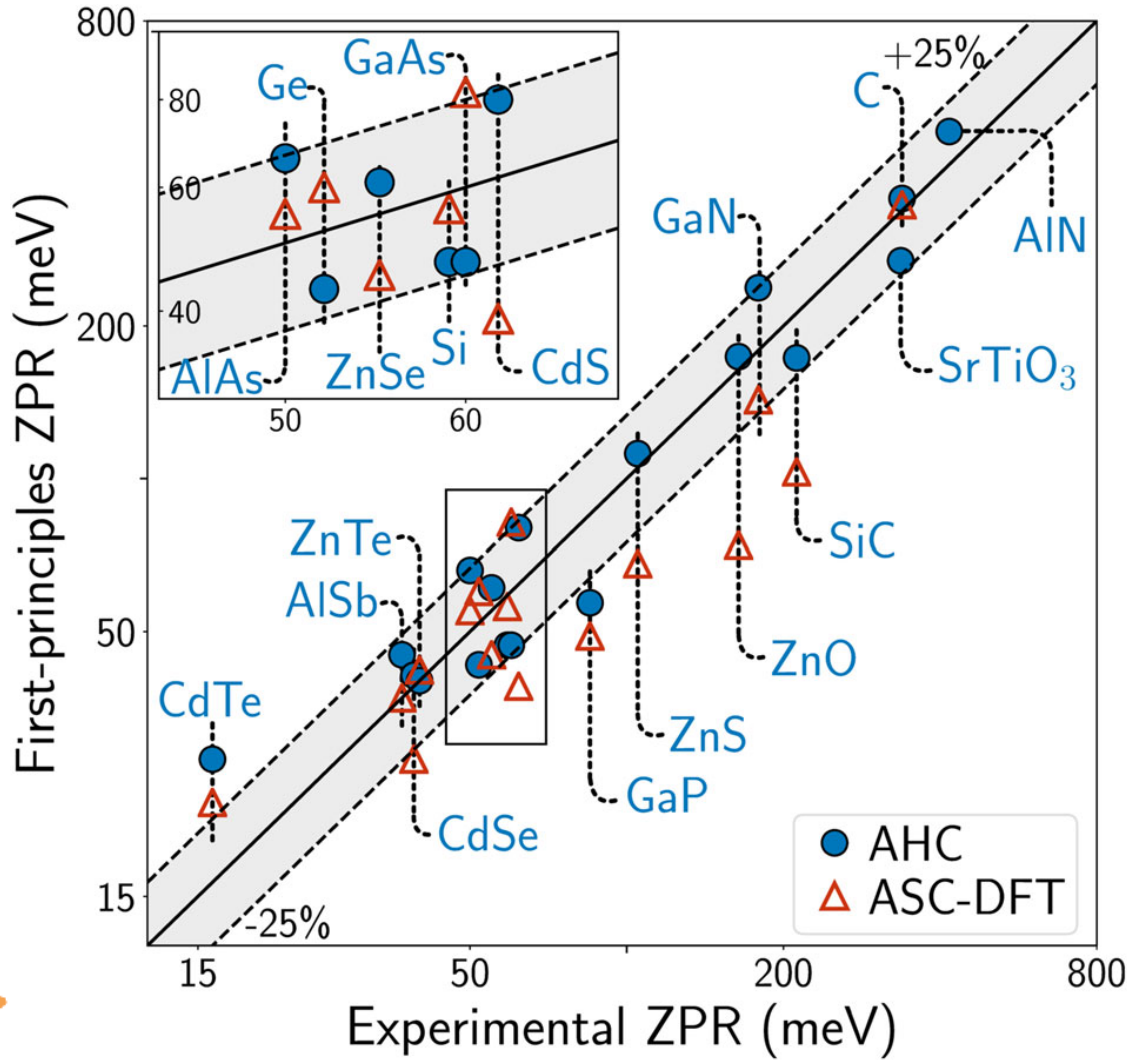
- $g^{\nu}_{mn}(\mathbf{k},\mathbf{q})$: electron-phonon matrix elements → from DFPT
- $\varepsilon_{n\mathbf{k}}$: single particle energy → from DFT
- $n_{\mathbf{q}\nu}(T) = [e^{\hbar\omega_{\mathbf{q}\nu}/k_BT} - 1]^{-1}$: Bose-Einstein distribution

Fully ab-initio have only "recently" become accessible

- Calculations require very dense grids to sample the integrals over the Brillouin zone (denser than 30×30×30)
- Interpolation using Maximally-localized Wannier function is required for $g^{\nu}_{mn}(\mathbf{k},\mathbf{q})$

Available in many ab-initio codes:

EPW exciting Yambo Abinit



Miglio, et al., npj Comput. Mater. **6**, 167 (2020)

Marzari et al., Rev. Mod. Phys. **84**, 1419 (2012)
Giustino et al., Phys. Rev. B **76**, 165108 (2007)

Many-body perturbation theory (MPBT) of electron-phonon coupling

Consider a perturbation acting on the electron Hamiltonian : $\hat{H}^{el} = \hat{H}_0^{el} + \Delta\hat{V}$

Consider a perturbation acting on the **lattice** Hamiltonian : $\hat{H}^{ph} = \hat{H}_0^{ph} + \Delta\hat{V}$

Electron Green's function

$$G_{ij}(t_1, t_2) = -i\hbar^{-1}\langle\Psi|\hat{T}[\hat{\psi}_i(t_1)\hat{\psi}_j^{\dagger}(t_2)]|\Psi\rangle$$

$\vert\Psi\rangle$:	electron ground-state wave function
$\hat{\psi}^{\dagger}, \hat{\psi}$:	creation/annihilation operators
$\hat{T}$:	Wick's time-ordering operator

Phonon Green's function

$$D_{\alpha\beta}(t_1, t_2) = -i\hbar^{-1}\langle\Phi|\hat{T}\Delta\hat{\tau}_\alpha(t_1)\Delta\hat{\tau}_\beta(t_2)|\Phi\rangle$$

$\vert\Phi\rangle$:	**phonon** ground-state wave function
$\Delta\hat{\tau}_\alpha$:	displacement operator
$\hat{T}$:	Wick's time-ordering operator

Direct access to physical properties (spectral function, observables, total energy, ect)

Formally exact treatment of the perturbation

G: the (exact) Green's function.

G_0: the non-interacting Green's function.

Σ: the electron self-energy

The Dyson equation

$$G = G_0 + G_0\Sigma G$$

coupled by the electron-phonon interactions

Perturbative treatment of the phonon Green's function

D: the (exact) **phonon** Green's function.

D_0: the non-interacting **phonon** Green's function.

$\Pi^{(na)}$: the non-adiabatic phonon self-energy

The Dyson equation

$$D = D_0 + D_0\Pi^{(na)}D$$

Exact self-consistent equations for the electron and phonon Green's functions

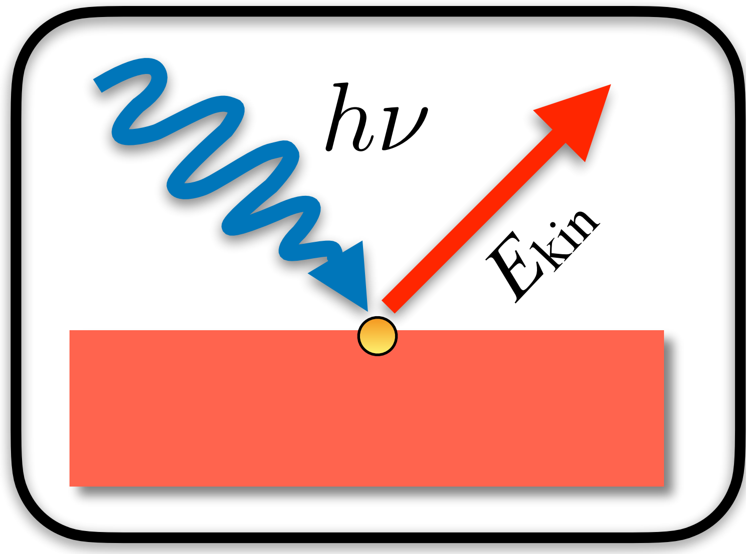
Description	Expression
Electronic charge density	$\langle \hat{n}_{\rm e}(1)\rangle = -i\hbar \sum_{\sigma_1} G(11^+)$
Nuclear charge density	$\langle \hat{n}_{\rm n}(\mathbf{r}t)\rangle = n^0_{\rm n}(\mathbf{r}) - (i\hbar/2)\sum_{\kappa p,\alpha\alpha'} Z_\kappa \partial^2\delta(\mathbf{r}-\boldsymbol{\tau}^0_{\kappa p})/\partial r_\alpha \partial r_{\alpha'} D_{\kappa\alpha p,\kappa\alpha' p}(t^+t)$
Total electrostatic potential	$V_{\rm tot}(1) = \int d2 v(12)[\langle \hat{n}_{\rm e}(2)\rangle + \langle \hat{n}_{\rm n}(2)\rangle]$
Equation of motion, electrons	$[i\hbar\partial/\partial t_1 + (\hbar^2/2m_{\rm e})\nabla^2(1) - V_{\rm tot}(1)]G(12) - \int d3\Sigma(13)G(32) = \delta(12)$
Equation of motion, nuclei	$\sum_{\kappa''\alpha''p''}[M_\kappa\omega^2\delta_{\kappa\alpha p,\kappa''\alpha''p''} - \Pi_{\kappa\alpha p,\kappa''\alpha''p''}(\omega)]D_{\kappa''\alpha''p'',\kappa'\alpha'p'}(\omega) = \delta_{\kappa\alpha p,\kappa'\alpha'p'}$
Electron self-energy	$\Sigma(12) = i\hbar\int d(34)G(13)\Gamma(324)[W_{\rm e}(41^+) + W_{\rm ph}(41^+)]$
Screened Coulomb, electrons	$W_{\rm e}(12) = v(12) + \int d(34)v(13)P_{\rm e}(34)W_{\rm e}(42)$
Electronic polarization	$P_{\rm e}(12) = -i\hbar\sum_{\sigma_1}\int d(34)G(13)G(41^+)\Gamma(342)$
Electronic dielectric matrix	$\epsilon_{\rm e}(12) = \delta(12) - \int d(3)v(13)P_{\rm e}(32)$
Vertex	$\Gamma(123) = \delta(12)\delta(13) + \int d(4567)[\delta\Sigma(12)/\delta G(45)]G(46)G(75)\Gamma(673)$
Screened Coulomb, nuclei	$W_{\rm ph}(12) = \sum_{\kappa\alpha p,\kappa'\alpha'p'}\int d(34)\epsilon_{\rm e}^{-1}(13)\nabla_{3,\alpha}V_\kappa(\mathbf{r}_3-\boldsymbol{\tau}^0_{\kappa p})$
	$\times D_{\kappa\alpha p,\kappa'\alpha'p'}(t_3t_4)\epsilon_{\rm e}^{-1}(24)\nabla_{4,\alpha'}V_{\kappa'}(\mathbf{r}_4-\boldsymbol{\tau}^0_{\kappa'p'})$
Phonon self-energy	$\Pi_{\kappa\alpha p,\kappa'\alpha'p'}(\omega) = \sum_{\kappa''p''}Z_\kappa Z_{\kappa''}(\partial^2/\partial r_\alpha\partial r'_{\alpha'})$
	$\times[\delta_{\kappa'p',\kappa''p''}W_{\rm e}(\mathbf{r},\mathbf{r}',\omega) - \delta_{\kappa p,\kappa'p'}W_{\rm e}(\mathbf{r},\mathbf{r}',0)]_{\mathbf{r}=\boldsymbol{\tau}^0_{\kappa p},\mathbf{r}'=\boldsymbol{\tau}^0_{\kappa''p''}}$

Giustino, Rev. Mod. Phys. (2017)

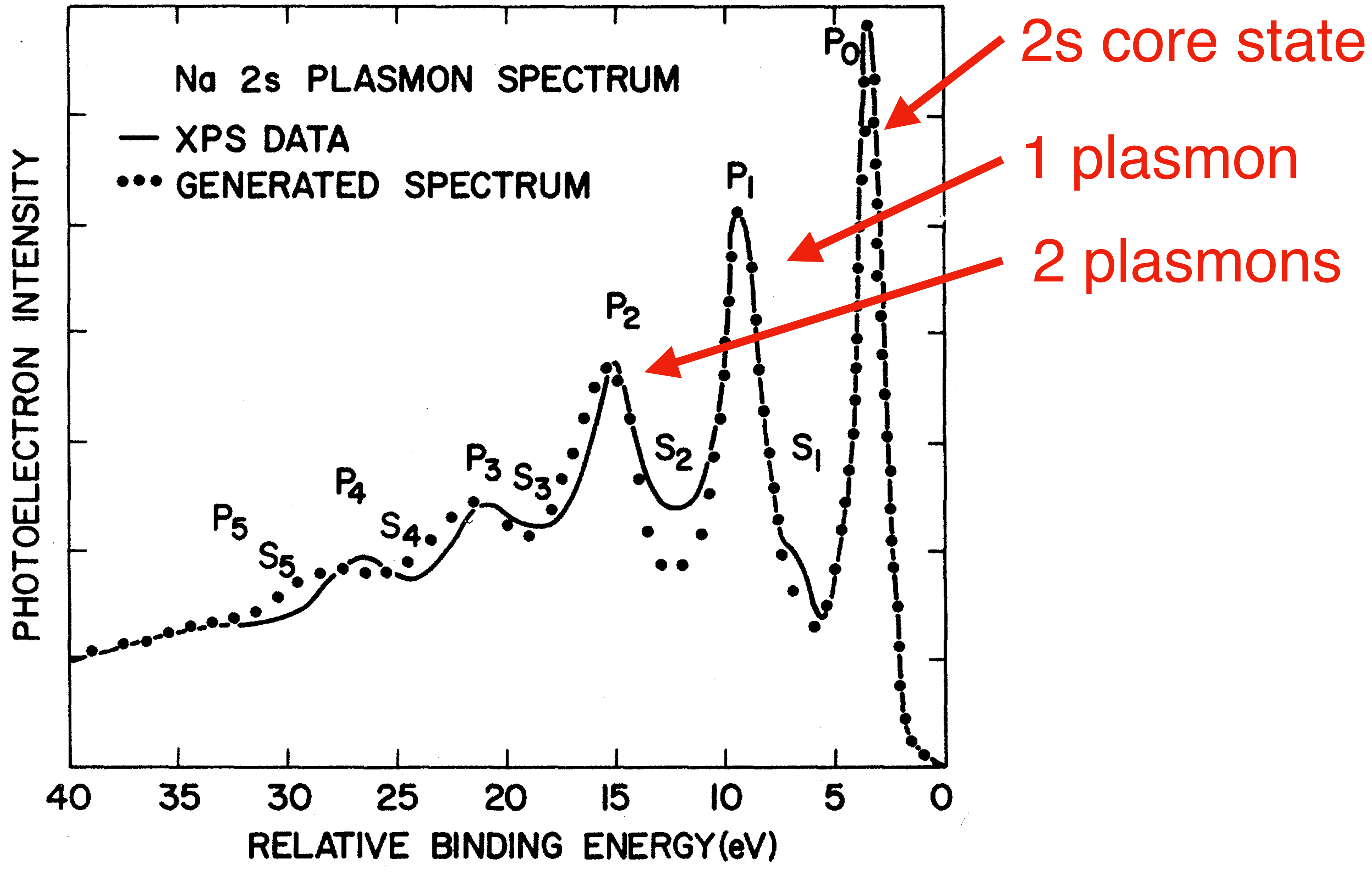
Part 2

Polaronic satellites in
angle-resolved photoemission spectroscopy (ARPES)

Satellites in photoemission: a hallmark of electron-boson interaction

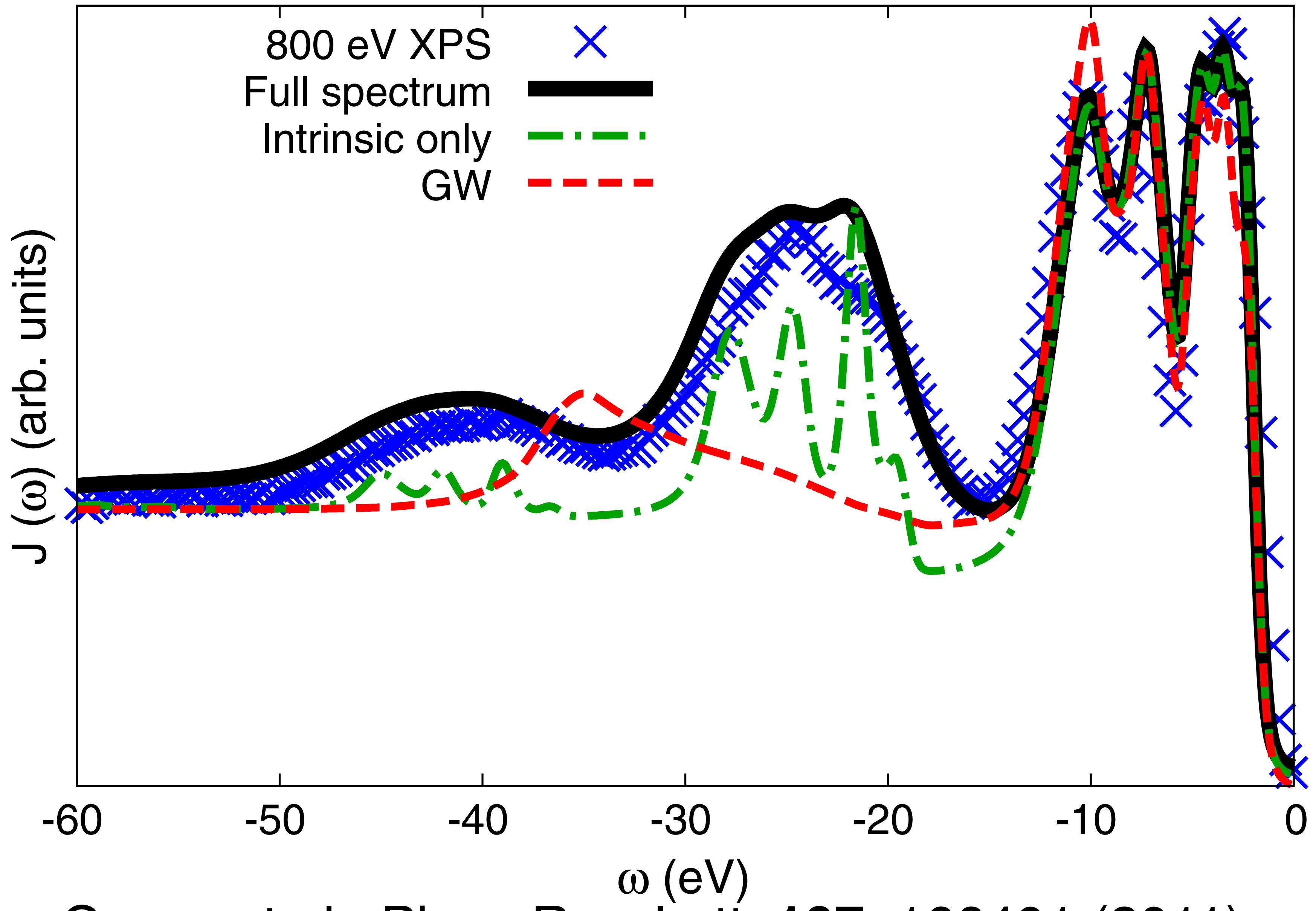


Metals



Pardee et al., Phys. Rev. B **11**, 3614 (1975)

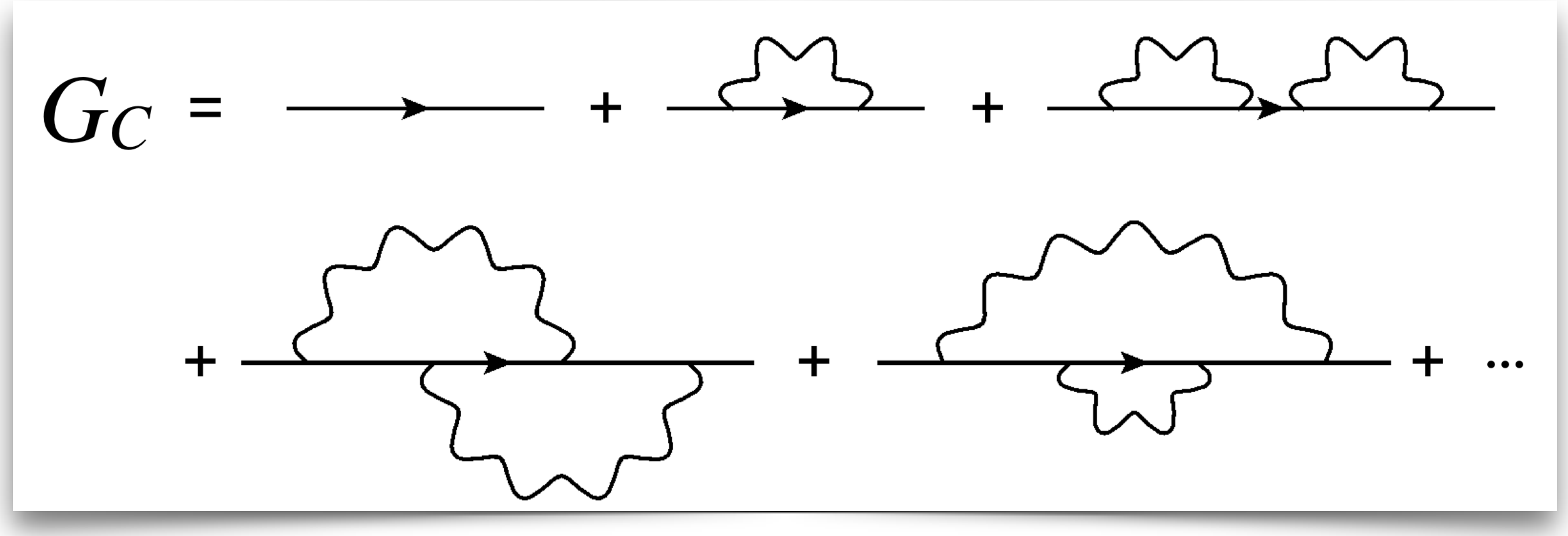
Semiconductors



Guzzo et al., Phys. Rev. Lett. **107**, 166401 (2011)

A strong stimulus for the development of (ab-initio) theories of the electron-boson interaction

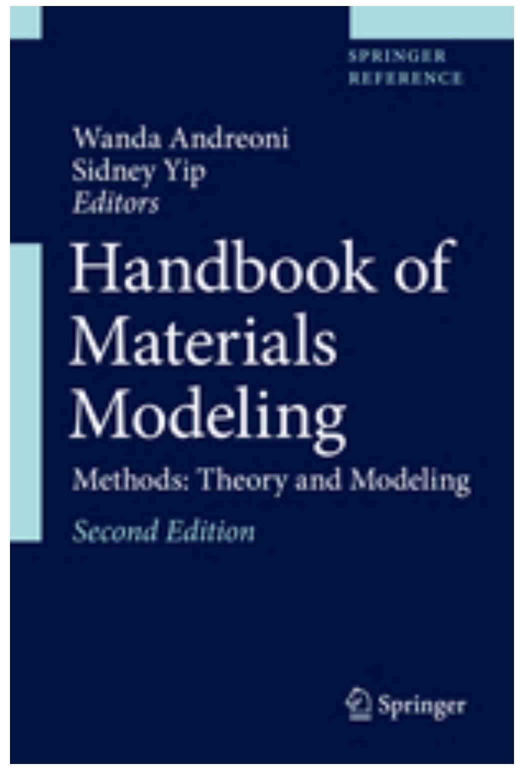
Example: the cumulant expansion approach



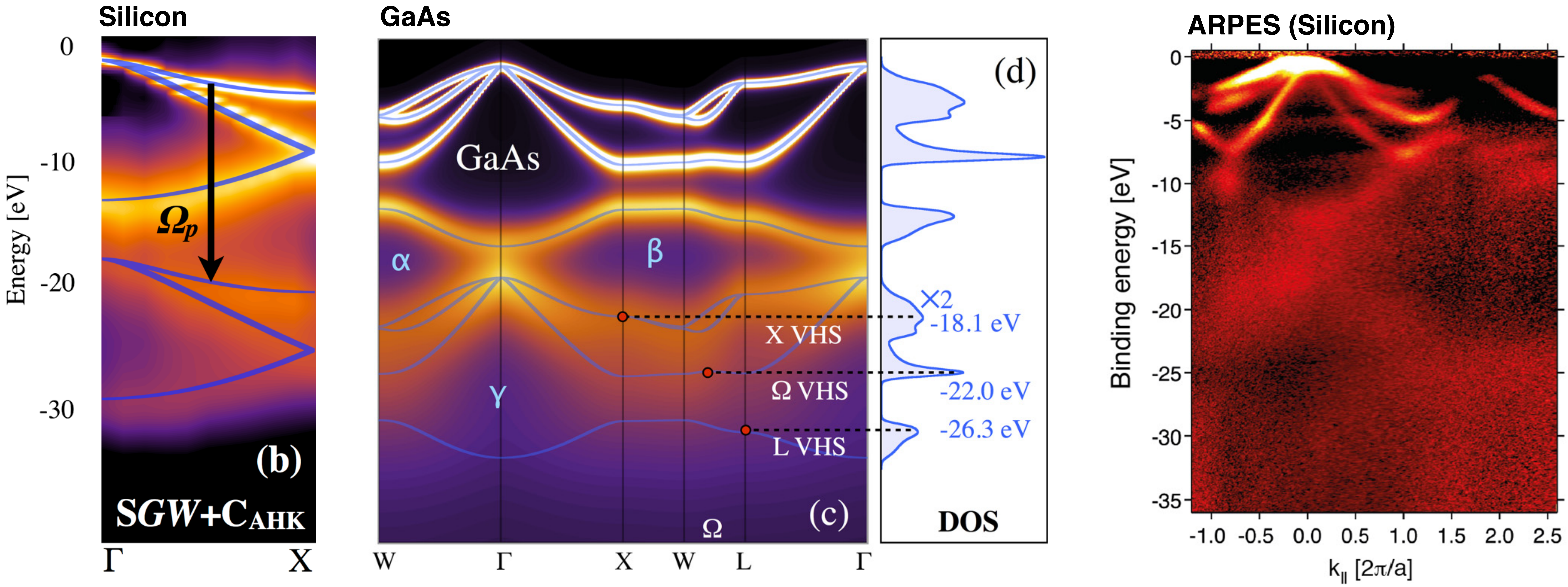
Cumulant representation of the spectral function

$$A(\mathbf{k},\omega) = \sum_n e^{A^{\rm S1}_{n\mathbf{k}}(\omega)} * A^{\rm QP}_{n\mathbf{k}}(\omega)$$

Caruso, Verdi, Giustino,
Handbook of Materials Modeling
Springer (2018)



Band structures of plasmonic polarons

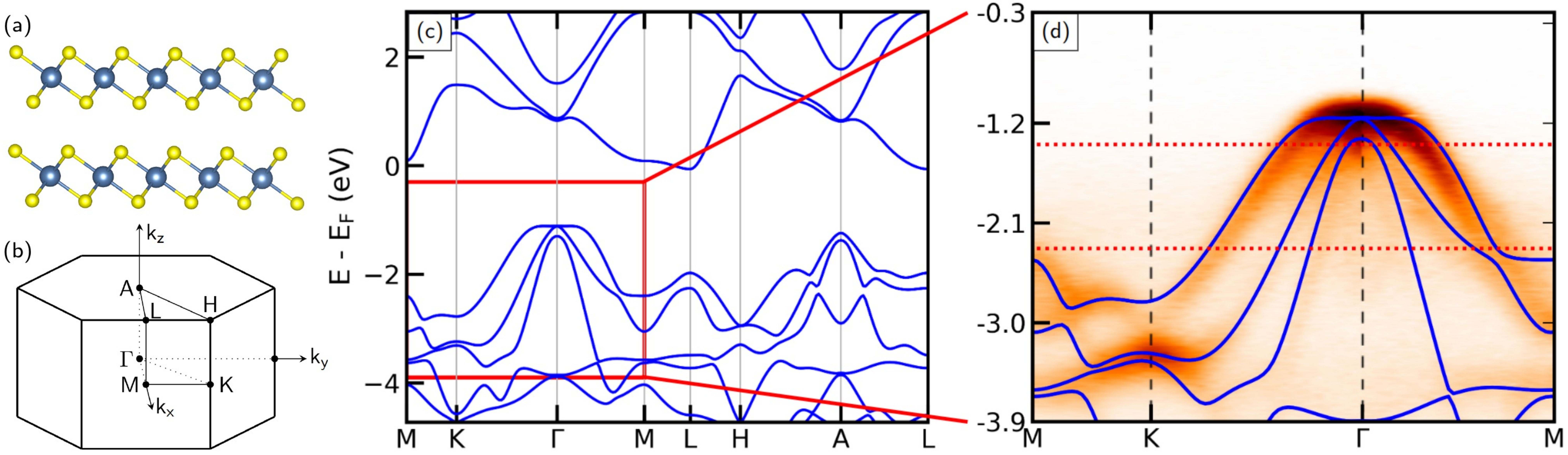


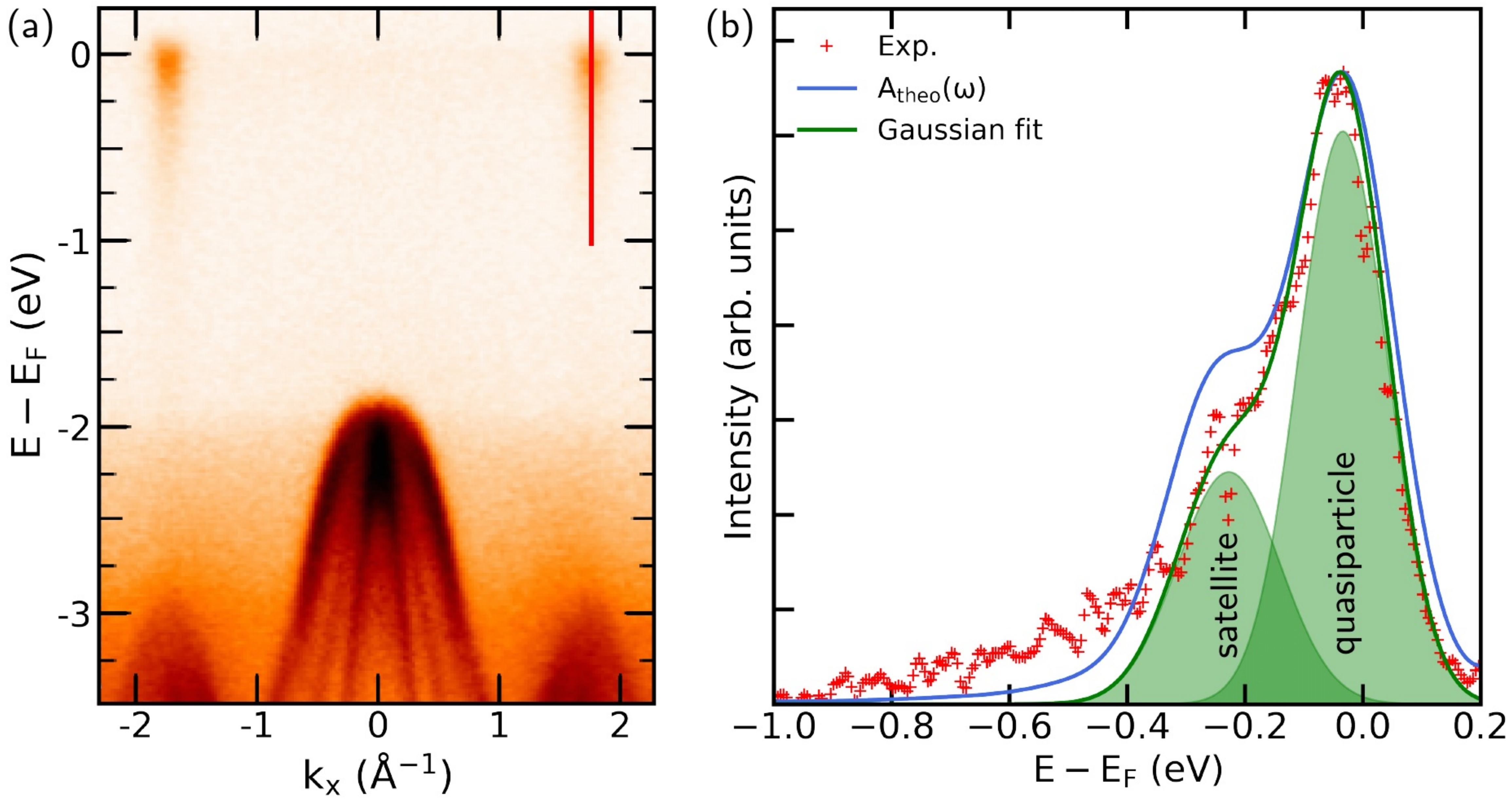
Full replicas of the band structure due to the electron-plasmon interactions

Caruso et al., Phys. Rev. Lett. **114**, 146404 (2015)
Caruso et al., Phys. Rev. B, **92**, 045123 (2015)

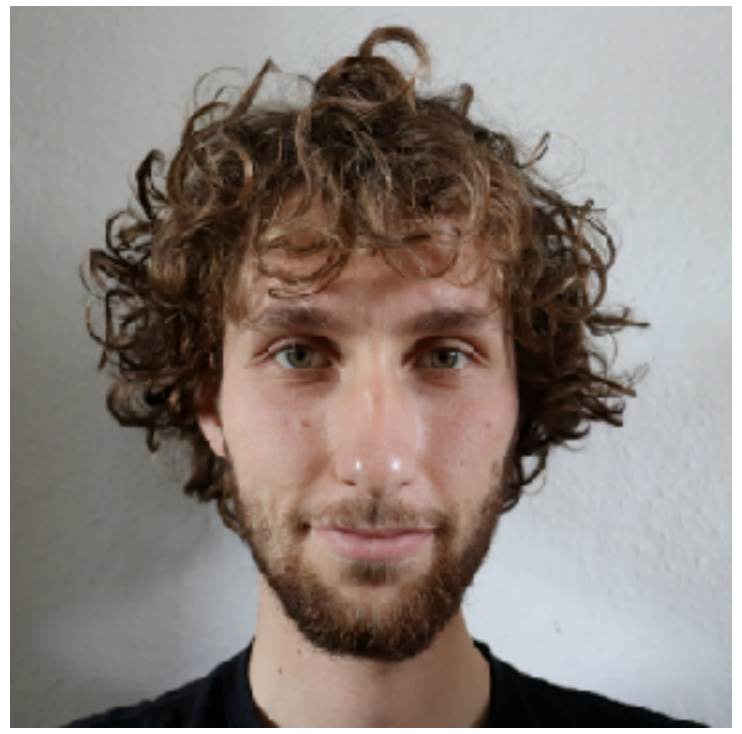
Lischner et al., Phys. Rev. B, **91,** 205113 (2015)

Satellites due to the electron-plasmon coupling in highly-doped HfS2





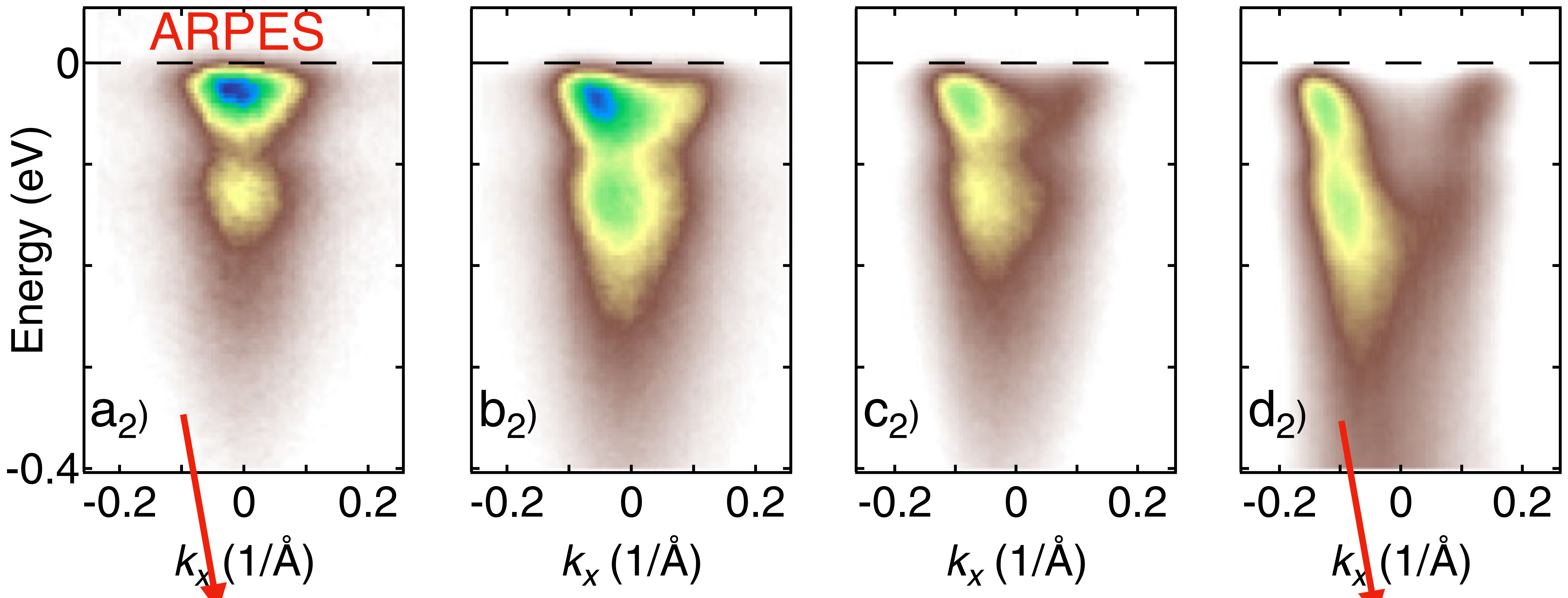
Poster!!!



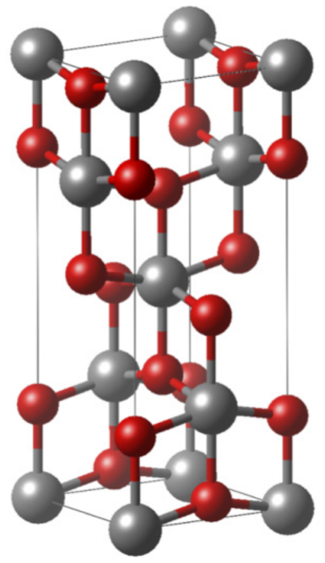
C. Emeis

Satellites due to the electron-phonon coupling: highly-doped polar semiconductors

increasing doping



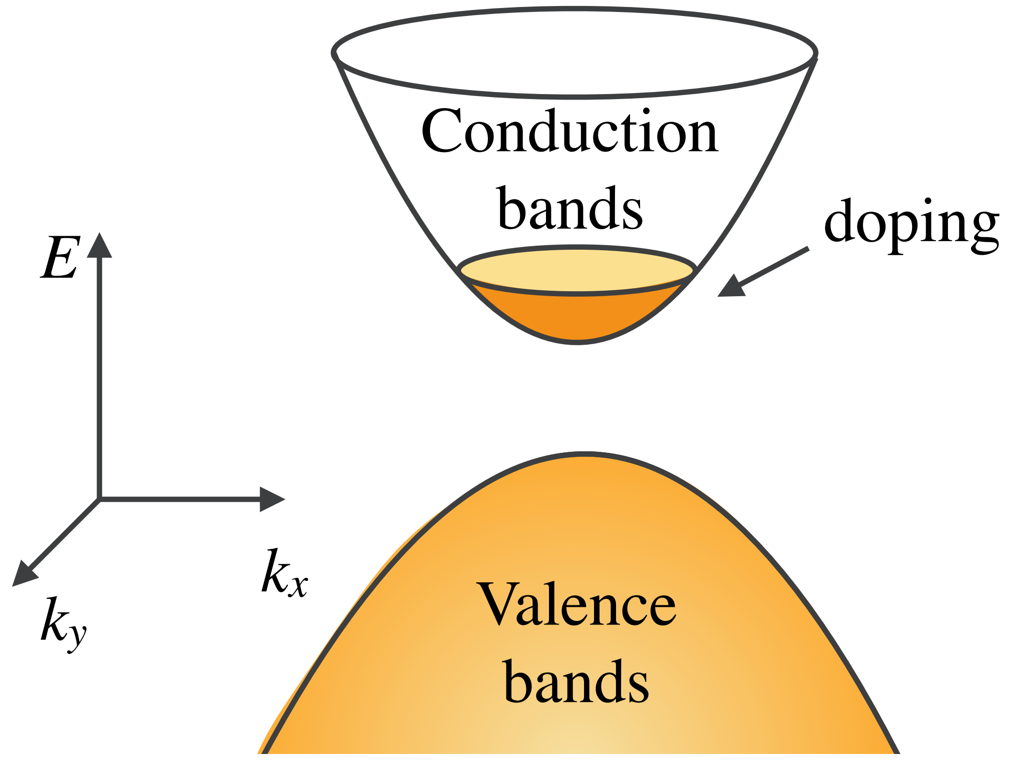
TiO2



satellite (strong coupling)

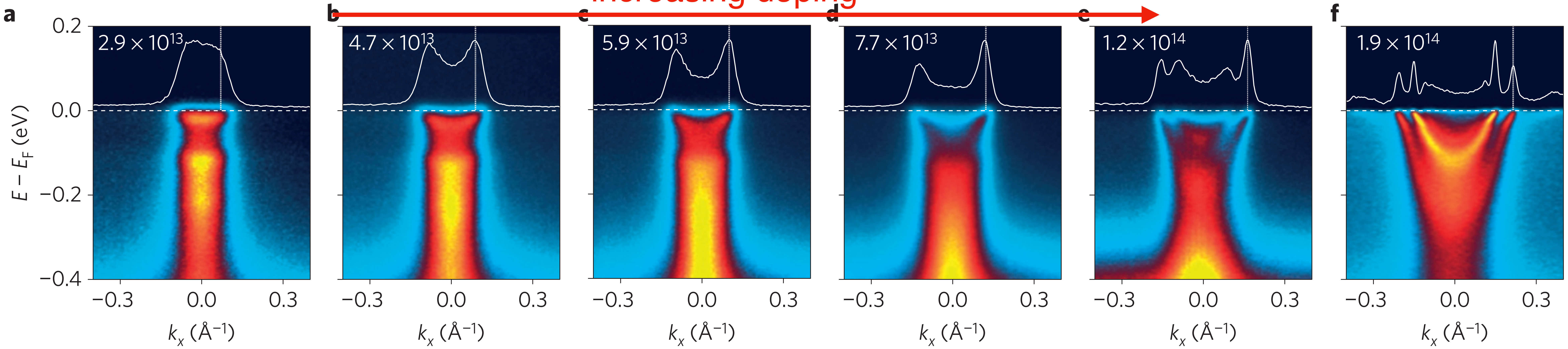
kink (weak coupling)

Moser et al., Phys. Rev. Lett. **110,** 196403 (2013)

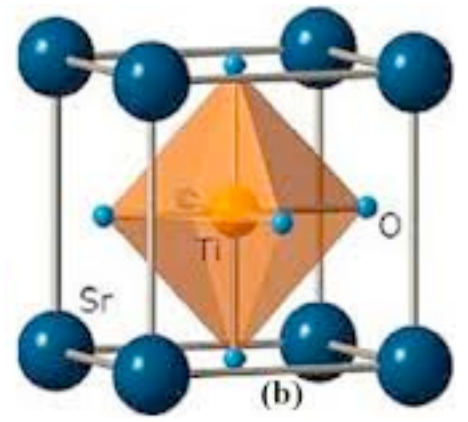


What is the origin of polaronic satellites?
What is the influence of doping?

increasing doping



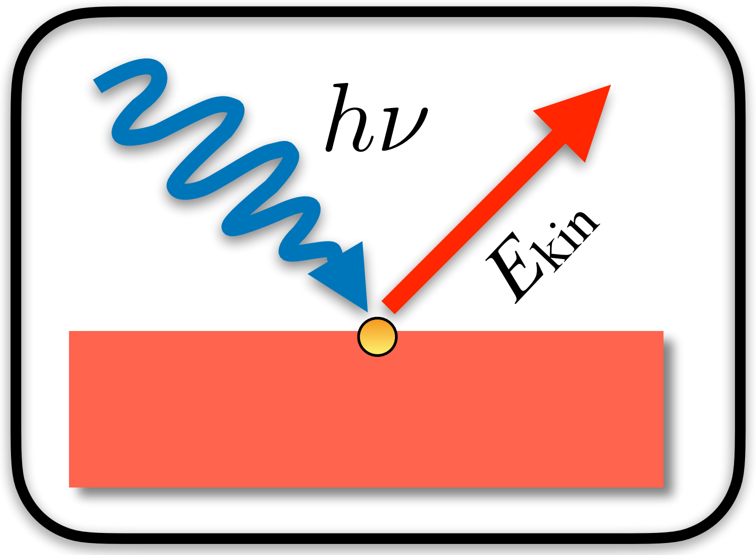
2D electron gas
at the surface of $SrTiO_3$



Wang et al., Nat. Mater. **15,** 835 (2016)

First-principles theory of photoemission spectroscopy

photoemission spectroscopy



Photoelectron current (Fermi's golden rule):

$$J_{\mathbf{k}}(\omega) = \sum_s |\langle \Psi_{\mathbf{k},s} | \Delta | \Psi_i \rangle|^2 \delta(\omega - \varepsilon_{\mathbf{k}} + \varepsilon_s)$$

final state — perturbation — initial state — energy conservation

$$= \sum_{ij} \Delta_{\mathbf{k}j} A_{ji}(\varepsilon_k - \omega) \Delta_{i\mathbf{k}}$$

[1] sudden approximation

Spectral function

$$A(\mathbf{k},\omega) = -\frac{1}{\pi} \sum_n \mathrm{Im}\, G_{n\mathbf{k}}(\omega)$$

Migdal (diagonal) approximation:

$$= \frac{1}{\pi} \sum_n |\mathrm{Im}[\omega - \varepsilon_{n\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega)]^{-1}|$$

Electron-boson coupling self-energy (Fan-Migdal):

$$\Sigma_{n\mathbf{k}}(\omega) = \frac{1}{N_{\mathbf{q}}} \sum_{m\nu\mathbf{q}} |g^{\text{e-b}}_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \left[\frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} + \omega^{\text{b}}_{\mathbf{q}\nu} - i\eta} + \frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} - \omega^{\text{b}}_{\mathbf{q}\nu} - i\eta} \right]$$

+

Phonons: $\omega^{\text{b}}_{\mathbf{q}\nu} = \omega_{\mathbf{q}\nu}$

$$g^{\text{e-ph}}_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V | \psi_{n\mathbf{k}} \rangle$$

C. Verdi, F. Giustino, Phys. Rev. Lett. **115**, 176401(2015)

Fröhlich (polar) coupling:

$$g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q}) \propto \sum_\kappa \frac{\mathbf{Z}^*_\kappa \cdot \mathbf{e}_{\kappa\nu}(\mathbf{q})}{(\mathbf{q}+\mathbf{G})}$$

Electron-Phonon coupling with Wannier function (EPW)

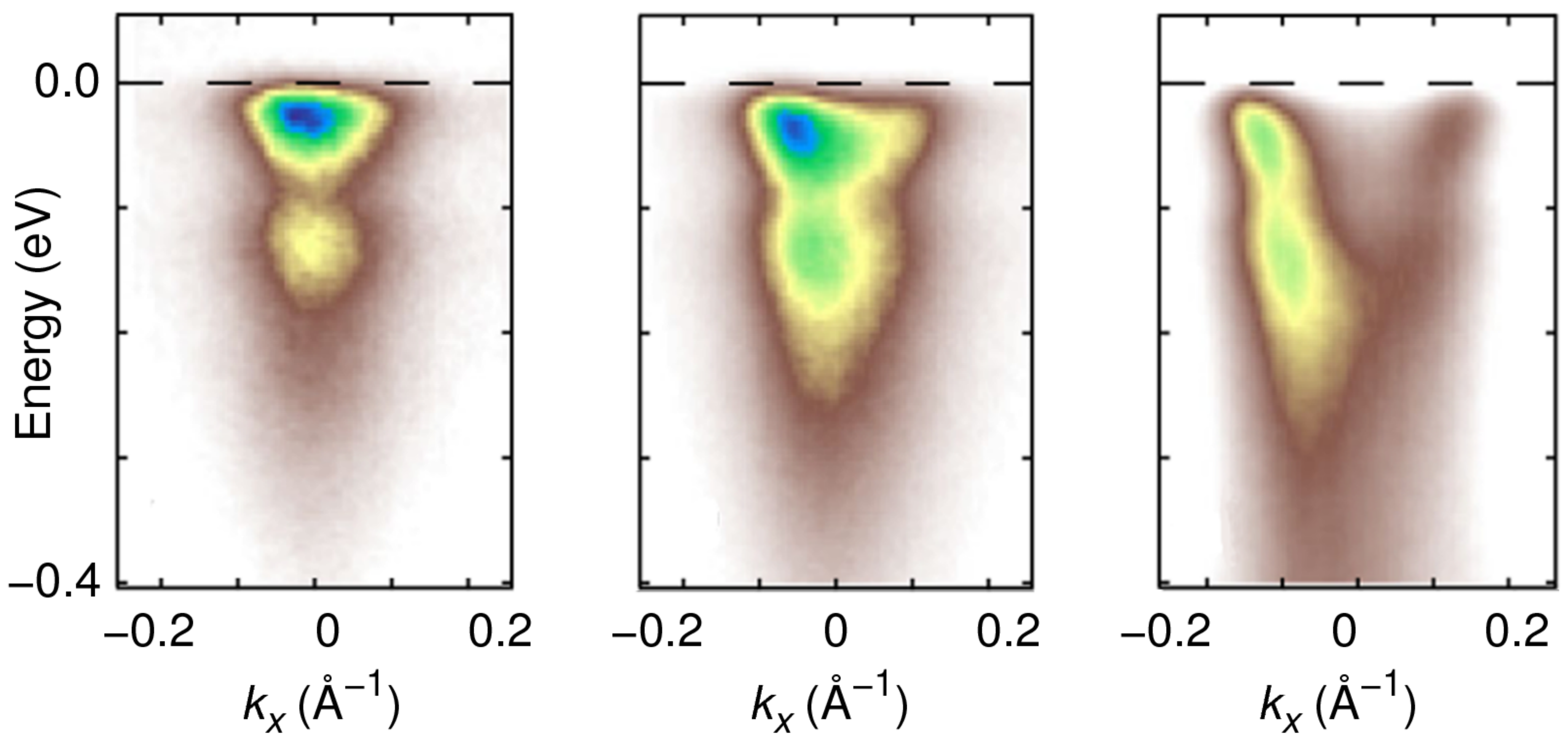
Cumulant expansion approach

$$A(\mathbf{k},\omega) = \sum_n e^{A^{\mathrm{S1}}_{n\mathbf{k}}(\omega)} * A^{\mathrm{QP}}_{n\mathbf{k}}(\omega)$$

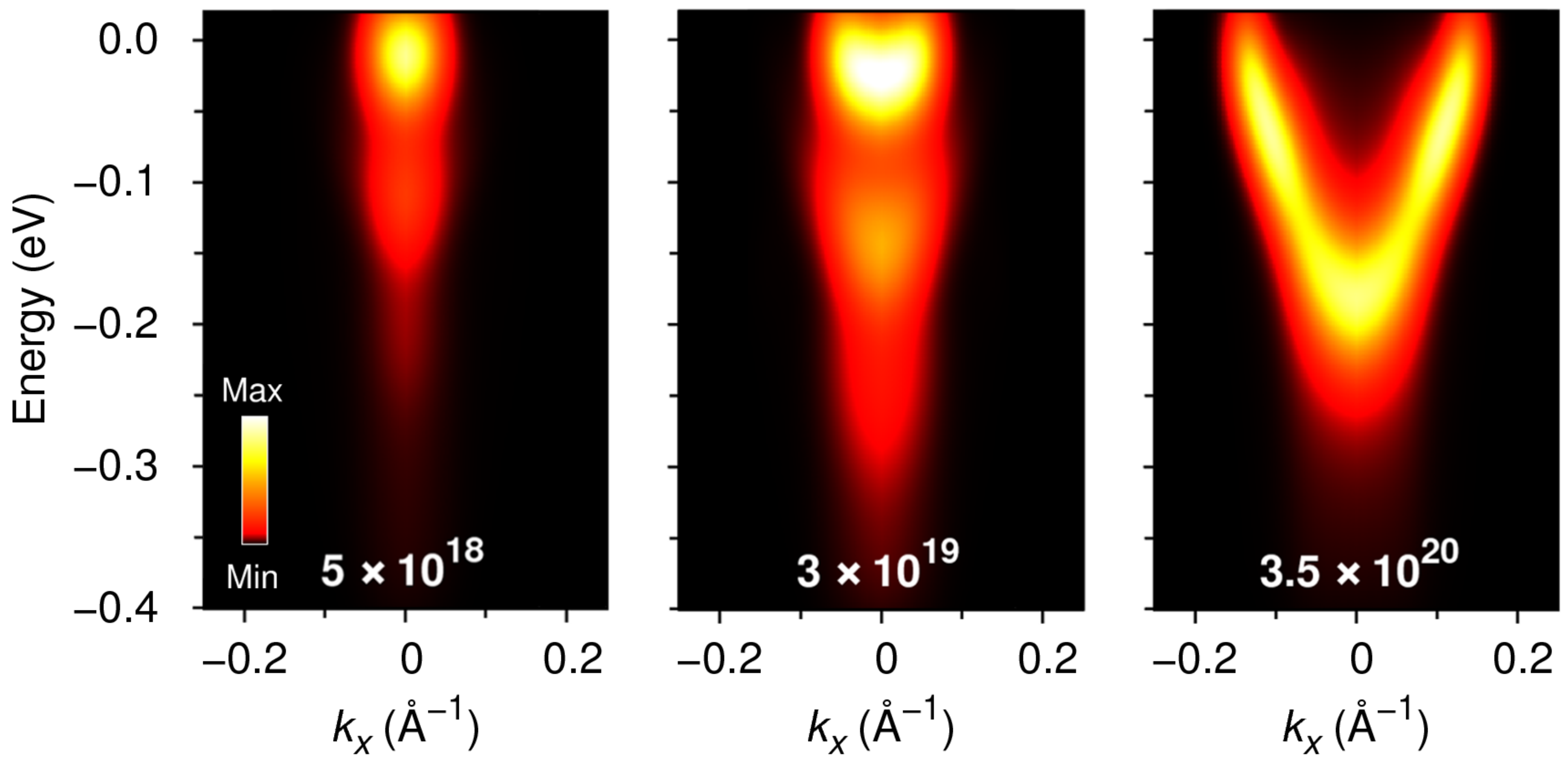
[1] L. Hedin, et al., Phys. Rev. B **58**, 15565 (1998)

Satellites due to the electron-phonon coupling: highly-doped polar semiconductors

ARPES measurements of highly-doped TiO_2



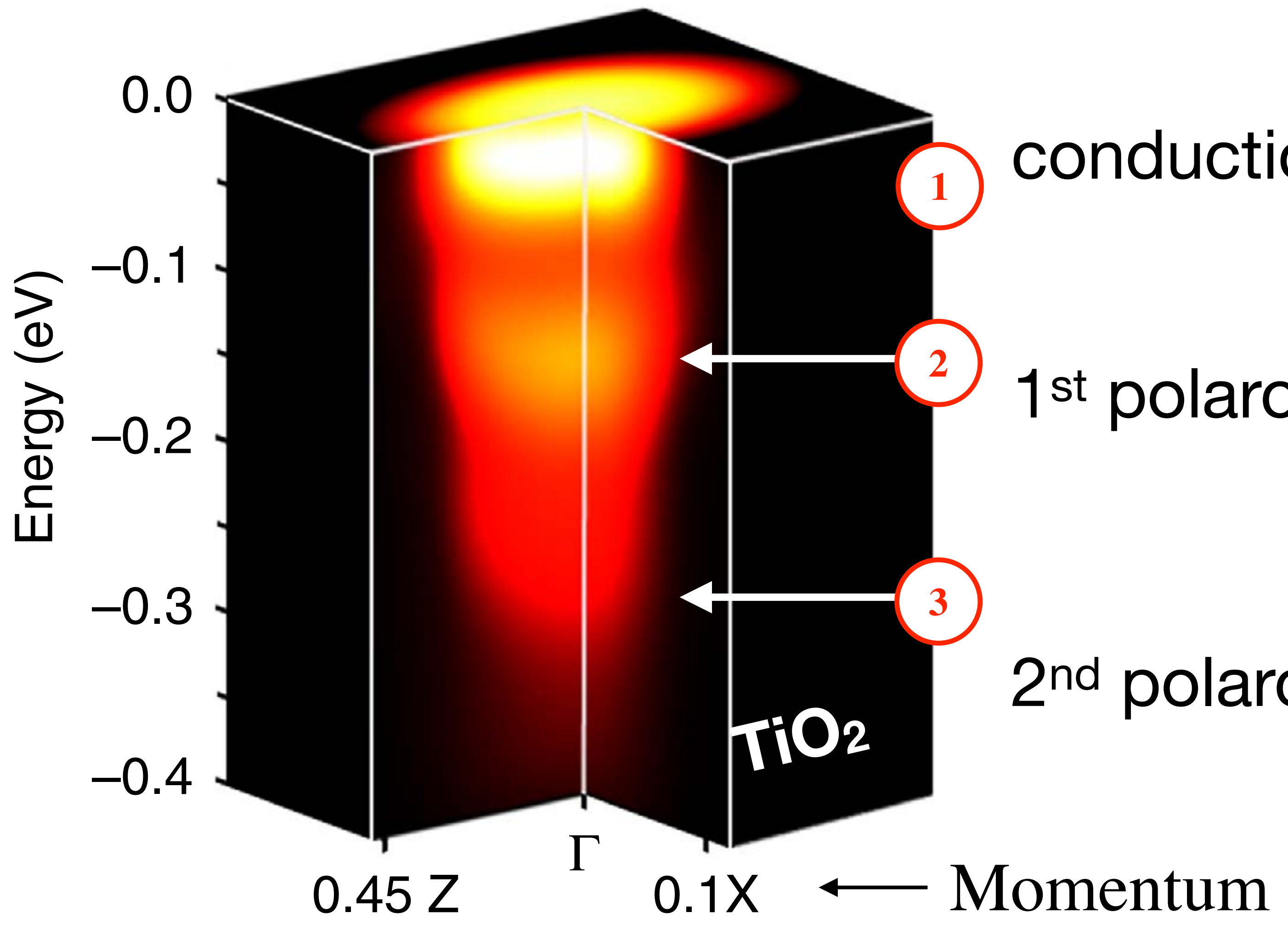
Spectral function including electron-phonon interactions:



ARPES: Moser et al., Phys. Rev. Lett. **110**, 196403 (2013)
Theory: Verdi, Caruso, Giustino, Nature Comm. **8**, 15769 (2017)

Free carriers screen the electron-phonon interactions (progressively reduce the coupling at higher doping)

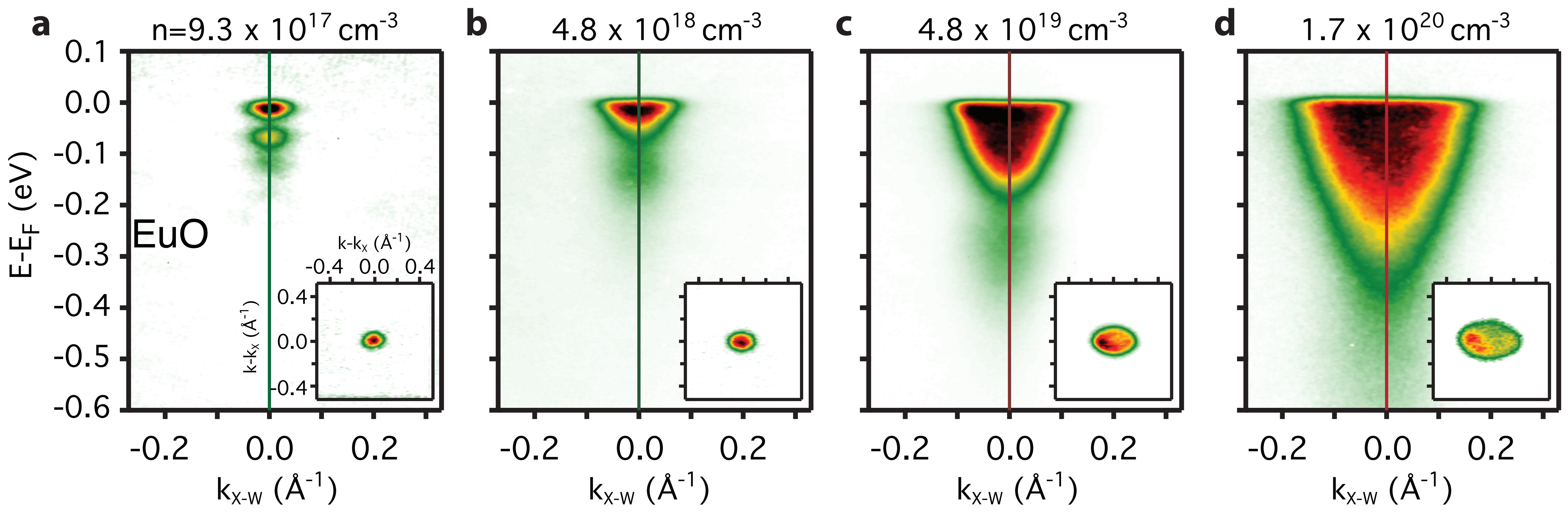
Doping-induced polaronic to Fermi liquid transition

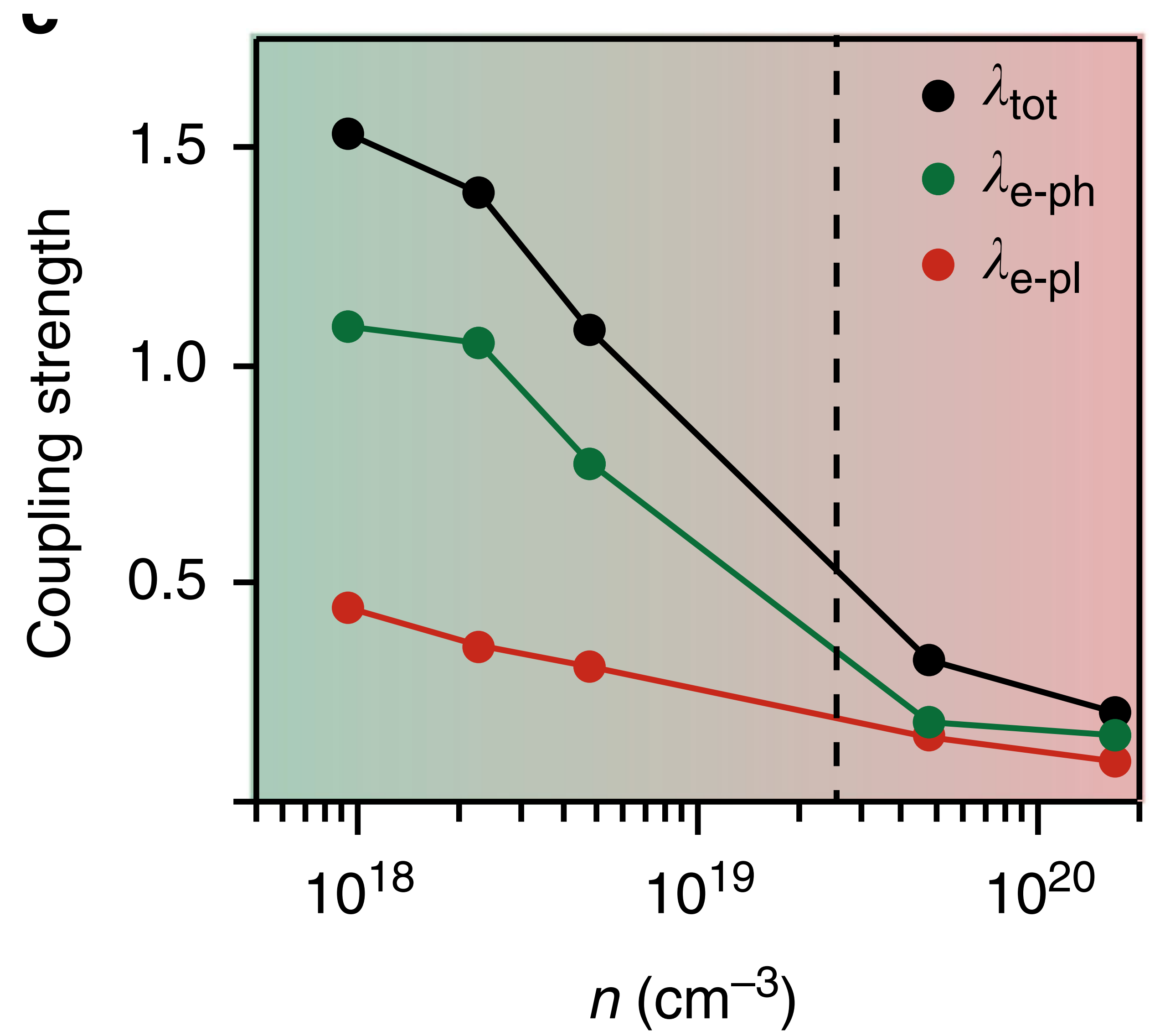


Carla Verdi

Feliciano Giustino

Doping-induced crossover from lattice to plasmonic polarons

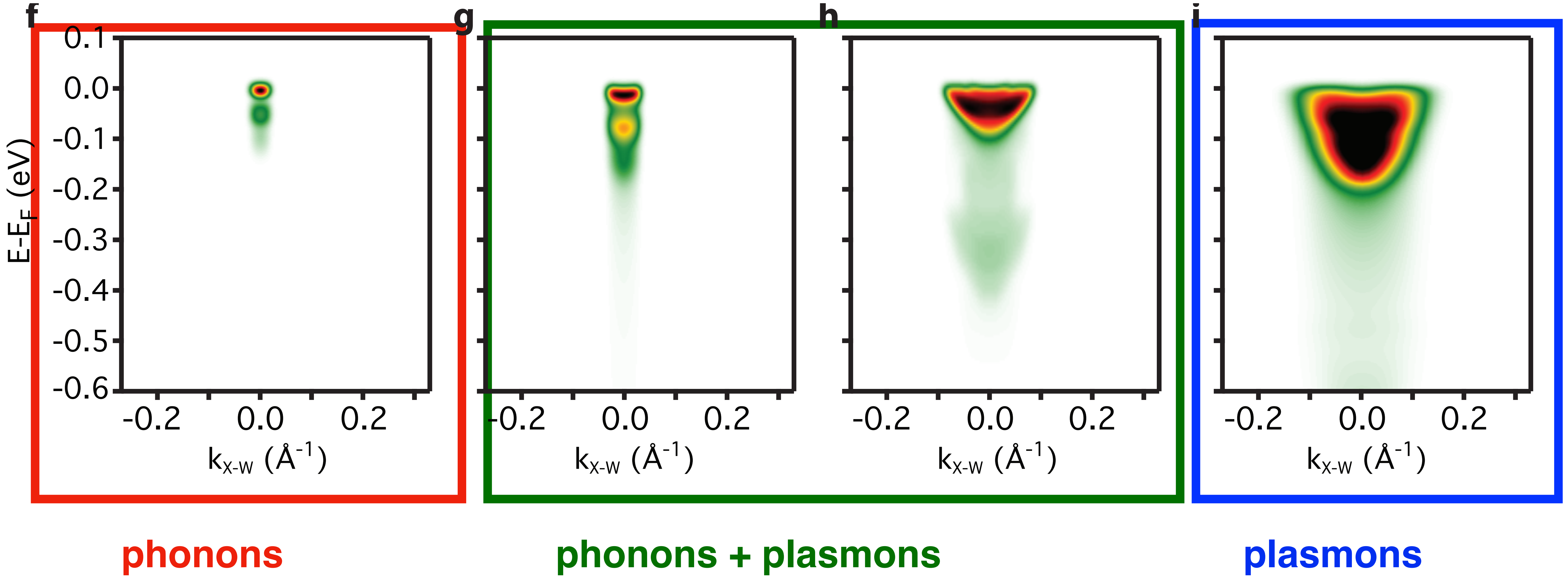




Spectral function with:

$$\Sigma(\mathbf{k},\omega) = \Sigma^{\mathrm{eP}} + \Sigma^{\mathrm{e-ph}}$$

F. Caruso, F. Giustino, Phys. Rev. B **94**, 115208 (2016)

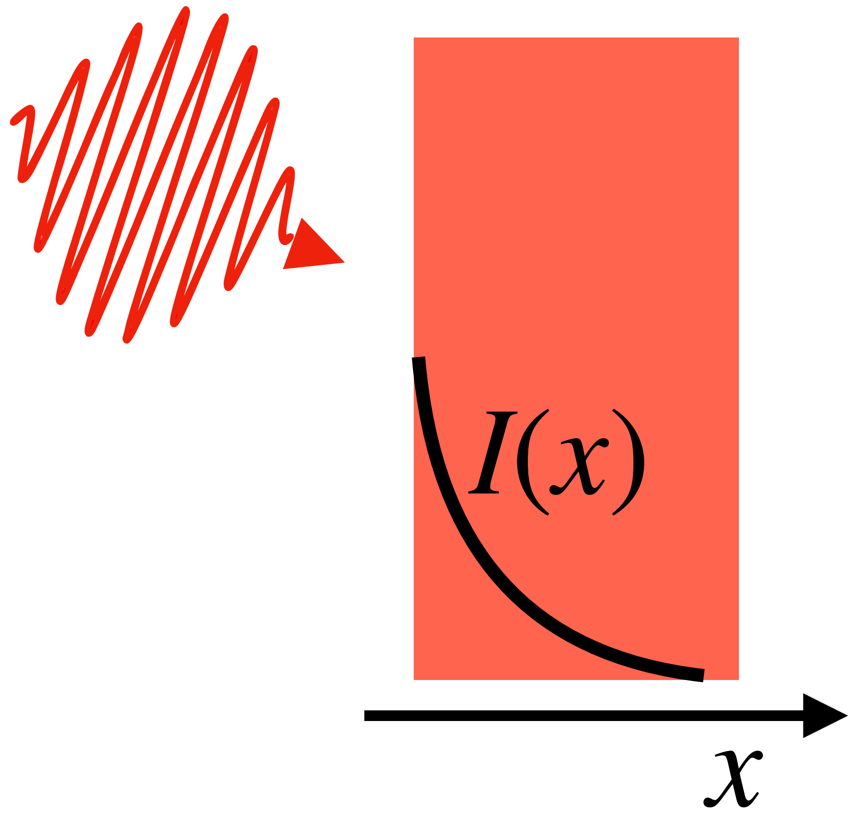


J. Riley, F. Caruso, C. Verdi, et al. Nature Comm. **9**, 2305 (2018)

Part 3

Phonon-assisted optical absorption in semiconductors

Optical absorption in semiconductors

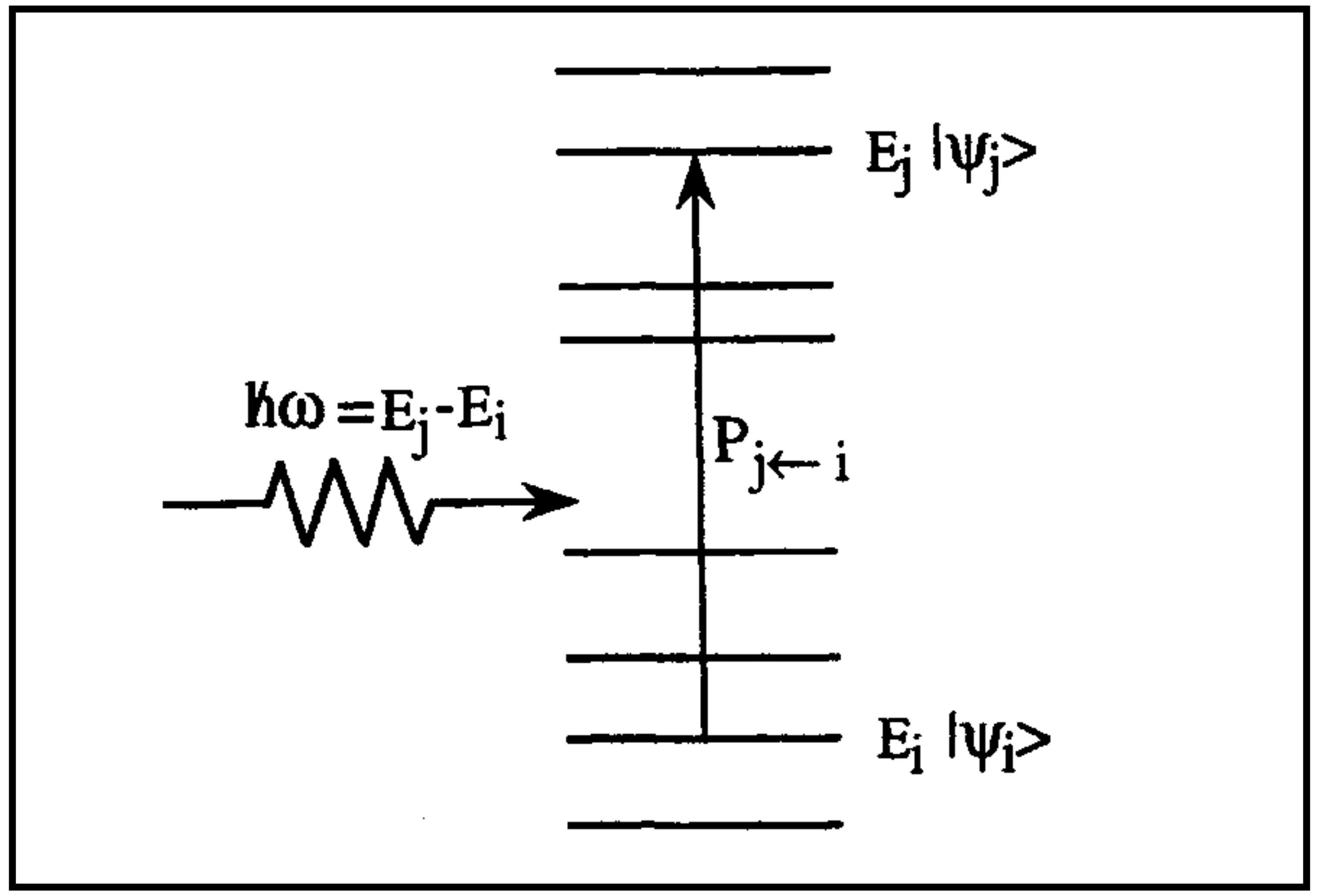


Intensity of radiation
propagating through the sample

$$I(\omega, x) = I_0\, e^{-\alpha(\omega)x}$$

α : absorption coefficient

Quantum picture of the absorption process



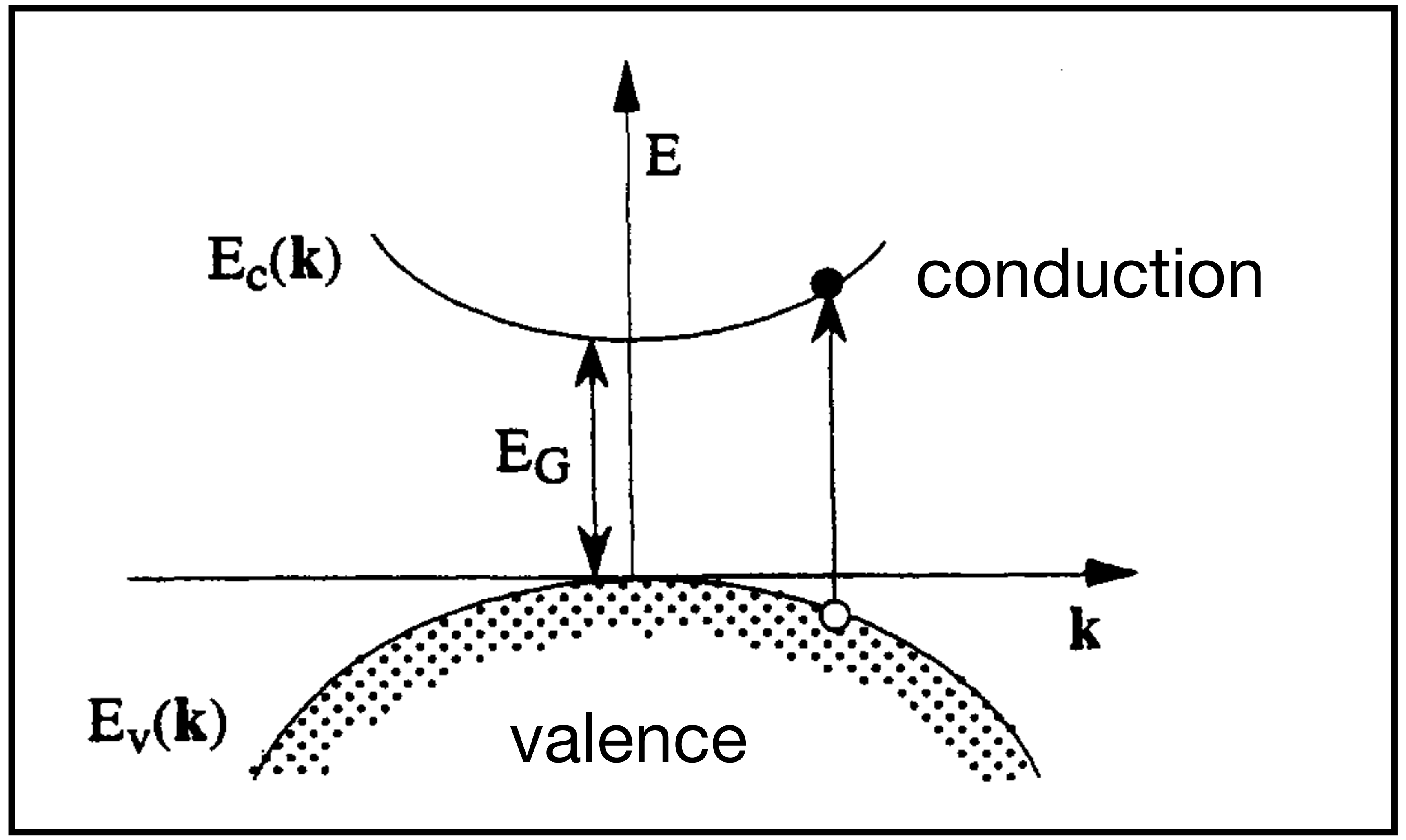
Why is it important?

- powerful characterization technique
- fundamental principle underlying solar energy conversion

In this lecture:
What is the role of phonons in the absorption of light in solids?

Phonon-assisted optical absorption in semiconductors

(direct) optical absorption



The absorption coefficient:

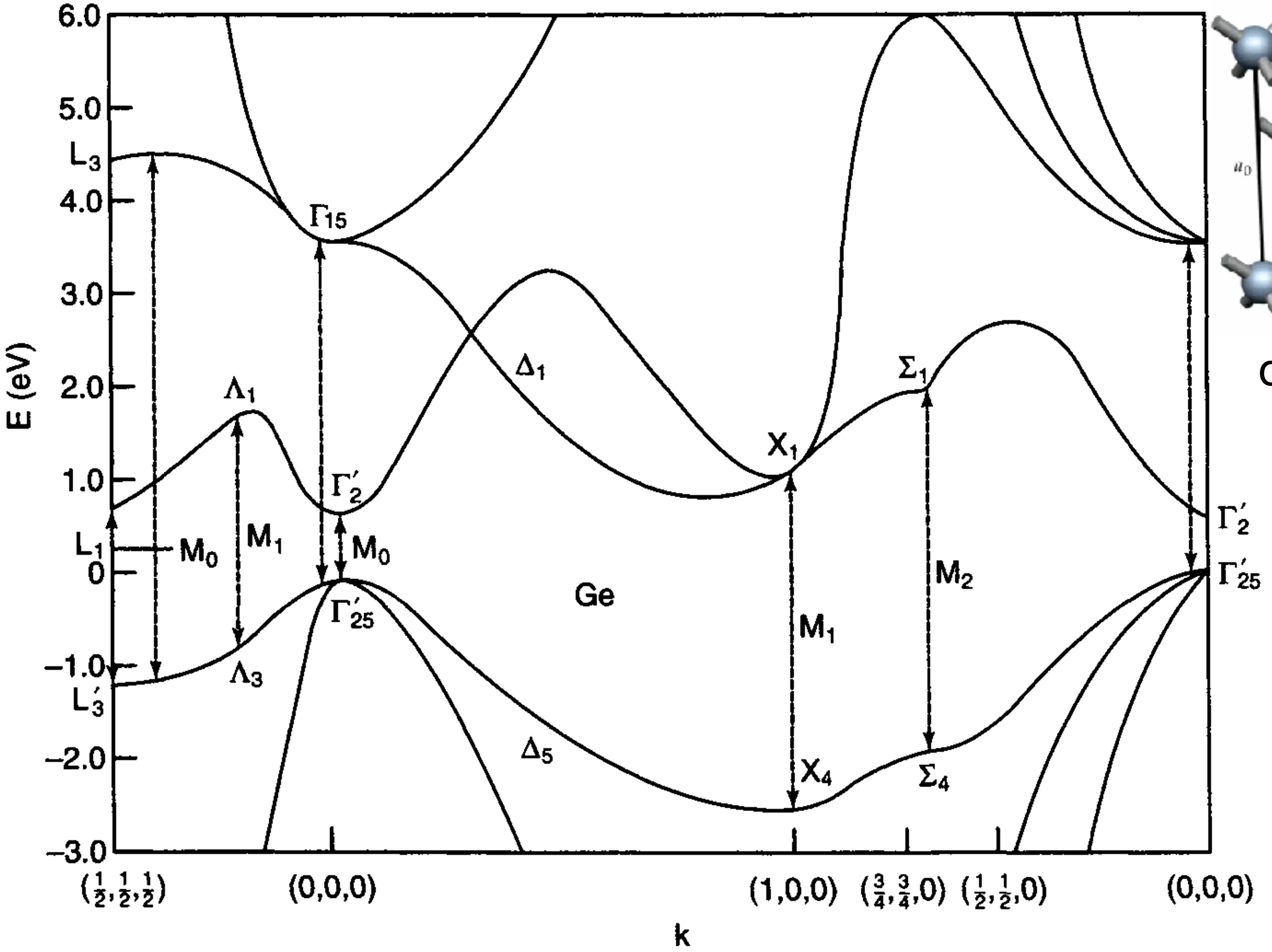
$$\alpha(\omega) = \frac{\omega}{c\,n(\omega)}\varepsilon_2(\omega)$$

speed of light

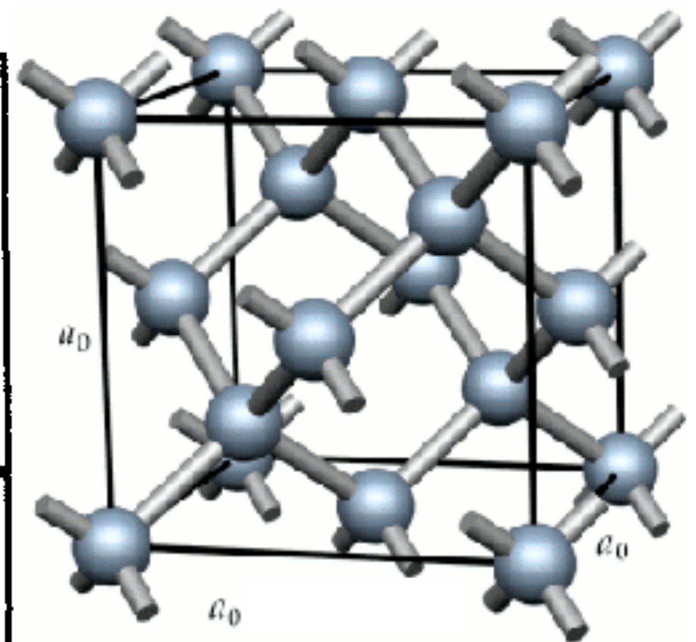
refractive index

dielectric fn.

Band structure of Germanium



Brust et al., Phys. Rev. Lett **9**, 94 (1962)



diamond-like structure

Phonon-assisted optical absorption in semiconductors

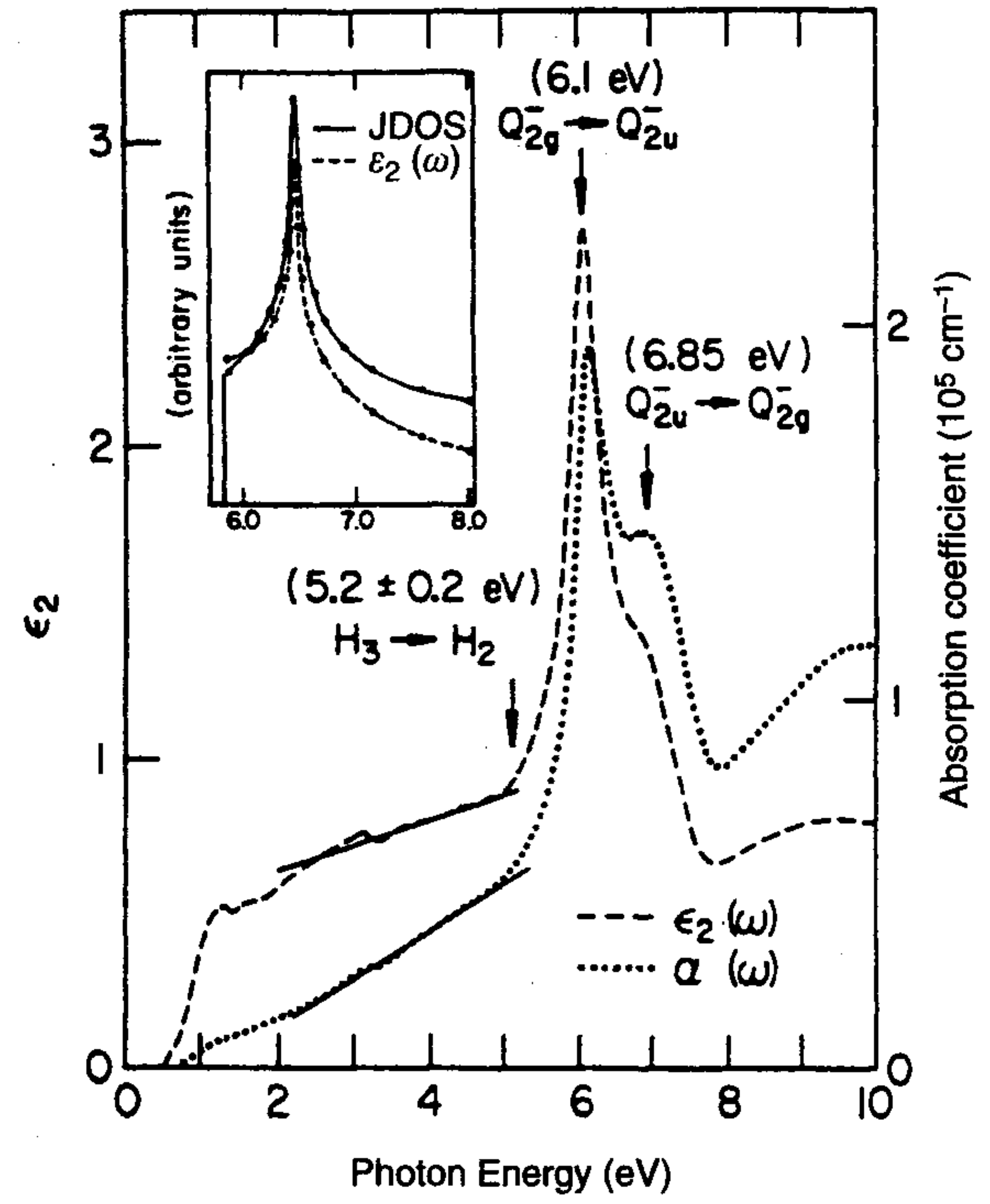
The absorption coefficient:

$$\alpha(\omega) = \frac{\omega}{c\,n(\omega)}\varepsilon_2(\omega)$$

speed of light

refractive index

dielectric fn.



Hoffman et al., Phys. Rev. B **30**, 6051 (1984)

The dielectric function independent particle approximation (IPA):

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{m^2\omega^2}\frac{1}{V}\sum_{cv}\sum_{\mathbf{k}} |\langle\psi_{c\mathbf{k}}|\,\mathbf{e}\cdot\mathbf{p}\,|\psi_{v\mathbf{k}}\rangle|^2\,\delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

matrix elements of the momentum operator

delta function for energy conservation

$\langle\psi_{c\mathbf{k}}|\,\mathbf{e}\cdot\mathbf{p}\,|\psi_{v\mathbf{k}}\rangle$: typically a slowly varying function

The joint density of states:

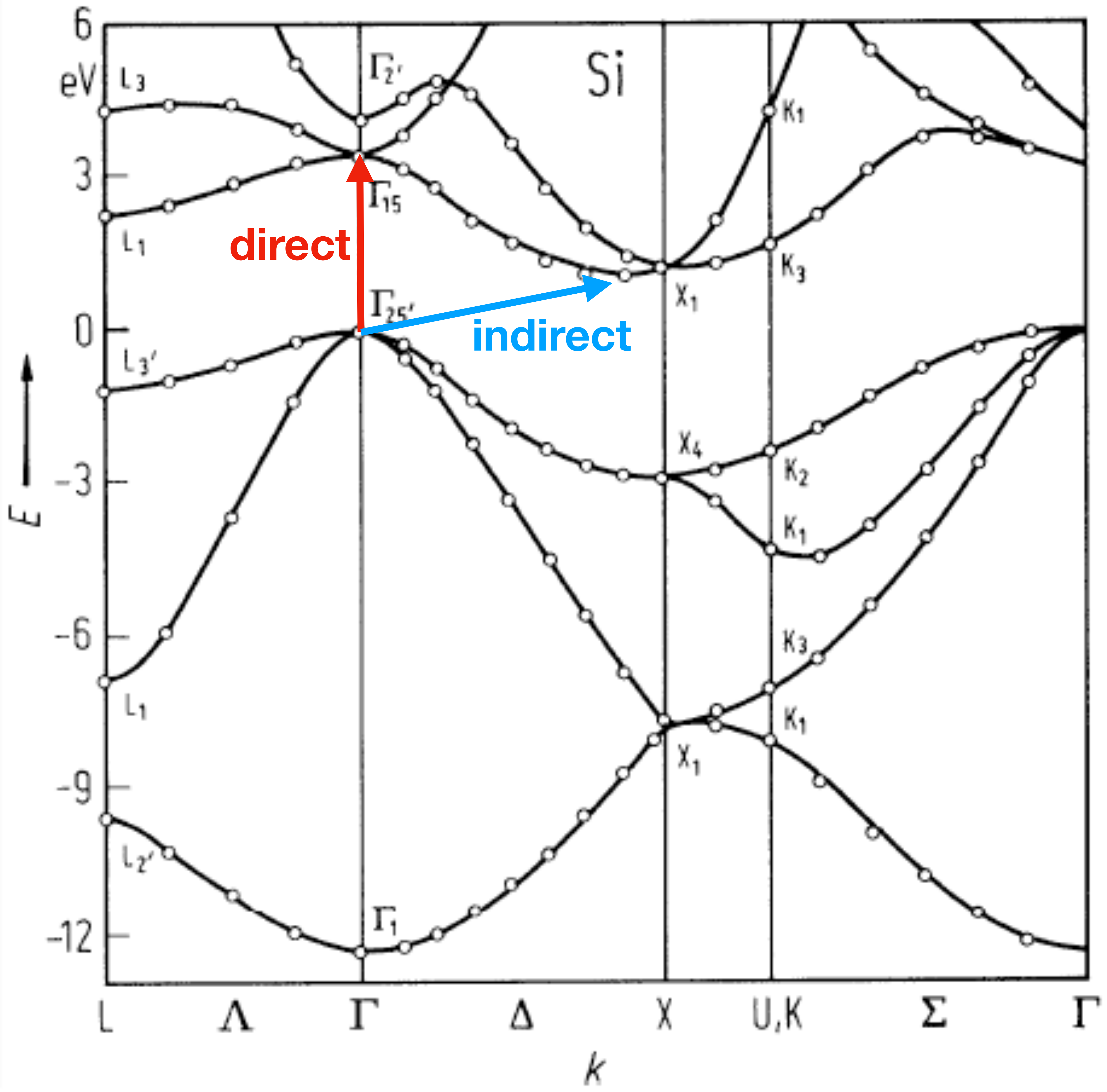
$$J_{cv}(\omega) = \int_{B.Z.} \frac{d\mathbf{k}}{(2\pi)^3}\,\delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

1. Structures in the absorption spectrum arise from peaks in the joint DOS
(exceptions: excitons, phonon assisted transitions)

2. No absorption for photon energies smaller than the band gap (exceptions: excitons)

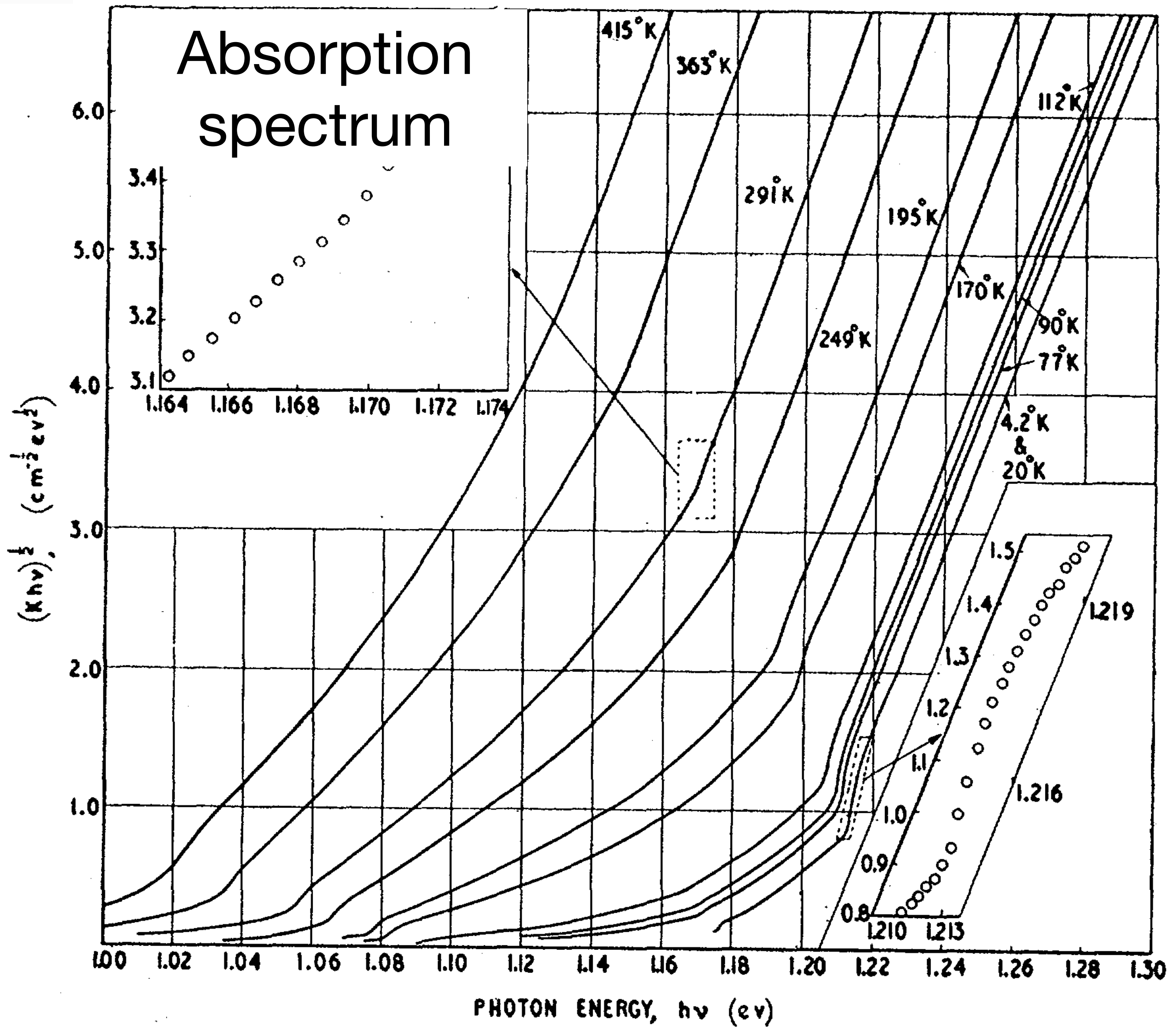
Optical absorption in INDIRECT-gap semiconductors: silicon

Band structure



Direct band gap: 3.5 eV **= minimum energy for direct transitions**
Indirect band gap: 1.12 eV

Absorption spectrum



Absorption of light occurs already for energy comparable with the indirect gap.

With strong temperature dependence (phonons?)

$1.0 < E < 1.3$ eV

Due to momentum conservation: only possible if a phonon is absorbed or emitted in the absorption process

Phonon assisted optical absorption

Macfarlane et al., Phys. Rev. **111**, 1245 (1958)

Phonon-assisted indirect optical absorption (emission)

Two possible processes:

1. One photon absorbed (emitted) & one phonon is absorbed
2. One photon absorbed (emitted) & one phonon is emitted

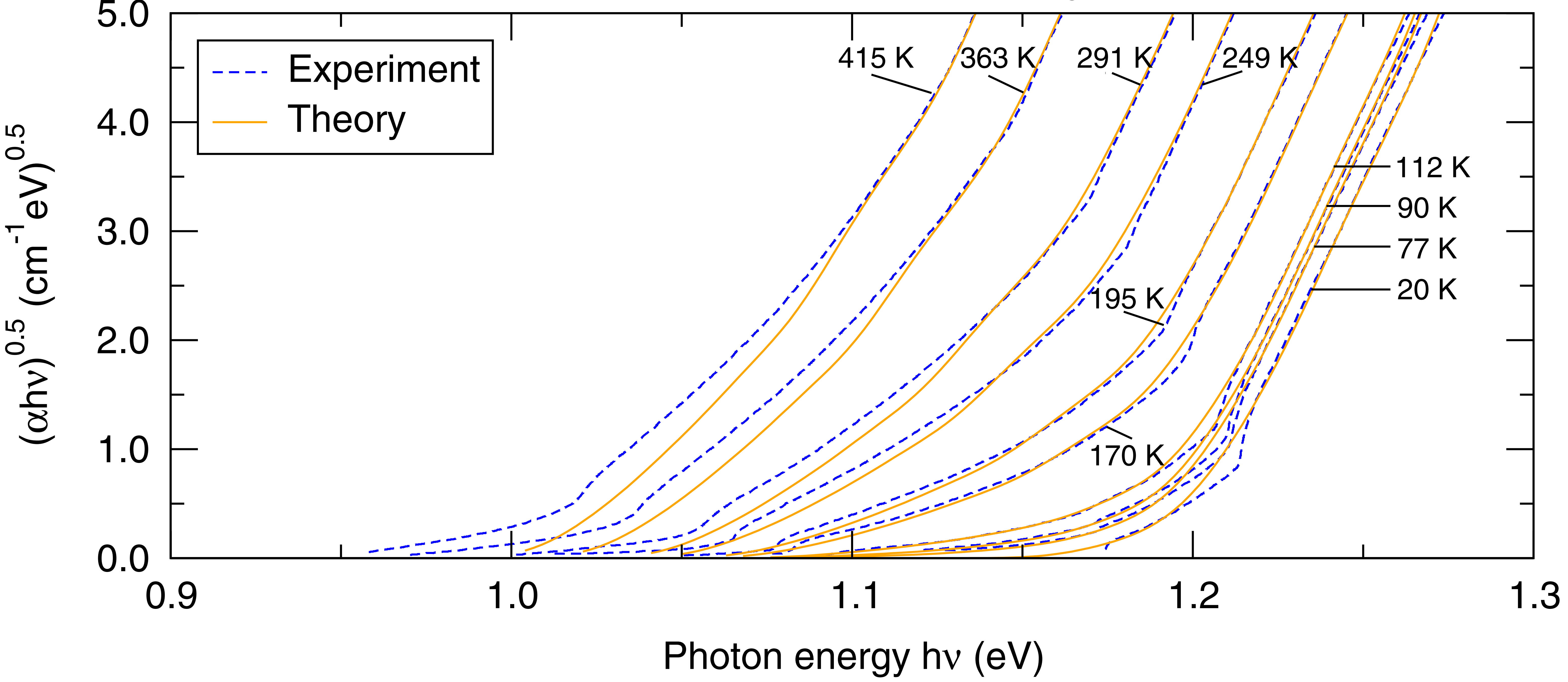
Theory: 2nd order Fermi golden rule + electron-phonon coupling

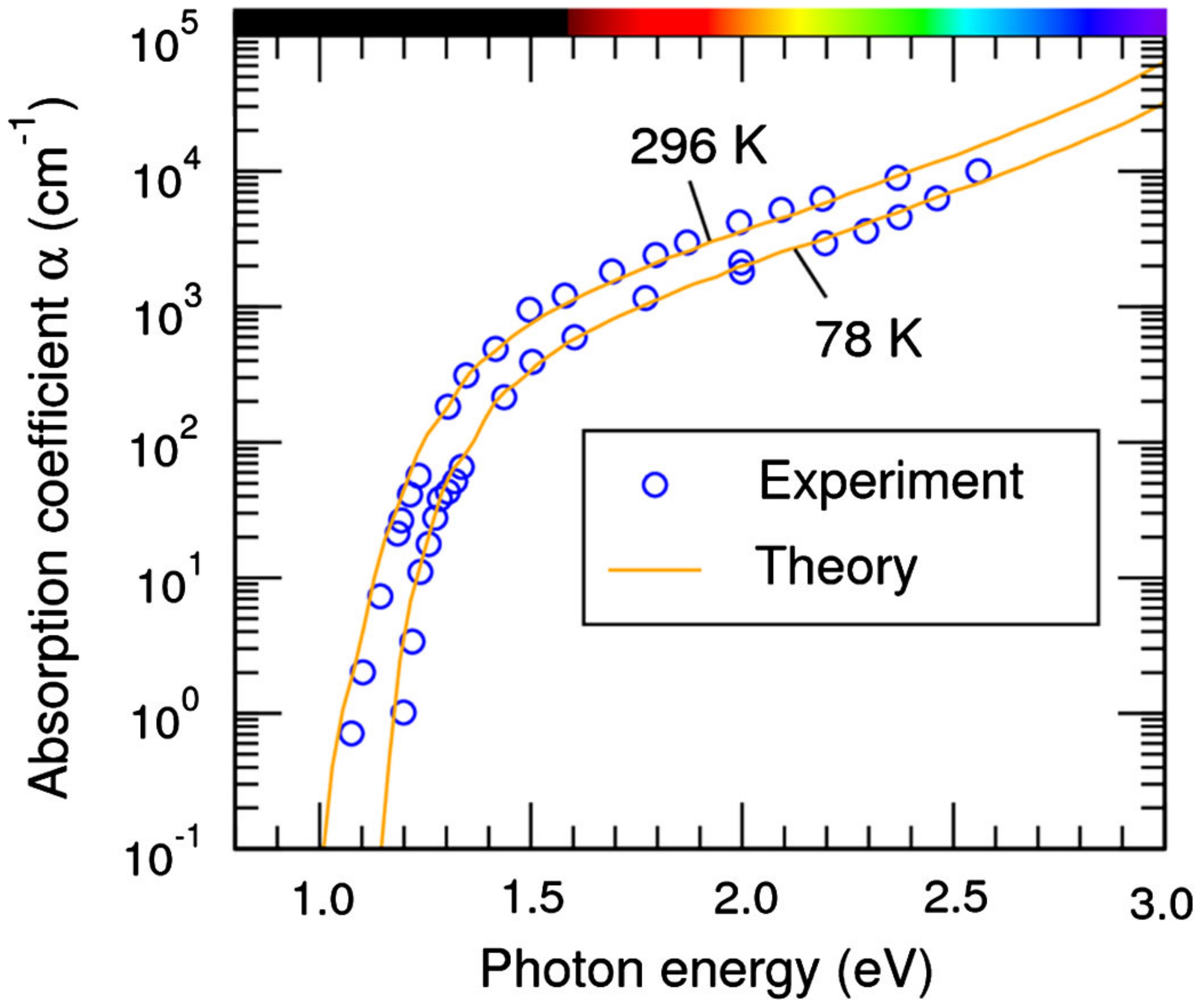
$$\alpha(\omega) = 2\frac{4\pi^2 e^2}{\omega c n_r(\omega)} \frac{1}{V_{\text{cell}}} \frac{1}{N_k N_q} \sum_{\nu i j \boldsymbol{k} \boldsymbol{q}} |\boldsymbol{\lambda} \cdot (\boldsymbol{S}_1 + \boldsymbol{S}_2)|^2 \, \delta(\epsilon_{j,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega \pm \hbar\omega_{\nu\boldsymbol{q}})$$

generalized matrix elements

delta function for energy conservation

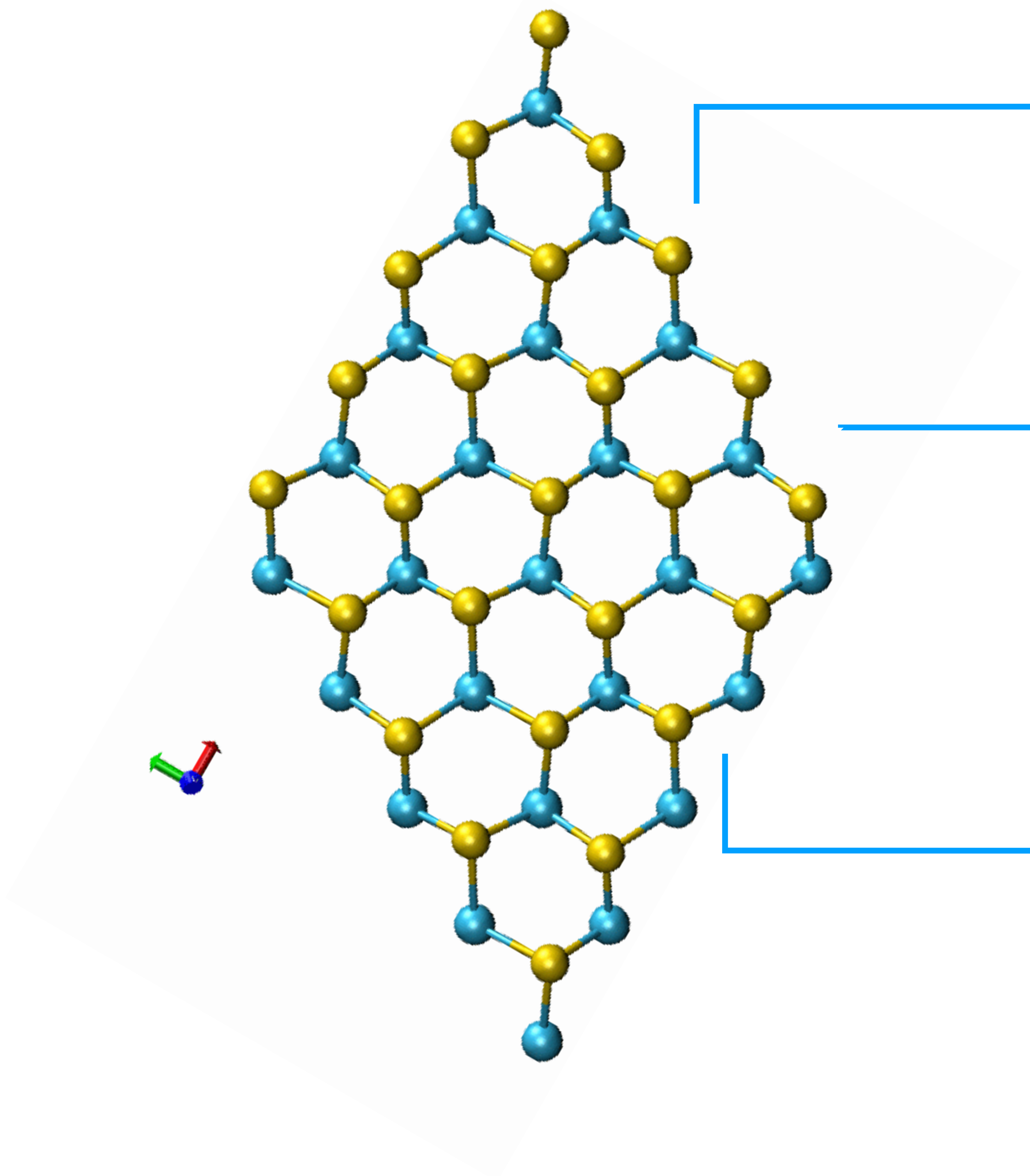
Indirect optical absorption in silicon (theory vs experiments)



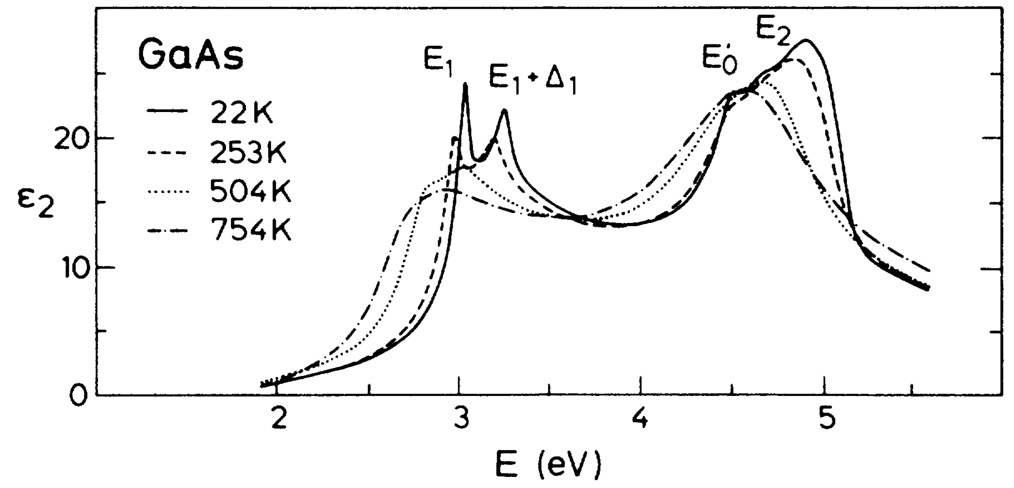


Noffsinger et al., Phys. Rev. Lett. **108**, 167402 (2012)

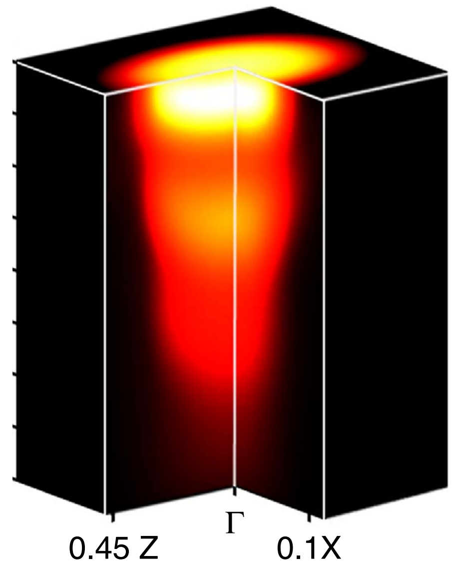
Outline



The temperature dependence of the band structure



Polaronic satellites in angle-resolved photoemission spectroscopy (ARPES)



Phonon-assisted optical absorption in semiconductors