Theory of NRIXS

A summary & discussion

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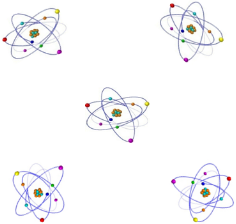
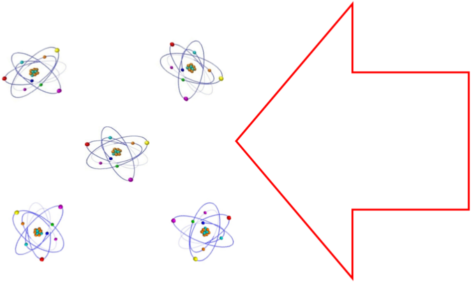
Theory of NRIXS

- Repetition, summary, Q&A
- *Caveat emptor*
- What happens in NRIXS
- What info we can get out of it
  - Debye sound velocity
  - Moments & thermodynamic quantities

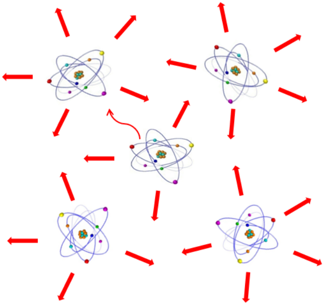
Scattering processes



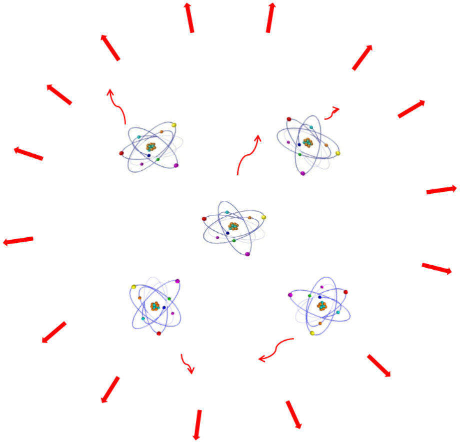
Scattering processes



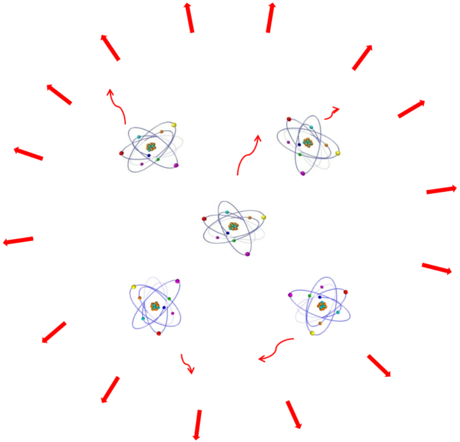
Scattering processes



Scattering processes

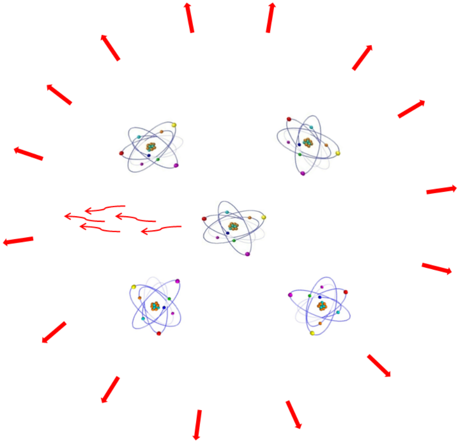


Scattering processes



@APS 3ID, 14.4 keV -
5 x 10^9 ph/sec/meV
800 ph/bunch/meV

Scattering processes



@APS 3ID, 14.4 keV -
5 x 10^9 ph/sec/meV
800 ph/bunch/meV
0.004 ph/bunch/5neV

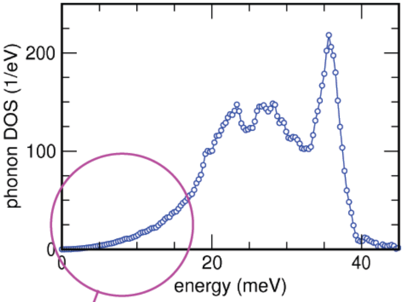
NRIXS process

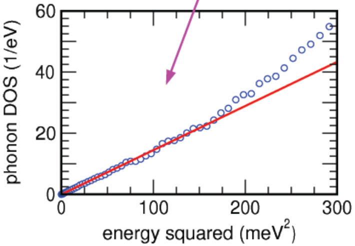
- Specific isotopes
- An absorption process
- Vibrations, phonons
- No HI considered
- Energy scales invovled
  neV, meV, keV
- Timing

What do we learn from NRIXS

- ppDOS
- **Debye sound velocity**
- **thermodynamic quantities**
- isotope fractionation factor
- anharmonic term of lattice potential
- sample temperature

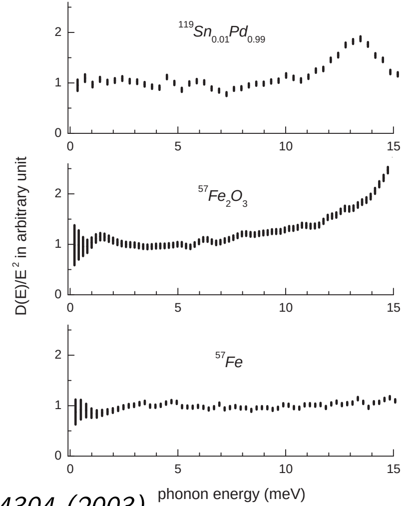
Low energy part of DOS





Sound velocity

The low-energy region of DOS: Debye behavior



Hu, et al., PRB 67, 094304 (2003)

NRIXS DOS & sound velocity

$$\mathcal{D}(\hat{\mathbf{k}}, E \sim 0) = \left(\frac{\tilde{m}}{m}\right) \frac{E^2}{2\pi^2 \hbar^3 n v_{\hat{\mathbf{k}}}^3}$$

$$\frac{1}{v_{\hat{\mathbf{k}}}^3} = \sum_{s=1}^{3} \int \frac{d\Omega_q}{4\pi} \frac{(\hat{\mathbf{k}} \cdot \hat{\epsilon}_{\hat{\mathbf{q}}s})^2}{c_{\hat{\mathbf{q}}s}^3}$$

For an isotropic sample, it reduces to Debye sound velocity,

$$\frac{3}{v_D^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}$$

Hu, et al., PRB 67, 094304 (2003)

Sound velocity & elasstic properties

$$\frac{3}{v_D^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}$$

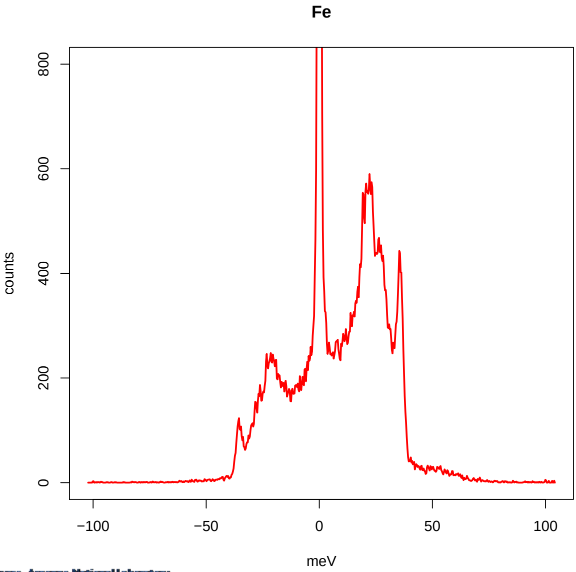
$$\frac{K}{\rho} = v_L^2 - \frac{4}{3} v_T^2$$

$$\frac{G}{\rho} = v_T^2$$

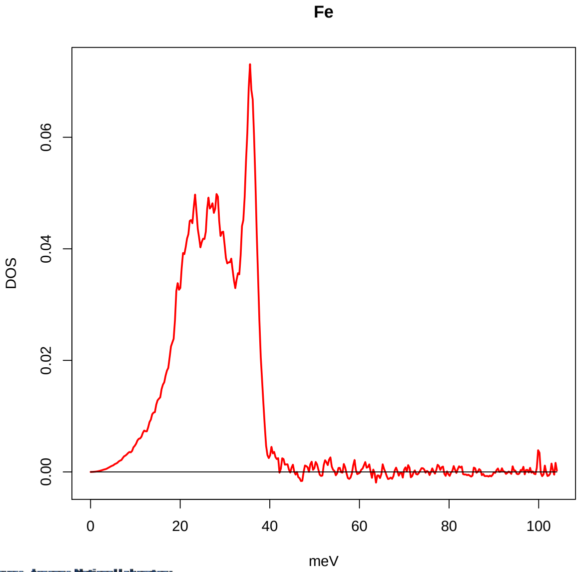
where K is the adiabatic bulk modulus, G the shear modulus, and ρ density.

Mao, et al., Science 292, 914 (2001)

NRIXS: S(E)



NRIXS: DOS



Moments

The central moments of S(E),

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

The moments of DOS,

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

The connection

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

Dynamics & thermodynamics

- Recoilless fraction, f-factor
- Mean square displacement
- Mean kinetic energy
- Force constants
- Internal energy
- Free energy
- Vibrational entropy
- Specific heat
- β-factor in Isotope fractionation

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

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,

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

Mean kinetic energy & internal energy

From $S(E)$,

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

From DOS,

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

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,

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

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,

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

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,

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

For an isotropic lattice,

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

For a powder sample,

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

Vibrational specific heat

From DOS,

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

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,

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

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

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

A high T approximation,

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

A critical temperature, Lamb-Mössbauer temperature

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

Since

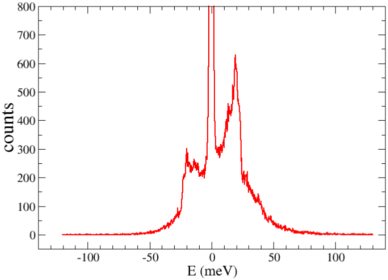
$$\langle z^2(T) \rangle \approx \langle z^2 \rangle \Big|_{T_0} + \frac{d\langle z^2 \rangle}{dT} \, \Delta T$$

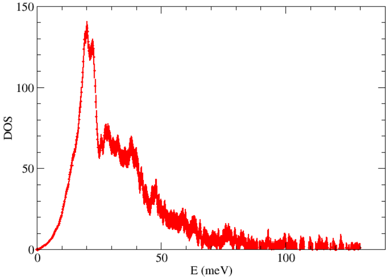
then,

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

A NRIXS study of Goethite

$FeO(OH)$, T$=$ 300.8 K.





Dauphas, et al., Geo. Cosmochimica Acta 94 (2012) 254 - 275

Thermodynamics: Goethite

	raw $S(E)$	corrected $S(E)$	$\mathcal{D}(E)$
Lamb-Mössbauer factor, f	0.769 ± 0.005	0.770	0.770
Mean square displacement, $\langle z^2 \rangle$ ($Å^2$)	0.00492 ± 0.00012	0.00490	0.00490
Mean kinetic energy, $T_{\hat{k}}$ (meV)	15.07 ± 0.13	15.09	15.08
Mean force constant, $K_{\hat{k}}$ (N/m)	305.2 ± 9.4	313.2	313.0
Characteristic force constant, $K^c_{\hat{k}}$ (N/m)	98.2 ± 2.6	98.7	98.7
Effective force constant, $K'_{\hat{k}}$ (N/m)			94.2
$d\langle z^2 \rangle/dT$ ($Å^2/K$)			0.000015
Critical temperature, T_c (K)			1278
$d\langle z^2 \rangle/dT$ ($Å^2/K$), high T limit			0.000016
Critical temperature, T_c (K), high T limit			1207
Helmholtz free energy, $F_{\hat{k}}$ (meV)			4.88
Internal energy, $U_{\hat{k}}$ (meV)			30.2
Vibrational entropy, $S_{\hat{k}}$ (k_B)			0.976
Phonon specific heat, $C_{\hat{k}}$ (k_B)			0.859
Isotope fractionation factor, $ln\beta$ $(\Delta m/m)$	0.244 ± 0.015	0.246	0.246

Summary

- What is NRIXS process, what happens
- Info obtainable
  - ppDOS
  - debye sound velocity
  - thermodynamic quantities
  - isotope fractionation factor
  - anharmonic term of lattice potential
  - sample temperature
- Be skeptical, be critical.
- Congratulations!