Ultrafast processes in the solid state: Light scattering from elementary excitations

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Ultrafast Time Scales

Ultrafast Science explores the dynamics of the microscopic world:
- Making or breaking of chemical bonds
- Atomic and Electron dynamics in materials

attoseconds to femtoseconds:
  - electron motion/correlation,...

femtoseconds to picoseconds:
  - vibrational motion, electron-phonon and phonon-phonon scattering,...

Adapted from M. Murnane
First, some advantages of time-domain measurements

...separation of time-scales

Sheu et al. unpublished

...Excited State Dynamics

Murray et al. PRB 72, 060301 (R) 2005.

...sometimes just plain resolution!


\[ f = (2.9787 \pm 0.0002) \text{ THz} \]

\[ 1/\Gamma = (211 \pm 7) \text{ ps @ 5K} \]
For perfect crystal, can write down Hamiltonian, but cannot solve.

\[ H = H(r_i, p_i, R_j, p_j) \]

\[ H = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \frac{1}{2} \sum_{j' \neq j} \frac{Z_j' Z_j e^2}{|\vec{R}_j - \vec{R}_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} + \frac{1}{2} \sum_{i' \neq i} \frac{e^2}{|\vec{r}_i - \vec{r}_{i'}|} \]
For perfect crystal, can write down Hamiltonian, but cannot solve.

\[
H = H_{\text{ion}}(\mathbf{R}_j) + H_{\text{e}}(\mathbf{r}_i, \mathbf{R}_{j0}) \\
+ H_{\text{e-ion}}(\mathbf{r}_i, \delta \mathbf{R}_{j0}) + \ldots
\]

Born-Oppenheimer, valence/core and mean-field approximations, +pert. theory with help from translational and point-group symmetries... ...single-particle excitations (electron-hole) and collective vibrations (phonons)
Stir in your favorite terms in the Hamiltonian…

Adapted from A. Warhol
Light Scattering and connection with elementary excitations
Response to Applied Field

\[ P_i(\vec{r}, t) = \int \chi_{ij}(\vec{r}', \vec{r}, t', t) E_j(\vec{r}', t') d\vec{r}' dt' \]

\[ P_i(\vec{q}, \omega) = \chi_{ij}(\vec{q}, \omega) E_j(\vec{q}, \omega) \]

\[ \epsilon_{ij}(\vec{q}, \omega) = 1 + 4\pi \chi_{ij}(\vec{q}, \omega) \]

- In linear Response, \( \chi \) doesn’t depend on E
- Causality, P follows E
- We will see excitation spectrum related to peaks in imaginary \( \chi, \epsilon \)
- Also related to the dynamical structure factor and van Hove correlations
At long wavelengths local response

\[ P(t) = \int_{0}^{\infty} \chi(t') E(t - t') dt' \]

\[ \varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) = 1 + \int_{0}^{\infty} 4\pi \chi(t') e^{i\omega t'} dt' \]

Kramers-Kronig, follows from causality

\[ \varepsilon_r(\omega) - 1 = \frac{2}{\pi} Pr \int_{0}^{\infty} \frac{\omega' \varepsilon_i(\omega')}{\omega'^2 - \omega^2} d\omega' \]

\[ \varepsilon_i(\omega) = -\frac{2\omega}{\pi} Pr \int_{0}^{\infty} \frac{\varepsilon_r(\omega')}{\omega'^2 - \omega^2} d\omega' \]

Can obtain real from imaginary part and vice versa, given knowledge everywhere

However, note that primary contribution near \( \omega \)
Microscopic picture of light interacting with electrons/ions

Microscopic picture: Light-matter interaction as perturbation to (single electron, or ion) Hamiltonian

\[ H_0 = \frac{p^2}{2m} + V(\vec{r}) \]

\[ \vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \nabla \times \vec{A} \quad \Phi = 0, \nabla \cdot \vec{A} = 0 \]

\[ \vec{p} \rightarrow \vec{p} - \frac{e\vec{A}}{c} \]

\[ H = H_0 + H_{eR} = \frac{p^2}{2m} + V(\vec{r}) + \frac{e}{mc} \vec{A} \cdot \vec{p} + \frac{e^2 A^2}{2mc^2} \]

- In dipole approx. \( p \cdot A \) equivalent to \( \mu \cdot E \)
- \( A^2 \) term typically neglected at optical wavelengths in linear response regime
- \( A^2 \) dominant for x-ray scattering except very near resonance
Long-wavelength make dipole approximation

\[ \lambda \gg a, q \approx 0 \rightarrow \vec{A} \approx \vec{A}_0 e^{i\omega t} + c.c. \]

Time dependent perturbation theory gives transition rate for SPE...

\[ \omega(\omega) = \frac{2\pi}{\hbar} \left( \frac{e}{m\omega} \right)^2 \left( \frac{E(\omega)}{2} \right)^2 \sum_{\vec{k}} |P_{cv}|^2 \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega) \]

Same matrix elements appear in Im\{\varepsilon\}

\[ \epsilon_i(\omega) = \left( \frac{2\pi e}{m\omega} \right)^2 \sum_{\vec{k}} |P_{cv}|^2 \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega) \]

- Similar for phonons, plasmons and other excitations
- More generally for finite q
FIRST-ORDER COUPLING TO ELECTRONS

$q_e \approx q_h$

$q=0$ excitons

DISCRETE (exciton) vs. (interband) CONTINUUM

Adapted from R. Merlin.
FIRST-ORDER COUPLING TO PHONONS (FAR TO MID INFRARED)

GaAs

$q \approx 0$

$q_1 + q_2 \approx 0$

DISCRETE (1 phonon) vs. (2 phonon) CONTINUUM

Adapted from R. Merlin.
Phonons in 1D

\[
M \frac{d^2 u}{dt^2} = K(u_{j+1} - 2u_j + u_{j-1})
\]

Propose solutions:

\[
u_j = \epsilon e^{i(qR_j - \omega t)}
\]

relationship between \(\omega\) and \(q\), dispersion relation:

\[
\omega = 2\sqrt{\frac{K}{M}} |\sin(qd/2)|
\]

\(\omega\) linear for \(|q| \ll 1/d\) : acoustic phonons
Propose solutions: \( u^{(1,2)}_j = \epsilon^{(1,2)} e^{i(qR_j - \omega t)} \)

dispersion relation:

Now \( M_1 \neq M_2 \)

\[
M_1 \frac{d^2 u^{(1)}_j}{dt^2} = K (u^{(2)}_j - 2u^{(1)}_j + u^{(2)}_{j-1})
\]

\[
M_2 \frac{d^2 u^{(2)}_j}{dt^2} = K (u^{(1)}_{j+1} - 2u^{(2)}_j + u^{(1)}_j)
\]
\[ H = -\vec{u}_{\text{ions}} \cdot \vec{E} = - \left( \vec{\alpha} Q_0 + \sum_q \vec{\beta}^q Q_q^2 + \ldots \right) \cdot \vec{E} \]

\[ \ddot{Q}_0 + \Omega_0^2 Q_0 = \sum_i \alpha_i E_i \]

Driven Oscillator

Parametric Resonance

\[ \ddot{Q}_q + \Omega_q^2 Q_q = \left( \sum_i \beta_i^q E_i \right) Q_{-q} \]
DISPLACEMENTS
($u = \text{ions}; Q = \text{phonons}$)

\[ U = \varepsilon \left| E(r, t) \right|^2 / 8\pi \]

\[ \delta \varepsilon = \sum_{im} \left( \frac{\partial \varepsilon}{\partial u_{im}} \right) u_{im} + \sum_{jmn} \left( \frac{\partial^2 \varepsilon}{\partial u_{im} \partial u_{jn}} \right) u_{im} u_{jn} + \ldots \]

\[ \delta U \approx \delta \varepsilon_{q=0} \left| E(r, t) \right|^2 / 8\pi = \frac{\left| E(r, t) \right|^2}{8\pi} \times \]

\[ \sum_{s} \left( \frac{\partial \varepsilon}{\partial Q_{s,q=0}} \right) Q_{s,q=0} + \sum_{st,q} \left( \frac{\partial^2 \varepsilon}{\partial Q_{s,q} \partial Q_{t,-q}} \right) Q_{s,q} Q_{t,-q} + \ldots \]

\[ F \propto \left| E^2(t) \right| \]

\[ F \propto Q_k \left| E^2(t) \right| \]

FIRST-ORDER
IMPULSIVE FORCE

SECOND-ORDER
IMPULSIVE CHANGE OF FREQUENCY

IMPULSIVE STIMULATED RAMAN SCATTERING

RAMAN COUPLING TO PHONONS (TRANSPARENT MEDIA)
Non-Raman Mechanisms?

**Displacive Excitation of Coherent Phonons**

(Ti$_2$O$_3$)

WORKS ONLY FOR FULLY-SYMMETRIC MODES

FIG. 3. (a) The pump-induced coherent phonon amplitude produces a $\Delta R/R$ as large as 12% initially. This plot convolved with the optical pulse intensity profile yields the least-squares fit to the data in Fig. 2. The fitting function is taken to be an exponentially damped cosine, superimposed on an exponentially decaying background (Ref. 6). (b) The coherent phonon frequency is initially down-shifted by 7%, but subsequently decays back to the 7.0 THz Raman frequency. This plot was obtained by fitting 0.5 ps blocks of the data from Fig. 2 to a decaying sinusoid, superimposed on an exponentially decaying background.


Adapted from R. Merlin.
Comparison of spontaneous and pump-probe yield femtosecond decay of Raman coherences (Force)

Excitation has coherent and incoherent contribution

Li et al., Phys Rev. Lett. 110, 047401 (2013)
Squeezed Phonons, $q=0$ excitation and measurement

**Vacuum Squeezing of Solids: Macroscopic Quantum States Driven by Light Pulses**


Femtosecond laser pulses and coherent two-phonon Raman scattering were used to excite $\text{KTaO}_3$ into a squeezed state, nearly periodic in time, in which the variance of the atomic displacements dips below the standard quantum limit for half of a cycle. This nonclassical state involves a continuum of transverse acoustic modes that leads to oscillations in the refractive index associated with the frequency of a van Hove singularity in the phonon density of states.

**Squeezed states are quantum states of a harmonic oscillator in which the variance of two conjugate variables each oscillate out of phase.**

Ultraslow optical states, where the variance of the atomic displacement is bonding strength with femtosecond x-ray diffraction, conclude that they are consistent with a model in which a constant scaling factor.

**Bi**


**Adapted from R. Merlin.**

Garrett, Science 275, 1638 (1997)
X-ray Scattering and connection with elementary excitations
Inelastic X-ray (and Neutron) Scattering

\[ \frac{d^2 \sigma}{d \Omega d \epsilon} = A S(\kappa, \omega), \]

\[ S(\kappa, \omega) = (2\pi)^{-1} N \int \exp[i(\kappa \cdot r - \omega t)] \cdot G(r,t) dr dt, \]

\[ G(r,t) = (2\pi)^{-3} N^{-1} \sum_{l,j=1}^{N} \int d\kappa \exp(-i\kappa \cdot r) \cdot \langle \exp\{-i\kappa \cdot r_l(0)\} \cdot \exp\{i\kappa \cdot r_j(t)\} \rangle. \]

\( S(Q, \omega) \) Related to the imaginary part of density-density response function
Inelastic X-ray Scattering: \( S(\vec{Q}, \omega) \propto \sum_j \int dt e^{i\omega t} \langle u_j, \vec{Q}(0)u_j, -\vec{Q}(t) \rangle \)

X-ray Diffuse Scattering: \( S(\vec{Q}) \propto \sum_j \langle u_j, \vec{Q}(0)u_j, -\vec{Q}(0) \rangle \)

M. Le Tacon et. al, Nat. Phys. 10,52 (2014)

M. Holt et al., PRL 83 (1999).
Time and momentum-domain x-ray scattering

\[ S(\vec{Q}; \tau) \propto \sum_{j,j'} \langle u_j, \vec{Q}(\tau) u_{j'}, -\vec{Q}(\tau) \rangle \]

Trigo et al. Nature Physics. 9, 790, 2013

Non-equilibrium populations

Non-equilibrium frequency (forces)

phonon-phonon interactions

Electron-phonon interactions
\[ u_n = u \cos(\Omega t + \delta) \cos(q \cdot \vec{R}_n) \]

\[ z_n = z(t) = \vec{K} \cdot \vec{u} \cos(\Omega t + \delta) \]

\[ I(\vec{K}, t) = I_e |f|^2 e^{-\frac{1}{2} z^2(t)} \left( N^2 \delta(\vec{K} - \vec{G}) + \right. \]

\[ \left. N^2 z^2(t) \delta(\vec{K} - \vec{G} \pm \vec{q}) + N z(t)) \delta(\vec{K} - \vec{G} \pm \vec{q}) \right) + \ldots \]
Change in forces induces temporal coherence

\[ \langle (\vec{Q} \cdot u\_q(t))(\vec{Q} \cdot u\_\bar{q}(t)) \rangle \]

Sudden Softening
squeezed thermal vibrations
A new era of hard x-ray sources

x-ray free-electron lasers (version 1):

http://www.psi.ch/swissfel/why-swissfel
Time and momentum-domain x-ray scattering:

\[ S(\mathbf{Q}; \tau) \propto \sum_{j,j'} \langle u_j, \mathbf{Q}(\tau) u_{j'}, -\mathbf{Q}(\tau) \rangle \]

Trigo et al. Nature Physics. 9, 790, 2013

50 fs, ~10 keV probe

3M pixel/120 Hz readout

\[ \mathbf{G}_{hk0} \]

Area detector

\[ \mathbf{k}_0 \]
Femtosecond time domain diffuse images:

t = -2 ps

Ge, differential signal after high-pass filter (for emphasis)
extracted TA phonon dispersion (Ge)

independent modes (oscillation at twice frequency):

\[
\langle u_q u_{-q} \rangle = \frac{1}{4m\omega_q} \left( \left(1 + \frac{\omega_{2q}^2}{\omega_q^2}\right) + \left(1 - \frac{\omega_{2q'}^2}{\omega_q^2}\right) \cos(2\omega'\tau) \right)
\]

Trigo, Zhu, et al. in preparation

Trigo et al. Nature Physics. 9, 790, 2013
Giant anharmonic phonon scattering in PbTe

Kirsten M. Ø. Jensen, Emil S. Božin, Christos D. Malliakas, Matthew B. Stone, Mark D. Lumsden, Mercouri G. Kanatzidis, Stephen M. Shapiro, and Simon J. L. Billinge

Lattice dynamics reveals a local symmetry breaking in the emergent dipole phase of PbTe

PHYSICAL REVIEW B 86, 085313 (2012)
PbTe differential scattering (2 µm pump, 1.4 Å probe)
PbTe near zone-center 100 fs steps (re-binned)

Approximately (0.01 .01 .01) – (0.05 0.0 .09)

M.P. Jiang et al., in preparation
PbTe ($\Gamma$ to $X$) 100 fs steps (re-binned)

Near $\Gamma$ [0 0.1 0] to $X$ [0 1 0] in 0.05 steps (with tolerance levels +/- 0.03)


M.P. Jiang et al., in preparation
Femtosecond x-ray scattering from large wave-vector phonon pairs excited by long-wavelength laser.

- harmonic crystal (Ge): coherences in $<x_{TA,q}x_{TA,-q}>$ at $2\omega_q$
- anharmonic crystal (PbTe): coherences in $<x_{j,q}x_{j',-q}>$ two-phonon combination modes ($j\neq j'$ as well as $j=j$).

Resolution limited by maximum delay (sub-meV demonstrated). Range limited by time-resolution (sub-80 fs demonstrated)

Broad-band x rays, no crystal analyzers and parallel detection of momentum transfer.

Applicable near and far from equilibrium.
This work was supported primarily by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Portions of this research were carried out at the Linac Coherent Light Source (LCLS) an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University.
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R. Loudon, The Raman Effect in Crystals, Advances in Physics, 13, 1964