Theory of NRIXS

A summary & discussion

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Theory of NRIXS

- What happens in NRIXS
- What info we can get out of it
  - Debye sound velocity
  - Dynamic & thermodynamic properties
  - ......

Rudolf Ludwig Mössbauer (1929 - 2011)

- Experiments 1955 - 1958
- Z. Phys. 151, 124 (1958)
  Naturwissenschaften 45, 538 (1958)
  Z. Naturforsch. A 14, 211 (1959)
- Nobel Prize 1961
  "for his researches concerning the resonance absorption of gamma radiation and his discovery in this connection of the effect which bears his name"
- An atomic probe into materials.

NRIXS: the beginning

1995: First PDOS from NRIXS spectrum
W. Sturhahn et al., PRL 74, 3832 (1995)

1995: First NRIXS spectrum
M. Seto et al., PRL 74, 3828 (1995)

1991: First successful NFS experiment
J. B. Hastings et al., Phys. Rev. Lett. 66, 770–773 (1991)

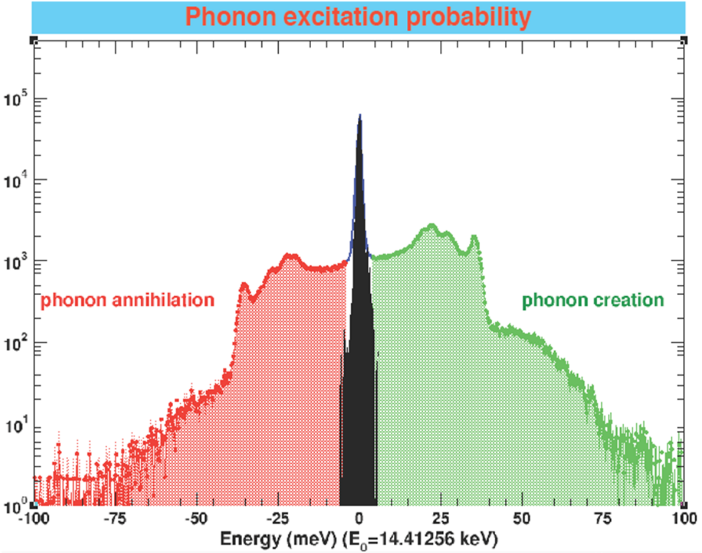
1985: First clear NBS spectrum using synchrotron radiation
E. Gerdau, et al. Phys. Rev. Lett. 54, 835–838 (1985)

1974: Proposal to use synchrotron radiation
S. L. Ruby, J Phys. (Paris) Colloq. 35, C6-209 (1974)

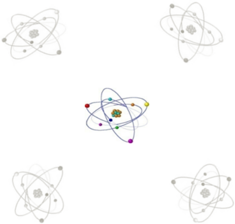
1962: Sum rules & moments of energy spectrum
H. J. Lipkin, Annals of Physics 18, 182 (1962)

1958: Discovery of the Mössbauer Effect

NRIXS: measured spectrum S(E)



Scattering processes



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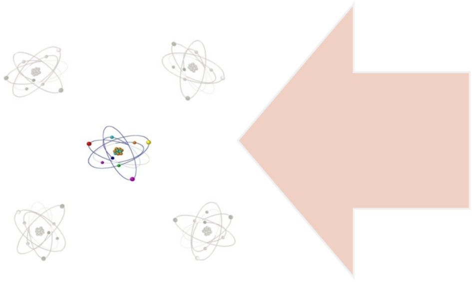
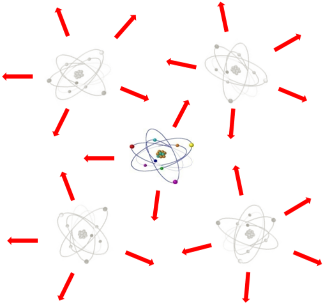


At APS/3ID, 14.4 keV, 24 bunch mode

$5 \times 10^9 ph/sec/meV$ (800 per bunch)

$2.5 \times 10^4 ph/sec/5neV$ (0.004 per bunch)

Scattering processes



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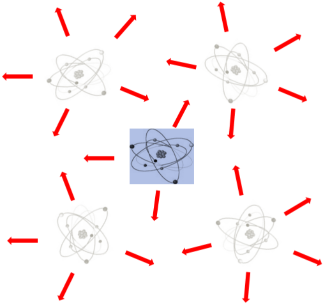

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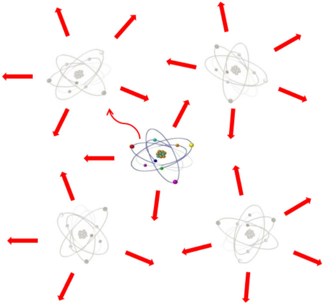
NRIXS



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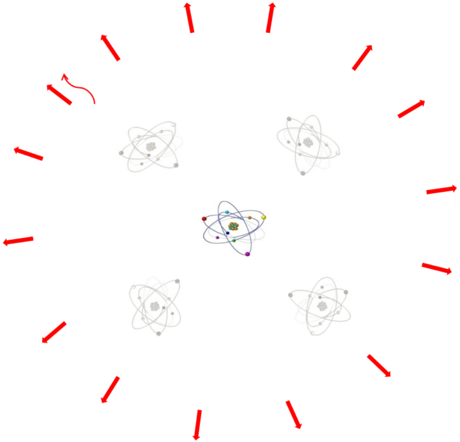

NRIXS

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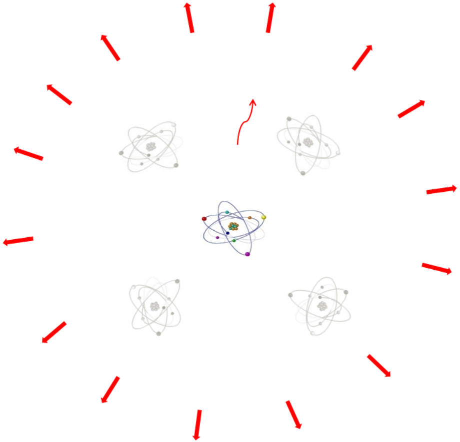
NRIXS



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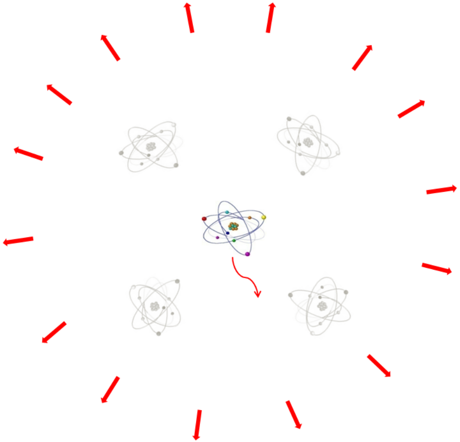
NRIXS



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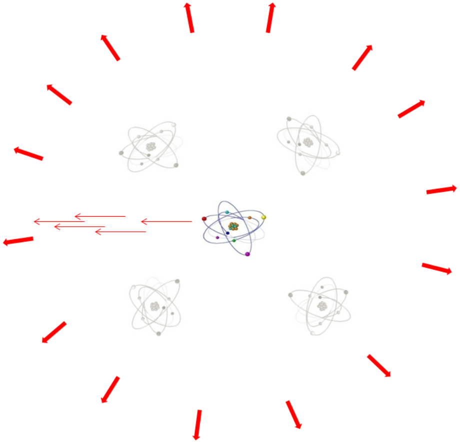
Scattering processes: on resonance



NFS
NBS
SMS

At APS/3ID, 14.4 keV, 24 bunch mode

$5 \times 10^9 ph/sec/meV$ (800 per bunch)

$2.5 \times 10^4 ph/sec/5neV$ (0.004 per bunch)

NRIXS cross-section

$$\begin{aligned}
\sigma(E,\mathbf{k}) &= \frac{\sigma_0\Gamma^2}{4}\sum_{i,f} g_i \sum_{\nu} \frac{\left|\langle \xi_f | e^{i\mathbf{k}\mathbf{r}_\nu} | \xi_i \rangle\right|^2}{(E+\varepsilon_i-\varepsilon_f-E_0)^2+\Gamma^2/4} \\
&= \frac{\pi}{2\hbar}\sigma_0\Gamma\,\frac{1}{2\pi}\int dtd\mathbf{r}\, e^{i(\mathbf{k}\mathbf{r}-\omega t)}G_s(\mathbf{r},t) \\
&= \frac{\pi}{2\hbar}\sigma_0\Gamma\, S(\omega,\mathbf{k})
\end{aligned}$$

where

$$G_s(\mathbf{r},t) = \left\langle \sum_{\nu}\int d\mathbf{r}'\,\delta\Big(\mathbf{r}+\mathbf{r}_\nu(0)-\mathbf{r}'\Big)\,\delta\Big(\mathbf{r}'-\mathbf{r}_\nu(t)\Big)\right\rangle_T$$

is the particle autocorrelation function of the system.

NRIXS: Harmonic lattice

The intermediate dynamic function

$$F_s(\mathbf{k}, t) = \int d\omega \, e^{i\omega t} \, S(\omega, \mathbf{k})$$

has the form of

$$F_s(\mathbf{k}, t) = e^{-2W(\mathbf{k})} \, e^{2M(\mathbf{k},t)}$$

under quasi-harmonic approximation.

NRIXS: Phonon DOS

$$S(E,\mathbf{k}) = S_0(E,\mathbf{k}) + S_1(E,\mathbf{k}) + S_2(E,\mathbf{k}) + \cdots$$

$$S_1(E,\mathbf{k}) = \frac{f\, E_R}{E\left(1 - e^{-\beta E}\right)}\, \mathcal{D}(|E|, \hat{\mathbf{k}})$$

$$\mathcal{D}(E,\hat{\mathbf{k}}) = \frac{1}{\tilde{N}} \sum_{\nu=1}^{\tilde{N}} \frac{1}{N} \sum_{l=1}^{3N} (\hat{\mathbf{k}} \cdot \epsilon_l^{\nu})^2\, \delta\Big(E - E_l\Big)$$

cf. The "total" phonon DOS,

$$\nu(E) = \frac{1}{3N} \sum_{l=1}^{3N} \delta\Big(E - E_l\Big)$$

NRIXS process

- Specific isotopes
- An absorption process
- Vibrations, phonons
- No HI considered
- Energy scales invovled
  neV, meV, keV
- Timing

What do we learn from NRIXS

- ppDOS
- Atomic dynamics
- Thermodynamics
- Debye sound velocity
- Isotope fractionation
- Lattice anharmonicity
- Sample temperature

NRIXS: Dynamics & Thermodynamics

- Atomic dynamics
  - Recoilless fraction, f-factor
  - Mean square displacement
  - Mean kinetic energy
  - Force constants, of several flavors
  - Vibration mode frequencies, amplitudes
  - Anharmonic term of lattice potential
- Thermodynamics
  - Free energy
  - Vibrational entropy
  - Specific heat
  - Isotope fractionation factor
  - Grüneisen parameters

Note: "**projected**" *and* "**partial**" *quantities.*

Moments

The central moments of S(E),

$$R_n \equiv \int_{-\infty}^{+\infty} (E - E_r)^n \, S(E) \, dE$$

The moments of DOS,

$$g_n \equiv \int_0^{+\infty} E^n \, \mathcal{D}(E) \, dE$$

$$\tilde{g}_n \equiv \int_0^{+\infty} \frac{\coth(\beta E/2)}{2} \, E^n \, \mathcal{D}(E) \, dE$$

The connection

$$
\begin{aligned}
R_0 &= 1 \\
R_1 &= 0 \\
R_2 &= 2\,E_r\,\tilde{g}_1 \\
R_3 &= E_r\,g_2 \\
R_4 &= 12\,E_r^2\,\tilde{g}_1^2 + 2\,E_r\,\tilde{g}_3 \\
R_5 &= 20\,E_r^2\,\tilde{g}_1\,g_2 + E_r\,g_4
\end{aligned}
$$

Lamb-Mössbauer factor

From measured spectrum,

$$f = 1 - \int S'(E)dE$$

From ppDOS,

$$f(\mathbf{k}) = e^{-k^2\langle z^2\rangle}$$

Mean square displacement

From measured spectrum,

$$\langle z^2 \rangle = -\frac{1}{k^2} ln(f)$$

From DOS,

$$\langle z^2 \rangle = \int \frac{\hbar^2}{\tilde{m}E} \left[n(E) + \frac{1}{2} \right] \mathcal{D}(E, \mathbf{k})\, dE = \frac{\hbar^2}{\tilde{m}} \tilde{g}_{-1}(\mathbf{k})$$

Mean kinetic energy & internal energy

From $S(E)$,

$$T_{\hat{k}} = \frac{1}{4\,E_r}\,R_2(\hat{k})$$

From DOS,

$$U_{\hat{k}} = \int E\left[n(E) + \frac{1}{2}\right]\mathcal{D}(E,\mathbf{k})\,dE = \tilde{g}_1(\mathbf{k})$$

For an isotropic lattice,

$$U_{\hat{k}} = \int E\left[n(E) + \frac{1}{2}\right]g(E)\,dE = \frac{1}{3}\,U$$

For a powder sample,

$$U_{\hat{k}} = \int |\epsilon|^2\,E\left[n(E) + \frac{1}{2}\right]g(E)\,dE$$

ppDOS & phonon polarization vectors

Projected partial phonon DOS,

$$\mathcal{D}(E,\mathbf{k}) = \frac{1}{\tilde{N}} \sum_{\nu=1}^{\tilde{N}} \frac{1}{N} \sum_{s=1}^{3N} (\hat{\mathbf{k}} \cdot \epsilon_s^{\nu})^2 \, \delta\Big(E - E_s\Big)$$

For an isotropic crystal, the coordinate system can be chosen so that

$$|\hat{\mathbf{k}} \cdot \epsilon_s^{\nu}|^2 = \frac{1}{3}\,,$$

while for a powder sample, it has to be averaged over all directions,

$$\frac{1}{4\pi} \int |\hat{\mathbf{k}} \cdot \epsilon_s^{\nu}|^2 d\Omega_k = \frac{|\epsilon_s^{\nu}|^2}{3}\,.$$

Helmholtz free energy

From DOS,

$$F_{\hat{k}} = k_B T \int \ln\left(2\sinh\frac{\beta E}{2}\right)\mathcal{D}(E,\mathbf{k})\, dE$$

For an isotropic lattice,

$$F_{\hat{k}} = k_B T \int \ln\left(2\sinh\frac{\beta E}{2}\right) g(E)\, dE = \frac{1}{3} F$$

For a powder sample,

$$F_{\hat{k}} = k_B T \int |\epsilon|^2 \ln\left(2\sinh\frac{\beta E}{2}\right) g(E)\, dE$$

Vibrational entropy

From DOS,

$$S_{\hat{k}} = k_B \int \Big[\frac{\beta E}{2}\,\coth(\frac{\beta E}{2}) - \ln\Big(2\sinh\frac{\beta E}{2}\Big)\Big]\mathcal{D}(E,\mathbf{k})\,dE$$

For an isotropic lattice,

$$S_{\hat{k}} = k_B \int \Big[\frac{\beta E}{2}\,\coth(\frac{\beta E}{2}) - \ln\Big(2\sinh\frac{\beta E}{2}\Big)\Big]g(E)\,dE = \frac{1}{3}\,S$$

For a powder sample,

$$S_{\hat{k}} = k_B \int |\epsilon|^2\Big[\frac{\beta E}{2}\,\coth(\frac{\beta E}{2}) - \ln\Big(2\sinh\frac{\beta E}{2}\Big)\Big]g(E)\,dE$$

Vibrational specific heat

From DOS,

$$C_{\hat{k}} = k_B \int (\frac{\beta E}{2})^2 csch^2(\frac{\beta E}{2}) \mathcal{D}(E, \mathbf{k})\, dE$$

For an isotropic lattice,

$$C_{\hat{k}} = k_B \int \left(\frac{\beta E}{2}\right)^2 csch^2(\frac{\beta E}{2})\, g(E)\, dE = \frac{1}{3}\, C$$

For a powder sample,

$$C_{\hat{k}} = k_B \int |\epsilon|^2 \left(\frac{\beta E}{2}\right)^2 csch^2(\frac{\beta E}{2})\, g(E)\, dE$$

Force constant (I): mean

From $S(E)$,

$$K_{\hat{k}} = \frac{\tilde{m}}{\hbar^2 E_r} R_3(\hat{k})$$

From DOS,

$$K_{\hat{k}} = \int \tilde{m} \left(\frac{E}{\hbar}\right)^2 \mathcal{D}(E, \mathbf{k})\, dE = \frac{\tilde{m}}{\hbar^2} g_2(\mathbf{k})$$

For an isotropic lattice,

$$K_{\hat{k}} = \int \tilde{m} \left(\frac{E}{\hbar}\right)^2 g(E)\, dE = K$$

For a powder sample,

$$K_{\hat{k}} = \int |\epsilon|^2\, \tilde{m} \left(\frac{E}{\hbar}\right)^2 g(E)\, dE$$

Force constant (II): characteristic

$$K^{c}_{\hat{k}} \equiv \frac{2\,T_{\hat{k}}}{\langle z^2 \rangle} = \frac{\tilde{m}}{\hbar^2}\,\frac{\tilde{g}_1}{\tilde{g}_{-1}}$$

Force constant (III): effective, resilience

$$K'_{\hat{k}} \equiv \frac{k_B}{d\langle z^2\rangle / dT}$$

where

$$\frac{d\langle z^2\rangle}{dT} = \frac{\hbar^2}{\tilde{m} k_B T^2} \int \frac{e^{\beta E}}{(e^{\beta E} - 1)^2} \mathcal{D}(E, \mathbf{k})\, dE$$

A high T approximation,

$$\frac{d\langle z^2\rangle}{dT} \simeq \frac{\hbar^2 k_B}{\tilde{m}} \int \frac{1}{E^2} \mathcal{D}(E, \mathbf{k})\, dE = \frac{\hbar^2 k_B}{\tilde{m}} g_{-2}(\mathbf{k})$$

A critical temperature, Lamb-Mössbauer temperature

$$\frac{1}{T_c} \equiv k^2 \frac{d\langle z^2\rangle}{dT}$$

Since

$$\langle z^2(T)\rangle \approx \langle z^2\rangle\Big|_{T_0} + \frac{d\langle z^2\rangle}{dT}\,\Delta T$$

then,

$$f(T) = e^{-k^2\langle z^2(T)\rangle} = f(T_0)\,e^{-(T-T_0)/T_c}$$

Summary: What

- What is NRIXS process, what happens
- Data measured: S(E), "the spectrum"
- Derived Info
  - ppDOS
  - debye sound velocity
  - atomic dynamics
  - thermodynamics
  - sample temperature

Summary: How

Things to keep in mind.

- For a measurement
  - Energy scan range
  - Total counts, statistical quality
  - Background counts, etc.
- For data analysis
  - Normalization of counts
  - Background subtraction
  - Consistency checks

Be skeptical, be critical.

Thank you.

&

Congratulations!