Phonons & electron-phonon coupling

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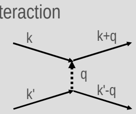
Some important phenomena

- Charge transport
- Heat transport
- Thermal expansion
- Electron (hole) lifetimes
- Superconductivity

effective electron-electron interaction



?

Aspects of e-ph Coupling

Basics

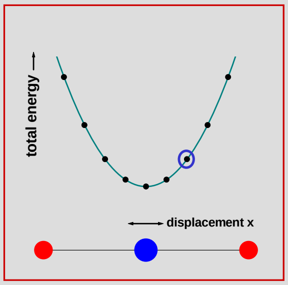
- The frozen phonon approach
- Lattice dynamics
- Atomic forces

Phonons and electron-phonon coupling

- Symmetry
- Vibrational frequencies
- Normal vectors
- Raman scattering
- Linear-response theory
- Comparison with experiment
- LAPW / WIEN2k specific aspects and examples

Outline

1D case:



$E_{tot}(x)=E_0+E_1x+E_2x^2+.....$

- Harmonic approximation

$$M\omega^2=\frac{\partial^2 E_{tot}}{\partial x^2}=2E_2$$

- Calculate energies
- Fit expansion coefficients

$\mathbf{F}(x) = E_1 + 2E_2\, x \; + \; .....$

The Frozen-Phonon Approach

General case:

$$E(R_{n\alpha i}+S_{n\alpha i}) = E(R_{n\alpha i})+\frac{1}{2}\sum_{n\alpha i}\sum_{m\beta j}\frac{\partial^2 E}{\partial S_{n\alpha i}\partial S_{m\beta j}}\bigg|_{R_{n\alpha i}} S_{n\alpha i}S_{m\beta j}+\cdots$$

Force constant: $\phi_{n\alpha i}^{m\beta j} = \frac{\partial^2 E}{\partial S_{n\alpha i}\partial S_{m\beta j}}\bigg|_{R_{n\alpha i}}$

change of the force acting on atom α in unit cell n in direction i, when displacing atom β in unit cell m in direction j.

Displacement wave:

$$S_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_n-\omega t)}$$

The Harmonic Approximation

Equation of motion:

$$-\omega^2 u_{\alpha i}(\mathbf{q})+\sum_{\beta j}\underbrace{\sum_{m}\frac{1}{\sqrt{M_\alpha M_\beta}}\phi_{n\alpha i}^{m\beta j} e^{i\mathbf{q}(\mathbf{R}_m-\mathbf{R}_n)}}_{D_{\alpha i}^{\beta j}(\mathbf{q})} u_{\beta j}(\mathbf{q}) = 0$$

Vibrational frequencies ω:

by diagonalization of the dynamical matrix D

$$\sum_{\beta j} D_{\alpha i}^{\beta j}(\mathbf{q}) u_{\beta j}(\mathbf{q}) - \omega^2 u_{\alpha i}(\mathbf{q}) = 0$$

- N atoms per unit cell
- $3N$ degrees of freedom
- Set of $3N$ coupled equations

The Harmonic Approximation

N atoms per unit cell

# displacements	Total energy	Forces
	$\frac{9N(N-1)}{2}+1$	$\frac{9N(N-1)+2}{2(3N-2)}+\frac{K}{2}$ $K=\begin{cases}0 & N \text{ odd}\\ 1 & N \text{ even}\end{cases}$
N=2	10	3
$YBa_2Cu_3O_7$: N=13	703	19
5 A_g modes	21	4

- Harmonic case only!
- Interpolation only – no fit!

Computational Effort

Many particle Schrödinger equation

$$\mathrm{H}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R}) = \mathrm{E}\Psi(\mathbf{r},\mathbf{R})$$

electronic coordinates ionic coordinates

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$$

groundstate wavefunction with respect to fixed ions

$$F_\alpha^x = -\frac{\delta E_0(\mathbf{R})}{\delta X_\alpha} = \underbrace{-\langle \frac{\delta \Psi_0}{\delta X_\alpha} | H | \Psi_0 \rangle - \langle \Psi_0 | H | \frac{\delta \Psi_0}{\delta X_\alpha} \rangle}_{0} - \langle \Psi_0 | \frac{\delta H}{\delta X_\alpha} | \Psi_0 \rangle$$

The Hellmann-Feynman Theorem

$$\frac{\delta E_0}{\delta X_\alpha} = \underbrace{\langle \Psi_0 | \frac{\delta T_e}{\delta X_\alpha} | \Psi_0 \rangle}_{0} + \underbrace{\langle \Psi_0 | \frac{\delta V_e}{\delta X_\alpha} | \Psi_0 \rangle}_{0} + \underbrace{\langle \Psi_0 | \frac{\delta V_I}{\delta X_\alpha} | \Psi_0 \rangle}_{\frac{\delta V_I}{\delta X_\alpha}\langle \Psi_0 | \Psi_0 \rangle} + \langle \Psi_0 | \frac{\delta V_{II}}{\delta X_\alpha} | \Psi_0 \rangle$$

$$\boxed{F_\alpha^x = -\sum_{\beta \neq \alpha} \frac{dV_{\alpha,\beta}}{dX_\alpha} - \int E_\alpha^x(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}}$$

component of the electric field caused by the nuclear charge

Hellmann-Feynman force:

total **classical Coulomb force** acting on the nucleus α stemming from all other charges of the system =
electrostatic force stemming from all other nuclei +
electrostatic force stemming from the electronic charges

The Hellmann-Feynman Force

Total energy:

$$\boxed{E[\rho] = E^{e}[\rho] + \frac{1}{2}\sum_{\gamma,\beta=1}^{N} \frac{q_\gamma q_\beta}{|\mathbf{R}_\gamma - \mathbf{R}_\beta|}}$$

$$E^{e}[\rho] = \sum_{n,\mathbf{k}} w(n,\mathbf{k})\varepsilon_{n,\mathbf{k}} - \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' -$$

$$\int \mu_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \int \varepsilon_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

Atomic force:

$$\boxed{\mathbf{F}_\alpha = \mathbf{F}_\alpha^{HF} - \frac{1}{\delta\mathbf{R}_\alpha}\left[\sum_{n,\mathbf{k}} w(n,\mathbf{k})\delta\varepsilon_{n,\mathbf{k}} - \int \rho(\mathbf{r})\delta V_{eff}(\mathbf{r})d\mathbf{r}\right]}$$

Pulay corrections

Forces in DFT

$$\boxed{\mathbf{F}_\alpha \equiv \frac{\delta E}{\delta \mathbf{R}_\alpha}} = \boxed{\mathbf{F}_\alpha^{HF}} + \boxed{\mathbf{F}_\alpha^{IBS}} + \boxed{\mathbf{F}_\alpha^{core}}$$

$$\boxed{\mathbf{F}_\alpha^{HF} = q_\alpha \frac{d}{d\mathbf{R}_\alpha}\left[\sum_{\beta,\alpha\neq\beta}\sum_{\mathbf{T}} \frac{-q_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta + \mathbf{T}|} + \int \frac{\rho(\mathbf{r})}{|\mathbf{R}_\alpha - \mathbf{r}|} d\mathbf{r}\right]}$$

Hellmann-Feynman force: classical electrostatic force excerted on the nucleus by the other nuclei and the electronic charge distribution

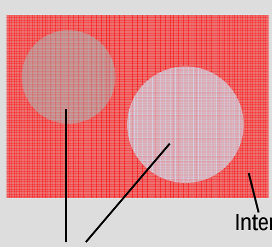
$$\boxed{\mathbf{F}_\alpha^{IBS} = -2\sum_i f_i \,\mathrm{Re}\left\langle \frac{d\Psi_i}{d\mathbf{R}_\alpha}\right| T + V_{eff} - \varepsilon_i \left|\psi_i\right\rangle - \frac{1}{\delta\mathbf{R}_\alpha}\sum_i f_i \left\langle \psi_i \right| \delta T \left|\psi_i\right\rangle}$$

IBS force: *incomplete basis set* correction due to the use of a finite number of position-dependent basis functions

$$\boxed{\mathbf{F}_\alpha^{core} = -\int \rho_\alpha^{core}(\mathbf{r})\, \nabla V_{eff}(\mathbf{r})\, d\mathbf{r}}$$

Core correction: contribution due to the fact that for core electrons only the spherical part of the potential is taken into account

Forces in the LAPW Basis

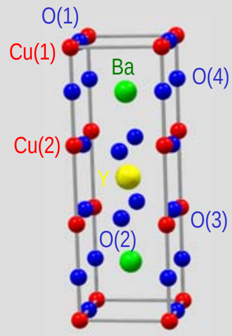


site-dependent!

The LAPW Method

Orthorhombic cell: Pmmm

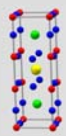
	position [a b c]	point symmetry
Y	(½ ½ ½)	mmm
Cu(1)	(0 0 0)	mmm
O(1)	(0 ½ 0)	mmm
Ba	(½ ½ z)	mm
Cu(2)	(0 0 z)	mm
O(2)	(½ 0 z)	mm
O(3)	(0 ½ z)	mm
O(4)	(0 0 z)	mm



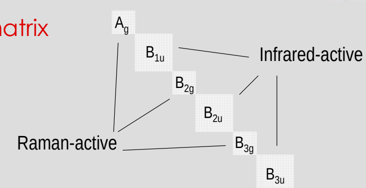
Example: $YBa_2Cu_3O_7$

Factor group analysis: q=0

$5\,A_g + 8\,B_{1u} + 5\,B_{2g} + 8\,B_{2u} + 5\,B_{3g} + 8\,B_{3u}$



Dynamical matrix



Bilbao Crystallographic Server: http://www.cryst.ehu.es/

Symmetry

Force contributions for a mixed distortion:

-O(2), -O(4)	Ba	Cu(2)	O(2)	O(3)	O(4)
position [c]	0.1815	0.3530	0.3740	0.3787	0.1540
F^{HF} [mRy / a.u.]	46.66	123.82	0.76	-8.77	290.52
F^{IBS} [mRy / a.u.]	-13.03	-35.22	6.50	7.91	-75.75
F^{core} [mRy / a.u.]	-36.08	-88.30	6.45	0.75	-188.87
F [mRy / a.u.]	-2.45	0.30	13.71	-0.09	25.90

Forces in $YBa_2Cu_3O_7$

A_g modes

Mode	ω LDA	ω GGA	ω Exp. [4]	rel. dev. LDA	rel. dev. GGA
Ba	103	115	118	-13%	-3%
Cu(2)	130	144	145	-10%	-1%
O(2)-O(3)	327	328	335	-2%	-2%
O(2)+O(3)	387	405	440	-12%	-8%
O(4)	452	452	500	-9%	-9%

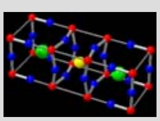
$YBa_2Cu_3O_7$: Phonon Frequencies

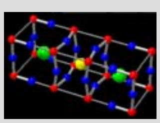
A_g modes

Mode	Ba	Cu(2)	O(2)	O(3)	O(4)
Ba	0.85	0.52	0.05	0.05	0.00
Cu(2)	0.53	-0.84	-0.08	-0.07	0.06
O(2)-O(3)	0.00	0.02	-0.81	0.59	-0.05
O(2)+O(3)	0.02	0.09	-0.51	-0.74	-0.43
O(4)	0.03	-0.11	0.28	0.32	-0.90

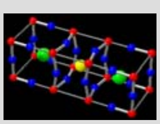
$YBa_2Cu_3O_7$: Normal Vectors

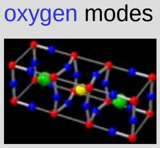
Ba / Cu modes

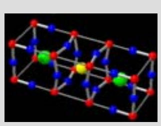




oxygen modes



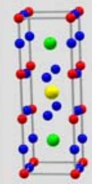




$YBa_2Cu_3O_7$: Lattice Vibrations

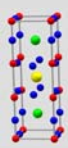
Phonon frequencies [cm^{-1}]

	Mode	Theory		Experiment
		Ref. [1-2]	optimized	Ref. [3-7]
A_{1g}	Ba	105 / 103	123	116-119
	Cu(2)	127 / 130	147	145-150
	O(2)-O(3)	312 / 327	338	335-336
	O(2)+O(3)	361 / 387	422	435-440
	O(4)	513 / 452	487	493-500
B_{2g}	Ba	57	65	70
	Cu(2)	133	142	142
	O(4)	185	222	210
	O(3)	365	389	370
	O(2)	568	593	579
B_{3g}	Ba	72	79	83
	Cu(2)	133	141	140
	O(4)	257	293	303
	O(2)	335	372	-
	O(3)	524	546	526

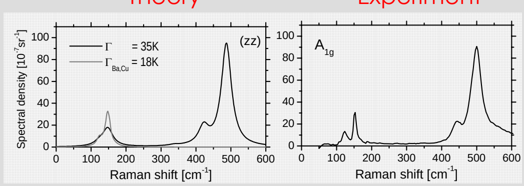


[1] R. E. Cohen et al., Phys. Rev. Lett. **64**, 2575 (1990).
[2] R. Kouba et al., Phys. Rev. B **56**, 14766 (1997).
[3] T. Strach et al., Phys. Rev. B **51**, 16460 (1995).
[4] G. Burns et al., Solid State Commun. **66**, 217 (1988).
[5] K. F. McCarty et al., Phys. Rev. B **41**, 8792 (1990).
[6] V. G. Hadjiev et al., Physica C **166**, 1107 (1990).
[7] B. Friedl et al., Solid State Commun. **76**, 217 (1990).
[8] K. Syassen et al., Physica C **153-155**, 264 (1988).

Raman Active Phonons



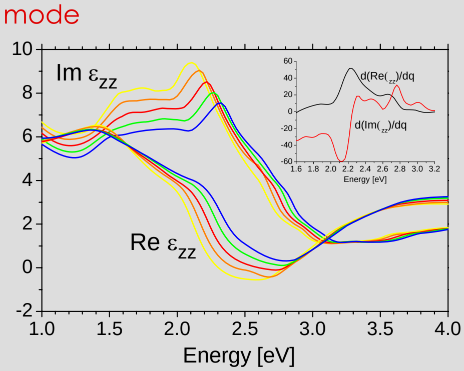
$$\boxed{S \sim \left|\frac{\partial \epsilon(\omega)}{\partial Q}\right|^2 |\langle \mu|Q|\nu\rangle|^2}$$



CAD, H. Auer, R. Kouba, E. Ya. Sherman, P. Knoll, M. Mayer, Phys. Rev. B 65, 064501 (2002).

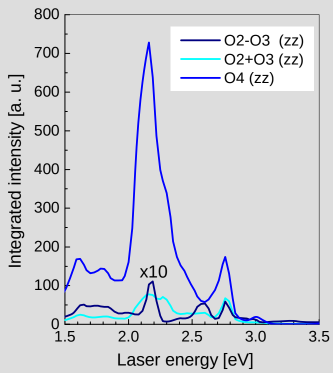
Raman Scattering Intensities

O(4) mode



Probing e-ph Coupling Strength

Resonance:



- Peak at 2.2 eV
- All oxygen modes
- O(4) displacement!

Probing e-ph Coupling Strength

Ba-Cu modes:

$$E(u_{Ba},u_{Cu}) = E_0 + \frac{1}{2}\Phi^{Ba}_{Ba}u_{Ba}^2 + \frac{1}{2}\Phi^{Cu}_{Cu}u_{Cu}^2 + \Phi^{Cu}_{Ba}u_{Ba}u_{Cu}$$

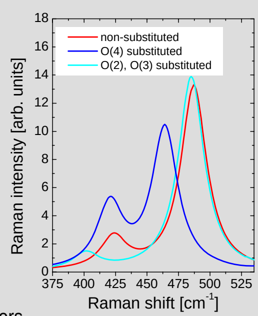
$$\begin{pmatrix} \frac{\Phi^{Ba}_{Ba}}{M_{Ba}} - \omega^2 & \frac{\Phi^{Cu}_{Ba}}{\sqrt{M_{Ba}M_{Cu}}} \\ \frac{\Phi^{Cu}_{Ba}}{\sqrt{M_{Ba}M_{Cu}}} & \frac{\Phi^{Cu}_{Cu}}{M_{Cu}} - \omega^2 \end{pmatrix} \begin{pmatrix} u_{Ba} \\ u_{Cu} \end{pmatrix} = 0$$

Force constant [N/m]	LDA	GGA	Experiment [3]
Ba	101	119	118.6 (-5.3 / +5.0)
Cu	69	77	81.3 (-2.2 / +2.5)
Ba-Cu	-17	-15	-16.3 (-3.3 / +5.6)

- Experiment: site-selective isotope substitution

Probing Normal Vectors

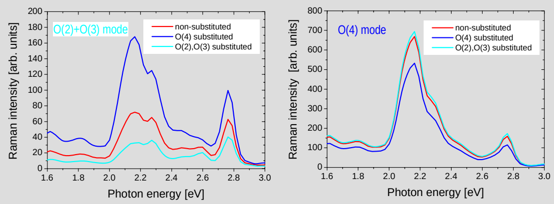
Raman scattering intensities:



- Influence of mass and eigenvectors

Isotope Substitution

Raman scattering intensities:



- Change of e-ph coupling strength through normal vectors

  CAD, H. Auer, R. Kouba, E. Ya. Sherman, P. Knoll, M. Mayer, Phys. Rev. B 65, 064501 (2002).
- Relevant for superconductivity

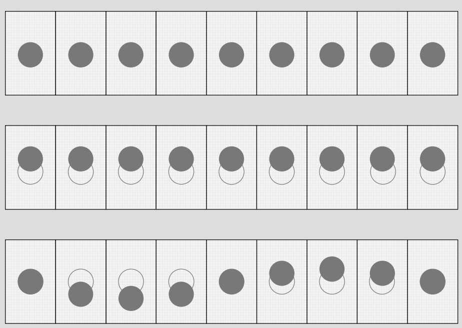
  E. Ya. Sherman and CAD, Eur. Phys. J. B 26, 323 (2002) .

Isotope Substitution

Equilibrium

q = 0

q ≠ 0



q-dependent Phonons

Supercell method:

- Unit cell commensurate with the **q**-vector (*supercell*)
- Computationally very demanding

Linear response theory:

N. E. Zein, Sov. Phys. Sol. State 26, 1825 (1984).
S. Baroni, P. Gianozzi, and A. Testa, Phys. Rev. Lett. 58, 1861 (1987).

- Starting point: undisplaced structure
- Treat **q**-dependent displacement as perturbation
- Self-consistent linear-response theory
- Keep single cell
- Computational effort nearly independent of **q**-vector
- Anharmonic effects neglected

Supercells vs. Perturbation Theory

Atomic displacement:

$$\delta \mathbf{S}_\alpha^{\mathbf{T}} = \delta^+ \mathbf{S}_\alpha e^{i\mathbf{q}\mathbf{T}} + \delta^- \mathbf{S}_\alpha e^{-i\mathbf{q}\mathbf{T}}$$

small polarization vector

- Superposition of forward and backward travelling wave
- Static first-order perturbation within density-functional perturbation theory (DFPT)
- Determine first-order response on the electronic charge, effective potential and Kohn-Sham orbitals

Linear Response Theory

Iterative solution of three equations:

$$\delta^+ V_{eff}(\mathbf{r}) = \delta^+ V_{nuc}(\mathbf{r}) + \int \frac{\delta^+ \rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d^3 r' + \delta^+ \rho(\mathbf{r}) \left. \frac{dV_{xc}}{d\rho} \right|_{\rho(\mathbf{r})}$$

$$\downarrow$$

$$(-\nabla^2 + V_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}}) \delta^+ \Psi_{n\mathbf{k}}(\mathbf{r}) = -\delta^+ V_{eff}(\mathbf{r}) \Psi_{n\mathbf{k}}(\mathbf{r})$$

$$\downarrow$$

$$\delta^+ \rho(\mathbf{r}) = 2 \sum_{n\mathbf{k}} w(n,\mathbf{k}) \delta^+ \Psi_{n\mathbf{k}}(\mathbf{r}) \Psi^*_{n\mathbf{k}}(\mathbf{r})$$

- Determine **q**-dependent atomic forces and dynamical matrix
- Alternatively compute second order changes (DM) directly

Linear Response Theory

Electron-phonon matrix element:

$$g^{\mathbf{q}\nu}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \left\langle \Psi_{m\mathbf{k}+\mathbf{q}} \left| \sum_{\alpha=1}^{N} \sum_{s=1}^{3} \frac{e_{\mathbf{q}\nu}(\alpha,s)}{M_\alpha \omega_{\mathbf{q}\nu}} \frac{\delta V_{eff}(\mathbf{r})}{\delta S_{\alpha s}} \right| \Psi_{n\mathbf{k}} \right\rangle$$

- Scattering process of an electron by a phonon with wavevector **q**

Need to evaluate matrix elements like:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} \equiv \left\langle \Psi_{m\mathbf{k}+\mathbf{q}} \left| \delta V_{eff}(\mathbf{r}) \right| \Psi_{n\mathbf{k}} \right\rangle$$

Matrix elements including Pulay-like terms:

S. Y. Savrasov and D. Y. Savrasov, Phys. Rev. B 54, 16487 (1996) .

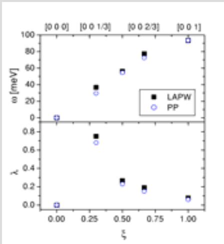
R. Kouba, A. Taga, CAD, L. Nordström, and B. Johansson, Phys. Rev. B 64, 184306 (2002).

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \sum_{\mathbf{G},\mathbf{G}'} C^*_{m\mathbf{k}+\mathbf{q}}(\mathbf{G}) (\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}) C_{n\mathbf{k}}(\mathbf{G}')$$

e-ph Matrix Elements

Coupling constant for a phonon branch ν:

$$\lambda_{q\nu} = \frac{1}{N(0)\,\omega_{q\nu}^2 \sum_\alpha M_\alpha (\hat{e}_{q\nu}^{\alpha})^2} \sum_{nmk} \frac{f(\epsilon_{nk}) - f(\epsilon_{mk+q})}{\epsilon_{mk+q} - \epsilon_{nk}} \left|M_{mn}^{q\nu}\right|^2 \delta(\epsilon_{mk+q} - \epsilon_{nk} - \omega_{q\nu})$$



$$\left|M_{mn}^{q\nu}\right|^2 = \frac{1}{2}\left[\left|M_{mk+q,nk}^{\alpha}\right|^2 + \left|M_{nk-q,mk}^{\alpha}\right|^2\right]$$

bcc S

R. Kouba, A. Taga, CAD, L. Nordström, and B. Johansson, Phys. Rev. B 64, 184306 (2002).

e-ph Coupling Constants

Comparison with experiment ....

- helps to analyze measured data
- contributes to assign modes

P. Puschnig, C. Ambrosch-Draxl, R. W. Henn, and A. Simon, Phys. Rev. B 64, 024519-1 (2001).

Theory can ....

- predict superconducting transition temperatures

J. K. Dewhurst, S. Sharma, and CAD, 68, 020504(R) (2003);
H. Rosner, A. Kitaigorodotsky, and W. E. Pickett, Phys. Rev. Lett. 88, 127001 (2002).

- predict phase transitions (phonon softening)
- much more ....

What Can We Learn?

Thank you for your attention!