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The electron-phonon coupling in ABINIT

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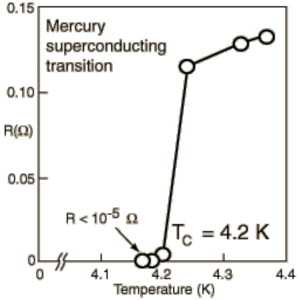
May 2014

Outline

Impact of phonons I

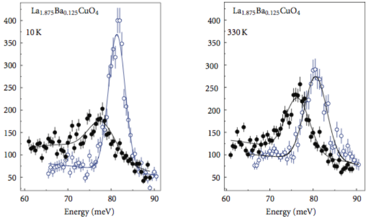
- Electrical resistivity
- Heat transport
- Superconductivity
- Thermoelectricity
- el-ph is 1 contribution
- + anharm, impurities, isotope...



Impact of phonons II

Inelastic/relaxation mechanism:

- IR
- ESR (w/ SO interaction)
- X Ray widths ⟶
- Raman



Reznik, Adv Cond Matt, 523549 (2010)

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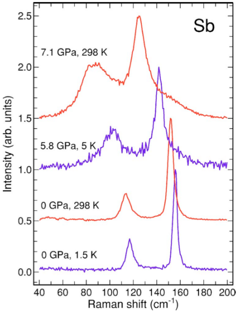
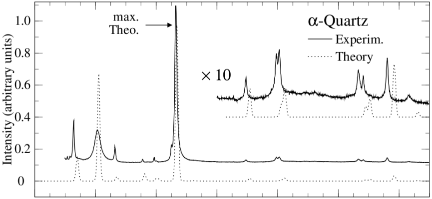
Raman linewidth



Wang et al. PRB **74** 134305 (2006)

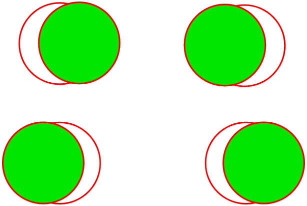


M. Lazzeri and F.Mauri, PRL **90**, 036401 (2003)

Linewidth contribution from el-ph processes

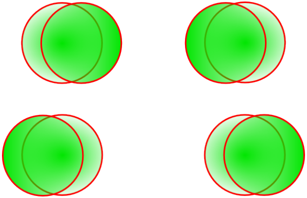
Outline

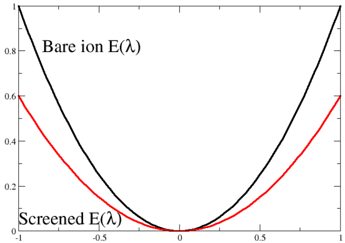
Bare phonons



- Rigid motion of ions (no screening)
- Completely unrealistic phonon frequencies (usu. too hard)

Screened phonons





- Screening of ion motion by electrons (SC DFT / DFPT)
- Very realistic phonon frequencies (max 10% error)

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Independent electrons...

- Perfect crystal and indep. e^- $\rightarrow$ no resistivity
- Electron-ion interaction is periodic:
- Renormalized e^- energies
- but still ideal "quasi-particles"
- KS states are in this category

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... & things that perturb them

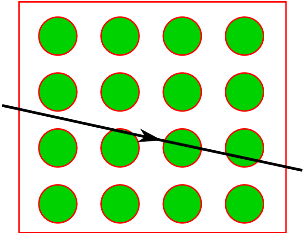
In real system, perturbations

- add to Hamiltonian $\mathcal{H} = \mathcal{H}^0 + \mathcal{H}^1$
- give finite lifetimes for indep. part. eigenstates
- interaction $\rightarrow$ only full MB Ψ has ∞ lifetime

Perturbations = Coulomb, photons, defects, impacts...
... and phonons
In many cases ($\pm$ high T) phonons dominate

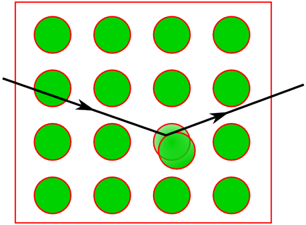
1. What is the system (and the "external" perturbation)?
2. Are the particles independent?

Bare electrons



- Self consistent screening of static el charge
- Decent BS within DFT treatment of Coulomb interaction

Perturbed electrons



- Finite lifetime for KS states
- EP coupling constants usually quite good

NB: Phonon eigenstates are Bloch-like $\rightarrow$
Figure shows localized phonon wavepacket

Energy scales

- Ion vibrations have low energy (0-20 max few 100 meV)
- $\sim$ photons in IR
- Electronic excitations:
  - Metals: $\simeq$ 0 eV: gold κ_T = 318 W/mK
  - Semiconductors ($> E_{gap} \simeq O(1)$ eV)
  - $\rightarrow$ no EPC with low ω
  - e.g. diamond κ_T = 1000-2000 W/mK
- Need strong coupling *and* large e$^-$ DOS

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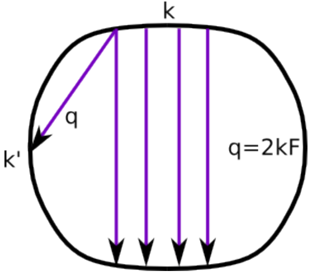
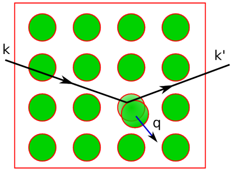
Temperature

- According to preceding energy scale:
- Low T: only FS electrons contribute
  ABINIT: = neglect ω wrt electronic energies
- High T: more phonon $\omega \rightarrow$ insulators have EPC too
- T $\gg$ Debye freq $\rightarrow$ classical Boltzmann stat.
- Hypothesis: phonons remain harmonic and ∞ lifetime

FS effects





- Phonon q connects k, k' $\in$ FS
- Nesting: many k-k' give same q
- And energy/frequency dependency
- Huge change in electron screening
- Kohn anomaly in e^- bands (PRL **2** 393 (1959))

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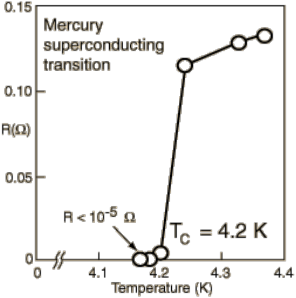
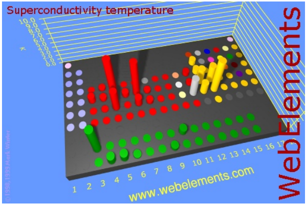
Superconductivity





- Effective e^- e^- interaction w/ phonons can be attractive
- $\rightarrow$ superconducting instability at low T
- New “mixed” quasiparticles have no resistance from EPC

Outline

Eliashberg Theory

- Coupling Hamiltonian (Frölich):

$$H_{ep} = \sum_{kq} < \vec{k} + \vec{q} | \delta V | \vec{k} > \vec{d}_q c^\dagger_{k+q} c_k$$

- Single phonon scattering (Migdal)
- Perturbed (electronic) potential δV from DFPT

Eliashberg Theory II

- Displacement operator:

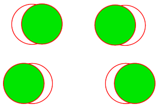
$$\vec{d}_q = \sum_j \left(\frac{\hbar}{2NM\omega_{qj}}\right)\vec{u}_{qj}(a_{qj} + a^\dagger_{-qj})$$

- gkk matrix elements:

$$g^{qj}_{k'k} = \frac{\hbar}{\sqrt{2NM\omega_{qj}}}\vec{u}_{qj} < \vec{k'}|\delta V|\vec{k} >$$

Eliashberg Theory III

- Perturbation theory in H_{ep}
- Use *spectral representations* of
  - Green's functions for e, ph
  - e-p and e-e self-energies
- Full phonon self-energy is *not* perturbational
- But pre-screened DFPT is ok



Spectral function

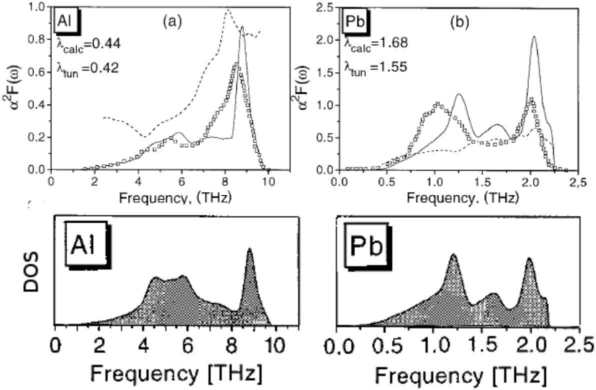
- Eliashberg spectral functions:

$$\alpha^2 F(\Omega) = N_F \sum_{kk'j} |g_{k'k}^{qj}|^2 \delta(\Omega - \omega_{qj})$$

- k-point sums over Fermi Surface
- Related to imaginary part of e^- self-energy

Spectral function II

Closely linked to phonon DOS $F(\Omega) = \sum_{qj} \delta(\Omega - \omega_{qj})$



Savrasov[2] PRB **54**, 16487 (1996)

EP quantities - Link to experiments starts here

- Superconducting coupling strength

$$\lambda = 2 \int \frac{d\Omega}{\Omega} \alpha^2 F(\Omega)$$

- Phonon lifetime from scattering with e$^-$:

$$\gamma^{ph}_{\vec{q}m} = 2\pi\omega_{\vec{q}m} \sum_{\vec{k}ii'} |g^{\vec{q}m}_{\vec{k}'i'\vec{k}i}|^2 \delta(\epsilon_{\vec{k}i} - \epsilon_F)\delta(\epsilon_{k\vec{+}qi'} - \epsilon_F)$$

- and electron lifetime due to phonons:

$$\begin{aligned} \gamma^{el}_{\vec{k}i} &= 2\pi \sum_{\vec{q}mi'} |g^{\vec{q}m}_{i'\vec{k}'i\vec{k}}|^2 \times \{[f_{\vec{k}'i'} + n_{\vec{q}m}]\delta(\epsilon_{\vec{k}i} - \epsilon_{k\vec{+}qi'} + \omega_{\vec{q}m}) \\ &+ [1 - f_{k\vec{+}qi'} + n_{\vec{q}m}]\delta(\epsilon_{\vec{k}i} - \epsilon_{k\vec{+}qi'} + \omega_{\vec{q}m})\} \end{aligned}$$

Further approximations

- Neglect band energy dependence in $\alpha^2 F$: $\omega \ll \epsilon$
- Bands are not too narrow and DOS varies slowly
- $\rightarrow$ Shouldn't be true for localized bands or low D!!

Coulomb interactions

- Most already in ω_q and ϵ_{nk} (DFT is a good start)
- Remaining e-e repulsion in "Retarded coulomb parameter":

$$\mu^* = N_F \int_{FS^2} V^c_{kk'} / (1 + log(\omega_{el}/\omega_D))$$

- ω_{el} Coulombic frequency $\sim$ 10eV
- *Approximate: only need the change btw SC and N states*
- McMillan formula for T_c (W. L. McMillan, Phys. Rev. 167, 331 (1968))

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Transport equations

- “Classical” statistical mechanics
- Boltzmann equations for flow of e^- and phonons
- Coupled by precisely the e-ph matrix elements $g_{kk'}$

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Boltzmann equations

$$
\begin{aligned}
\frac{\partial f_k}{\partial t} = -\frac{2\pi}{\hbar N_c} \sum_q |g_{kk+q}|^2 \{ f_k(1 - f_{k+q})[& \quad (N_q + 1) \quad \delta(\epsilon_k - \epsilon_{k+q} - \hbar\omega_q) \\
+ & \quad N_q \quad \delta(\epsilon_k - \epsilon_{k+q} + \hbar\omega_q)] \\
-(1 - f_k) f_{k+q}[& \quad (N_q + 1) \quad \delta(\epsilon_k - \epsilon_{k+q} + \hbar\omega_q) \\
+ & \quad N_q \quad \delta(\epsilon_k - \epsilon_{k+q} - \hbar\omega_q)]\}
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial N_q}{\partial t} = -\frac{4\pi}{\hbar N_c} \sum_k |g_{kk+q}|^2 f_k(1 - f_{k+q})[& \quad N_q \quad \delta(\epsilon_k - \epsilon_{k+q} + \hbar\omega_q) \\
- & \quad (N_q + 1) \quad \delta(\epsilon_k - \epsilon_{k+q} - \hbar\omega_q)]
\end{aligned}
$$

e.g. J.M. Ziman *Electrons and Phonons* Oxford U Press (1960)

Steady state solutions

- Relate κ_{ph}, σ_e to coupling btw fluxes of ph and e^-
- Steady state transport under T or E gradient
- $\partial f_k / \partial t =$ diffusion terms
- Linearize Boltzmann eqs and simplify k dependency

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Transport spectral function:

Generalization by Allen:

$$\alpha^2_{in(out)}F(\omega) = \frac{1}{N_0 < v_x^2 >} \sum_{\nu} \sum_{knk'n' \in FS} |g^{q\nu}_{k'n'kn}| v_x(\vec{k}) v_x(\vec{k}^{(')}) \delta(\omega - \omega_{q\nu})$$

$$\alpha^2_{tr}F(\omega) = \alpha^2_{out}F(\omega) - \alpha^2_{in}F(\omega)$$

Average velocity $< v_x^2 >$

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e- and ph- Resistivity

$$
\begin{aligned}
\rho(T) &= \frac{\pi\Omega_{cell}k_BT}{N_0 < v_x^2 >}\int_0^\infty \frac{d\omega}{\omega}\frac{x^2}{sinh^2x}\alpha_{tr}^2F(\omega) \\
w(T) &= \frac{6\Omega_{cell}}{\pi k_B N_0 < v_x^2 >}\int_0^\infty \frac{d\omega}{\omega}\frac{x^2}{sinh^2x} \\
&\times \left[\alpha_{tr}^2F(\omega) + \frac{4x^2}{\pi^2}\alpha_{out}^2F(\omega) + \frac{2x^2}{\pi^2}\alpha_{in}^2F(\omega)\right]
\end{aligned}
$$

where x = $\omega/2k_BT$

- Only lowest order approx. to full Boltzmann eq.
- Only electronic contribution to thermal resistance

$\rightarrow$ no lattice thermal conductivity

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Outline

Workflow (NEW!)

1. run ABINIT GS + phonons with minimal k-grid
2. run ABINIT for _GKK matrices on dense k-grid
   _DDB files = $E^{(2)}$ and _GKK = $< \vec{k'} | \delta V | \vec{k} >$
3. mrgddb pastes all $E^{(2)}$ into one file for ANADDB
4. mrggkk pastes all $< \vec{k'} | \delta V | \vec{k} >$ into one file
   3 N_{atom} perts grouped by qpoint, and complete!
5. Run anaddb with telphon = 1 and additional file names

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Getting EP matrix elements

- SCF phonon calculation yields $n^{(1)}$ and hence $H^{(1)}$
- Now do non-SCF, 1 step calculation of $< \vec{k'}|H^{(1)}|\vec{k} >$
- Can use any k-grid we want $\rightarrow$ converge EPC integration
- NB: still need all perturbations for each $\vec{q}$

$\rightarrow$ use prepgkk 1 in SCF phonon run

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Symmetries

- Symmetry operations complete $E^{(2)}$
- does not work for $< \vec{k'} | \delta V_{qj} | \vec{k} >$ (phase interference)
- $< \vec{k'} | \delta V_{qj} | \vec{k} >< \vec{k} | \delta V_{qj'} | \vec{k'} >$ eliminates gauge
- $\rightarrow$ need all 3$\times$N$_{atom}$ perturbations!
- Q-points completed by symmetry
- $k' = k + q$ so q-grid must be consistent with k-grid

Transport outputs

- Electrical resistivity/conductivity (_RHO)
- Thermal conductivity (_WTH)
- Lorentz coefficient (_LOR)
- Transport $\alpha^2 F_{tr}$ (_A2F_TR)

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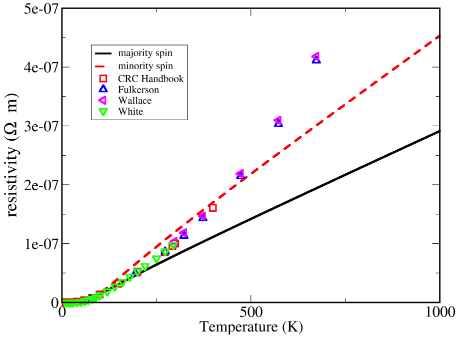
Transport outputs



- Electrical resistivity (_RHO)
- Spin polarized Fe (MJ Verstraete JPCM **25**, 136001 (2013))

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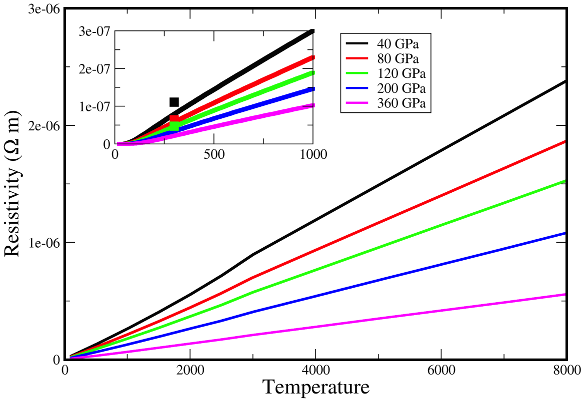

- Electrical resistivity (_RHO)
- High pressure Fe in Earth's core (Gomi et al. PEPI **224**, 88 (2013))

Conclusions

- Widely useful quantities
- Strong links to experiment
- Small cost beyond phonon calculation
- Many other processes involve EPC
- Should work in PAW as well (ASAP!)

Collaborators

Lots of input along the way

- Bin Xu, Momar Diakhate
- Matteo Giantomassi
- Jean-Paul Crocombette + the CEA boys
- Xavier Gonze, Samuel Poncé, Yannick Gillet

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References:

General:

- P.B. Allen and B. Mitrovic *Theory of Superconducting* T_c , Sol. State Phys., **37** (Academic Press, New York, 1982)
- J.M. Ziman *Electrons and Phonons* Oxford U Press (1960)
- G. Grimvall *The electron phonon interaction in metals* (North-Holland, Amsterdam, 1981)
- L. Hedin, S. Lundqvist Sol. Stat. Phys. **23** ed. Ehrenreich, Seitz, Turnbull (1969)

Implementation:

- Savrasov^2 PRB **54**, 16487 (1996)

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Beyond Eliashberg: Issues

- Strong coupling
- Anharmonic phonons
- Strong e-e correlation ($\rightarrow$ beyond Migdal)
- High T_c superconductivity

Beyond Eliashberg: Formalism

- Gross / Van Leeuwen formalism:
- Quantum ionic Density matrix
- No Born-Oppenheimer approx. in principle
- In practice: no external fitting of μ^*