PHOnon Excitation by Nuclear Inelastic X-ray scattering

Software for the evaluation of Nuclear Inelastic X-ray Scattering Spectra

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About PHOENIX:

- developed 1995 by W. Sturhahn at the APS
  - incoherent inelastic nuclear resonant scattering
  - explain first NRIXS experiments (Sturhahn et al. PRL 74, 1995)
  - FORTRAN code implemented on Sun UNIX
- improved 1995-2010 by W. Sturhahn at the APS
  - resolution function subtraction, 1997
  - ported to Linux in 2004
  - sound velocity treatment, 2007
  - runtime visualization, version 2.0.0 (2009)
- improved 2010-2017 by W. Sturhahn and *NRIXS software*
  - inverse construction (DOS to spectrum), version 2.1.0 (2012)
  - API for variable data input formats, version 2.1.0, (2012)

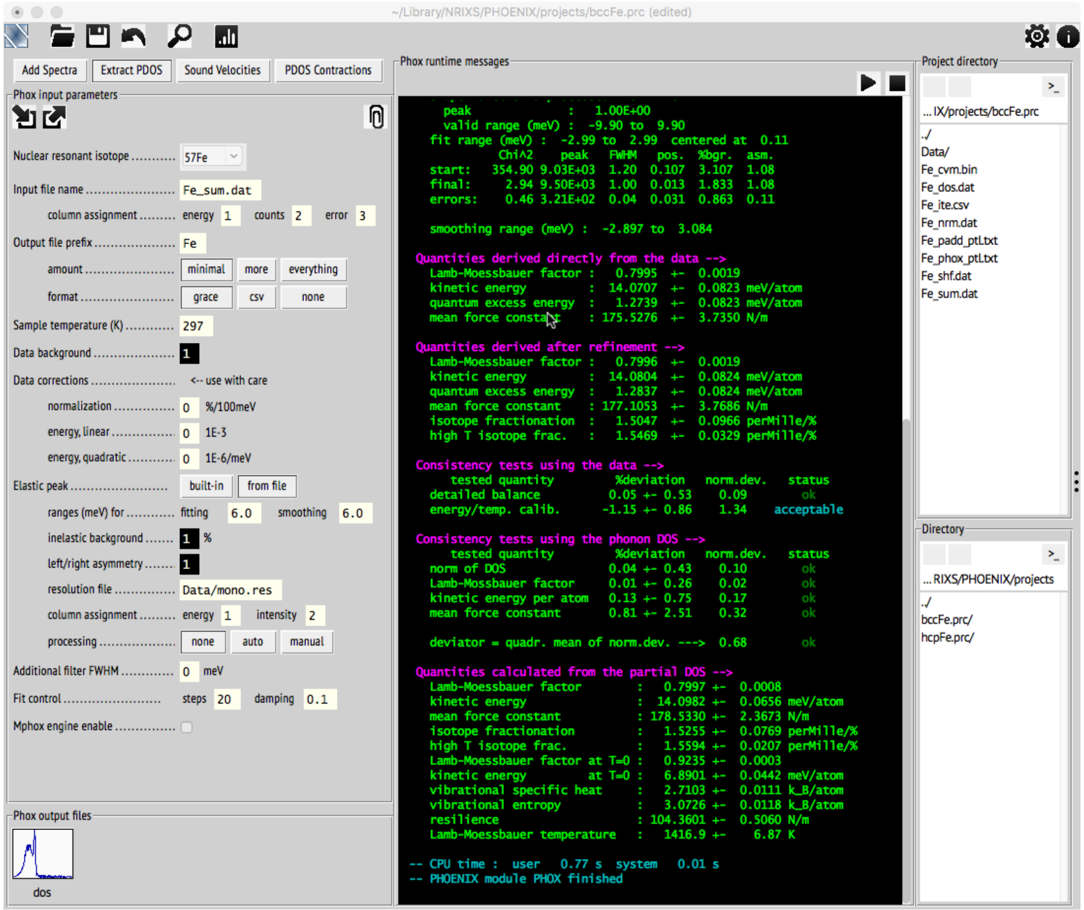
publications related to PHOENIX:
W. Sturhahn, Hyperfine Interact 125 (2000)

More on PHOENIX:

- has been used for data evaluation in numerous publications
- distributed under GPL, open source code, traceable evaluations
- can be obtained at http://www.nrixs.com – no charge
- a major upgrade, PHOENIX-2.0.0, was released in 2009
  - simple installation procedure for Unix and Mac OS X
  - all previous capabilities of PHOENIX
  - run-time graphics
- PHOENIX-2.1.4 until 2018
  - API for custom data input formats, e.g., SPEC or mda
  - inverse calculations, i.e., NRIXS spectra from DOS
  - options for output formats

The PHOENIX GUI:

- GUI upgrade, PHOENIX-3.x, supported by Caltech
  - ☆ translates functionality into Tcl/Tk for Unix and MacOS
  - ☆ maintains all previous capabilities of CLI
  - ☆ enhancements of core modules
  - ☆ cross-project analysis tools



- upgrades to core modules
  - ☆ consistency optimization
  - ☆ advanced elastic peak subtraction
  - ☆ probability distribution analysis for Debye velocity determination

- Thanks to Jennifer Jackson and her group at Caltech for continuous tests of the software and for ongoing discussions for improvements

PHOENIX core supports:

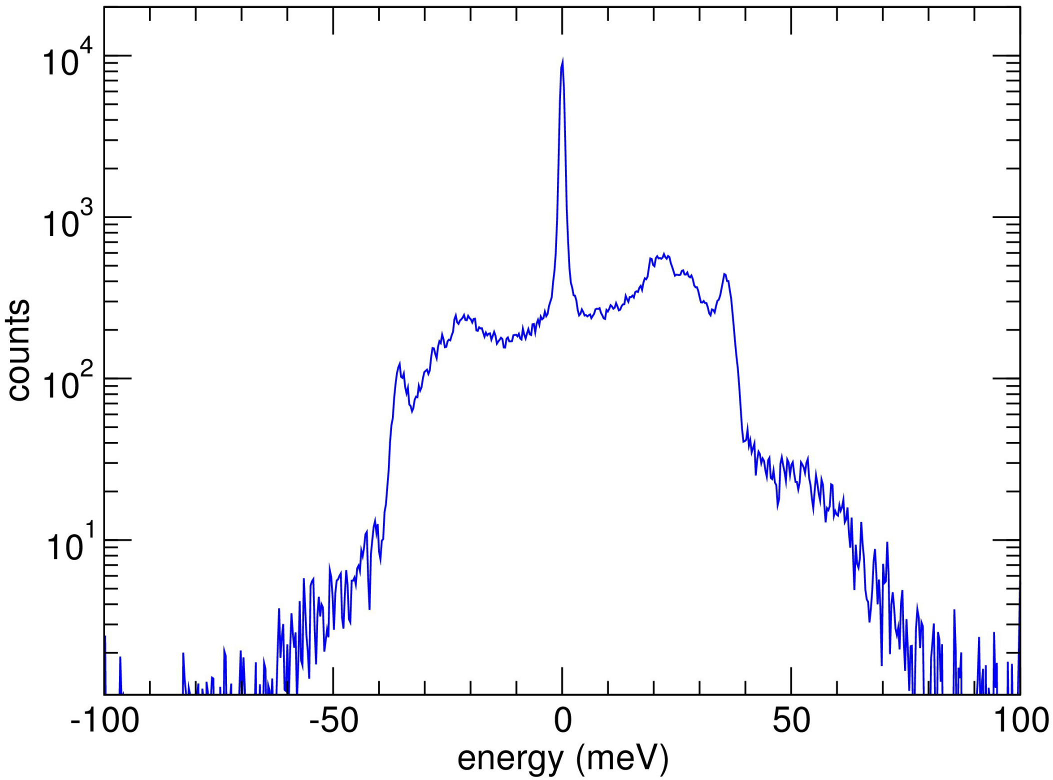
- all major Mössbauer isotopes
- addition of raw data sets including normalization
- creation of energy scale from angle/temperature data
- flexible procedure for subtraction of elastic peak
- data normalization
- correction routine for limited-range spectra
- detailed balance, energy calibration, and moment calculation
- partial phonon density-of-states extraction with Fourier-Log method
- consistency optimization of detailed balance, energy calibration, moments, and PDOS results
- probability distribution function for Debye sound velocity extraction
- aggregate compressional and shear sound velocities
- generation of spectra from measured or theoretical PDOS
- calculation of various thermodynamic quantities from PDOS

PHOENIX core modules:

- padd (GUI “Add Spectra”)
  - ✰ interface between data acquisition and user evaluation
  - ✰ creates energy scale, adds scans, normalizes data
  - ✰ features customizable API for arbitrary data formats
- phox (GUI “Extract PDOS”)
  - ✰ extracts phonon DOS from NRIXS spectrum
  - ✰ calculates moments of NRIXS spectrum
  - ✰ performs consistency optimization
- psvl (GUI “Sound Velocities”)
  - ✰ extracts Debye sound velocities from partial phonon DOS using probability distribution function approach
- psth (GUI “PDOS Contractions”)
  - ✰ generates NRIXS spectrum from phonon DOS
  - ✰ calculates temperature dependent contractions of phonon DOS

example bccFe – spectrum:

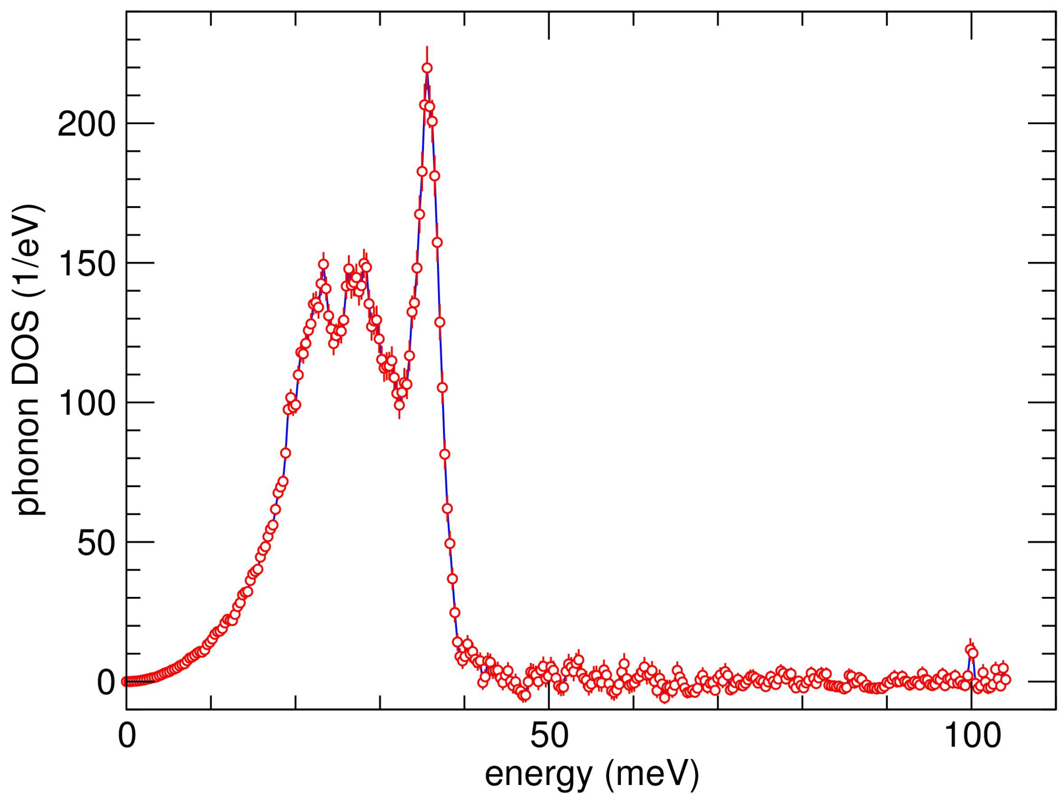
➢ add data of several NRIXS scans on bcc-Fe, ASCII input format



- ✰ open example bccFe
- ✰ GUI panel “Add spectra”
- ✰ inspect output files

example bccFe – DOS:

- ➢ extract phonon DOS from bcc-Fe spectrum created before



- ✰ open example bccFe
- ✰ GUI panel “Extract PDOS”
- ✰ inspect output files

The "deviator" definition:

- for N pairs of values A_n and B_n the deviator is

$$\Delta = \frac{1}{N} \sum_{n=1}^{N} w_n (A_n - B_n)^2$$

the weights w_n are derived from data statistics.

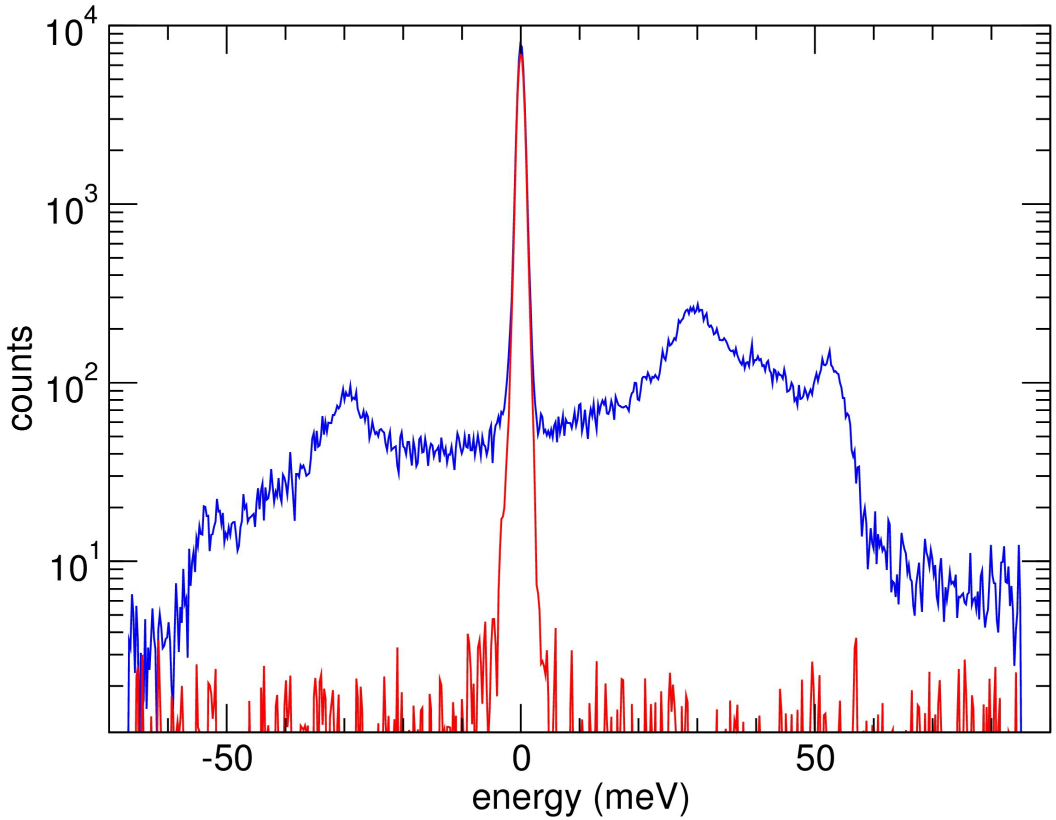
- list of used values
  - ✰ detailed balance
  - ✰ energy calibration
  - ✰ normalization of the PDOS
  - ✰ Lamb-Mössbauer factor
  - ✰ kinetic energy
  - ✰ force constant

Values to enter the deviator:

- detailed balance $$A_1 = \frac{\int_0^\infty \{S(\omega) - e^{\beta\omega} S(-\omega)\}\, d\omega}{\int_0^\infty \{S(\omega) + e^{\beta\omega} S(-\omega)\}\, d\omega}$$ $$B_1 = 0$$
- energy calibration $$\int \left\{ \frac{S(\omega) - S(-\omega)}{S(\omega) + S(-\omega)} - \tanh[A_2 \frac{\beta\omega}{2}] \right\}^2 d\omega \longrightarrow \min$$ $$B_2 = 1$$
- normalization $$A_3 = \int D(\omega)\, d\omega$$ $$B_3 = 1$$
- LM factor $$A_4 = 1 - \int \{S(\omega) - S(0)\}\, d\omega$$ $$\ln B_4 = -\int \frac{\omega_R}{\omega} \coth \frac{\beta\omega}{2} D(\omega)\, d\omega$$
- kinetic energy $$A_5 = \frac{1}{4\omega_R} \int (\omega - \omega_R)^2 S(\omega)\, d\omega$$ $$B_5 = \frac{1}{2} \int \omega \coth \frac{\beta\omega}{2} D(\omega)\, d\omega$$
- force constant $$A_6 = \frac{k^2}{2\omega_R^2} \int (\omega - \omega_R)^3 S(\omega)\, d\omega$$ $$B_6 = \frac{k^2}{2\omega_R} \int \omega^2 D(\omega)\, d\omega$$

example hcpFe – spectrum:

- add data of several NRIXS scans on hcp-Fe at 77 GPa,
  ASCII input format,
  simultaneous creation of resolution function



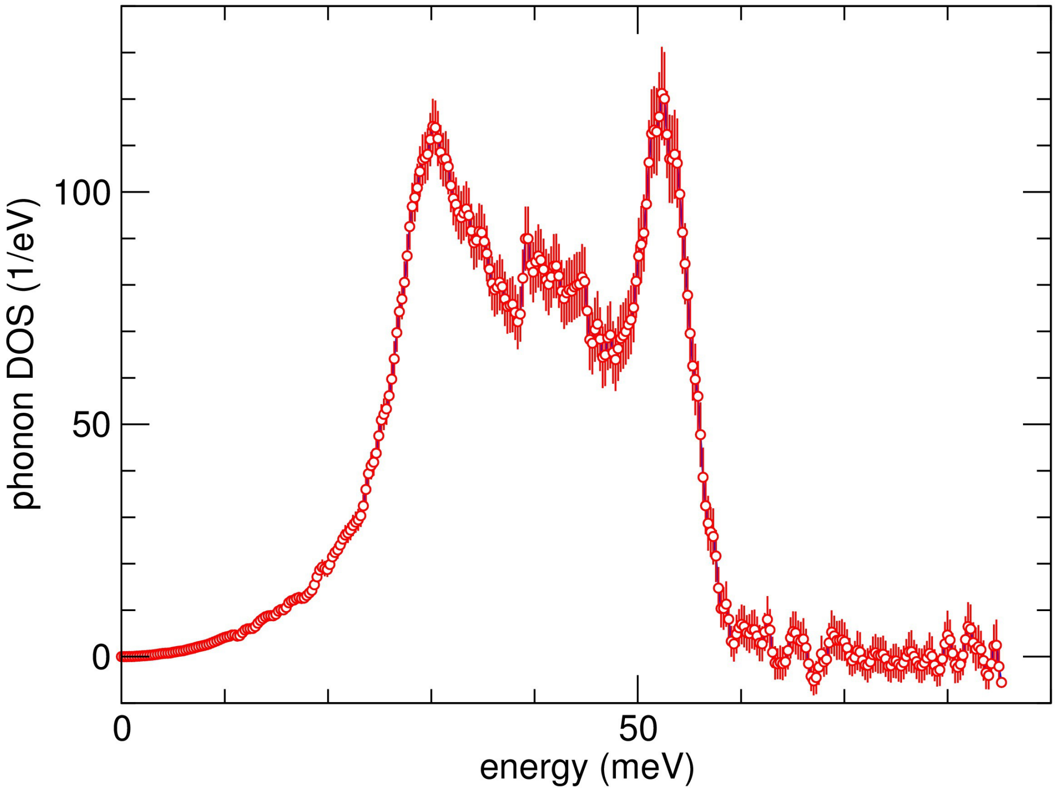
- ✫ open example hcpFe
- ✫ GUI panel "Add spectra"

- ✫ inspect output directories & files

Murphy et al., JGR 118 (2013)

example hcpFe – DOS:

- extract phonon DOS from hcp-Fe spectrum created before using data and resolution function



- ✰ open example hcpFe
- ✰ GUI panel “Extract PDOS”
- ✰ inspect output files

Murphy et al., JGR 118 (2013)

Create your own project:

- from scratch: GUI “New Project”
- copy an existing project using the GUI
- copy an existing project (directory) using a file manager
- copy an existing project (directory) using the command line
- convert previous PHOENIX input files into a project

example σ-FeCr:

- create new project

- add data of several NRIXS scans in folder data/FeCr
  - ASCII format
  - column assignment: a2 A3 D? t12 T14 with D9,D11 for NFS,NRIXS
  - monochromator identical to hcpFe example
  - create NRIXS spectrum and resolution function

- extract PDOS
  - temperature around 300 K

- evaluate problems in the experiment

The Debye sound velocity:

- The phonon DOS behaves Debye-like at low energies

$$\mathcal{D}(E \to 0) = \frac{M}{2\rho\pi^2\hbar^3}\,\frac{1}{\mathrm{v}_D^3}\,E^2$$

- The Debye sound velocity v_D is an average over all sound velocities

polarization vectors

$$\frac{1}{\mathrm{v}_D^3(\mathbf{k})} = \mathbf{k}\,\mathcal{Q}\,\mathbf{k} \qquad \mathcal{Q} = \frac{1}{3}\sum_{m,\mathbf{q}} \frac{\mathbf{e}_m(\mathbf{q}) \otimes \mathbf{e}_m(\mathbf{q})}{\mathrm{v}_m^3(\mathbf{q})}$$

x-ray direction

mode

direction

Aggregate sound velocities:

- For isotropic materials or cubic crystals, the definition of v_D gives

$$\frac{3}{v_D^3} = \frac{1}{v_p^3} + \frac{2}{v_s^3}$$

- A spatial average of the Christoffel equation results in

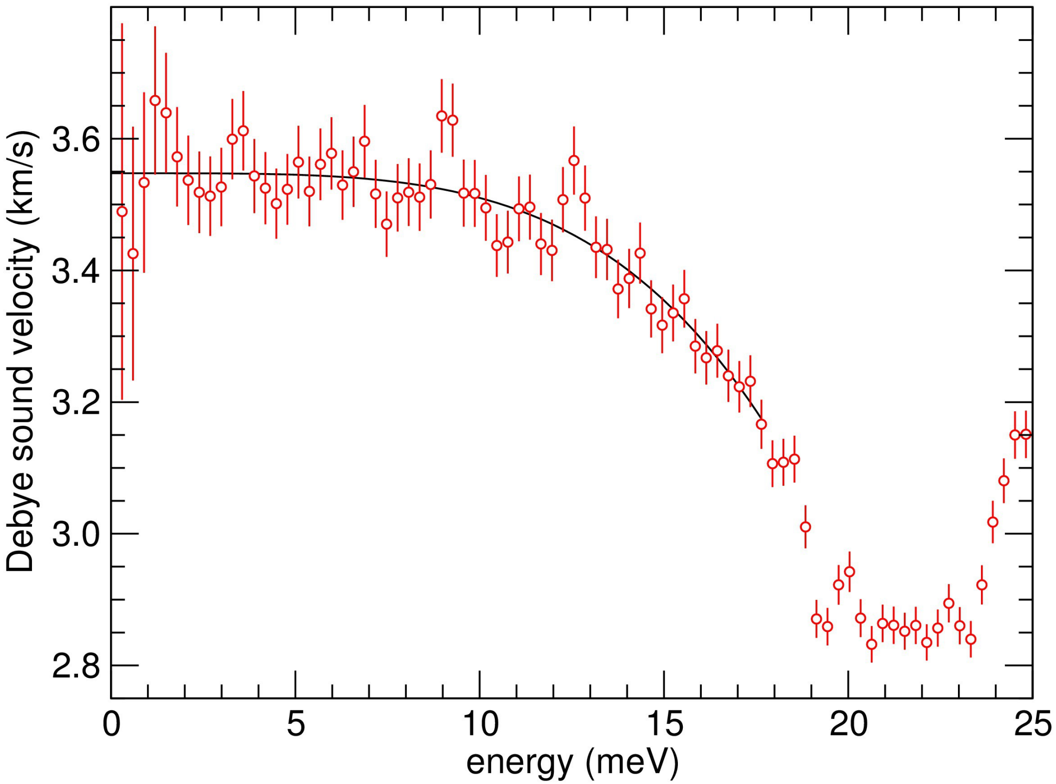
$$v_p^2 - \frac{4}{3}\, v_s^2 = \frac{K}{\rho} = v_\phi^2$$

- An excellent approximation for the solution is

$$v_s = 0.952\, v_D - 0.041\, v_\phi$$
$$v_p = 0.908\, v_\phi + 0.297\, v_D + 0.243\, v_D^2 / v_\phi$$

example bccFe:

➢ extract sound velocities from phonon DOS created earlier

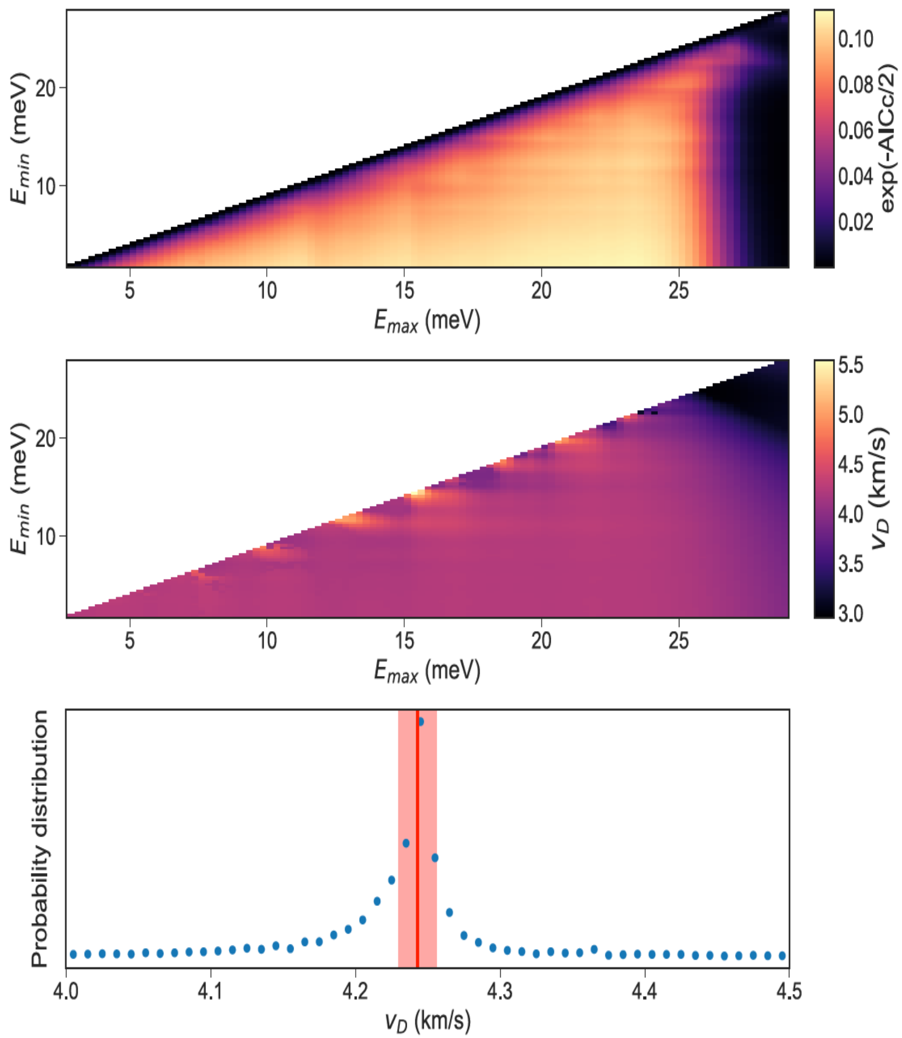


- ✰ open example bccFe
- ✰ GUI panel “Sound Velocities”

- ✰ focus of fit function selection

Probability distribution function:

R.A. Morrison, J.M. Jackson, W. Sturhahn, J. Zhao, and T.S. Toellner (2018): "High pressure thermoelasticity and sound velocities of Fe-Ni-Si alloys" under review



- Fit the Debye velocity function for various energy ranges
- Use the Akaike Information Criterium (AICc) and exp[-AICc/2] as likelyhood of fit results

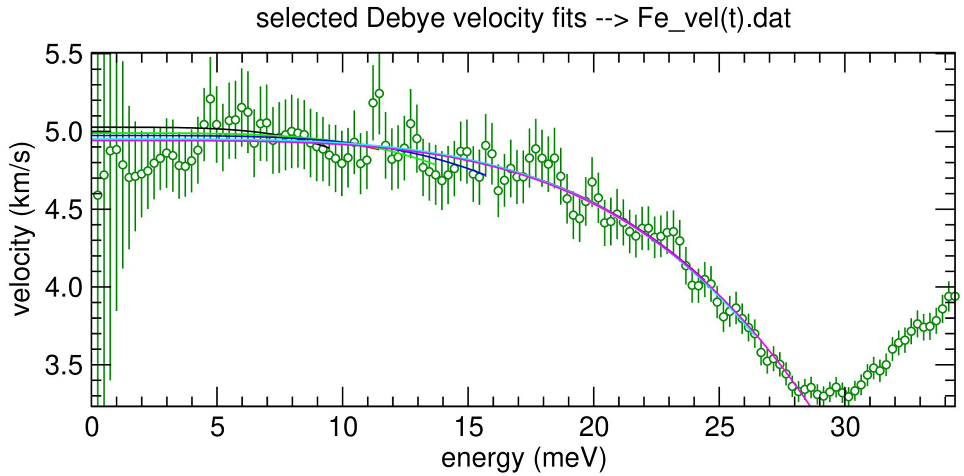
$$\mathrm{AICc} = \chi^2 + \frac{2\,M\,N}{N - M - 1}$$

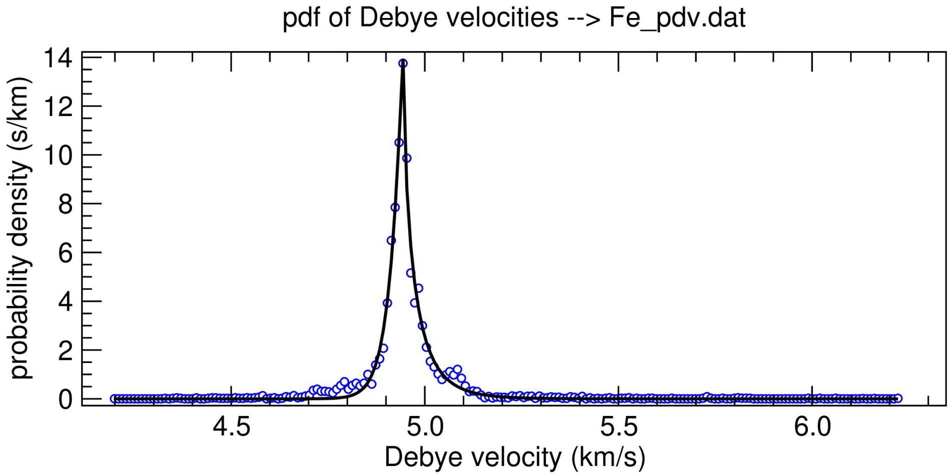
M = nr. of fit parameters, N = nr. data points

- Histogram of the AICc weighted Debye velocity fit results constitutes the pdf

example hcpFe:

➢ extract sound velocities from phonon DOS created earlier



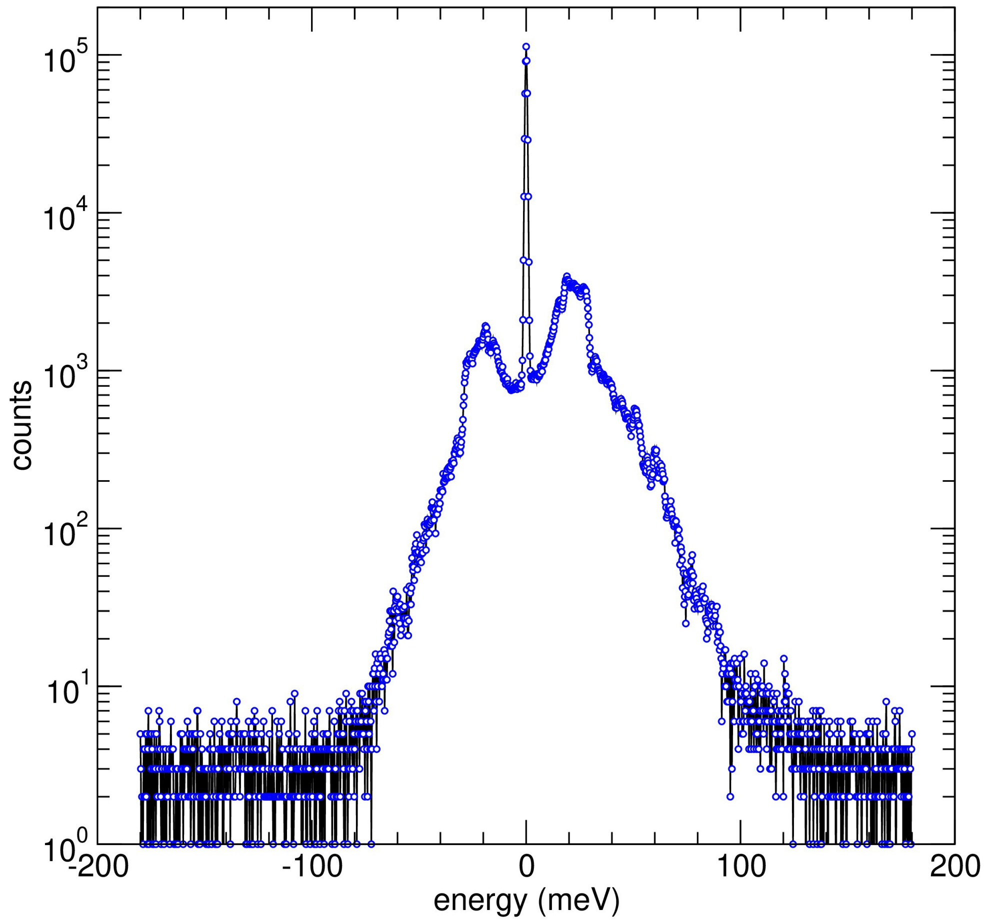


✰ open example hcpFe
✰ GUI panel "Sound Velocities"

✰ focus on the pdf

example oxide:

➢ determine an appropriate energy range for data collection



✰ create new project

✰ use NRXIS spectrum “oxide.dat”

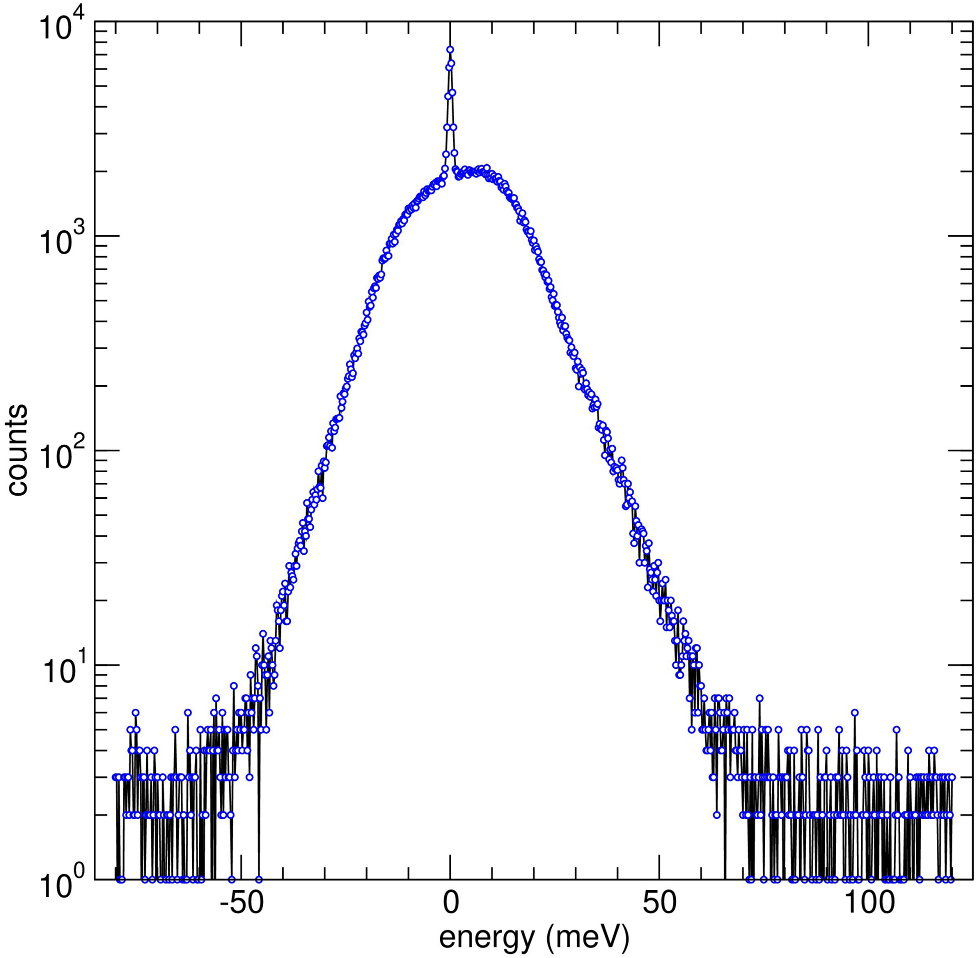
✰ extract PDOS
temperature around 300 K

✰ use mphox option

✰ use phoxalyzer to evaluate
choice of energy range

example glass:

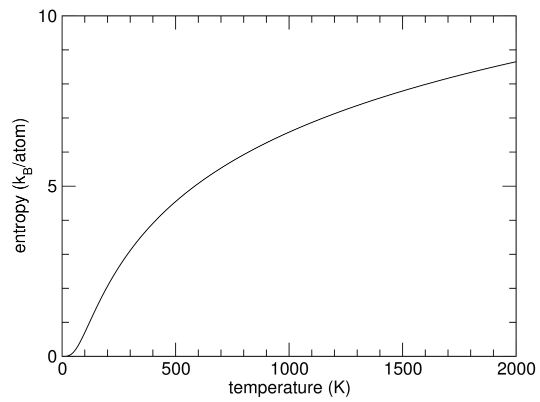
- difficult materials may torpedo your experimental plan



- ☆ create new project(s)
- ☆ use NRIXS spectra in folders
  "glass1" and "glass2"
- ☆ extract PDOS
  temperature around 300 K
- ☆ use phoxalyzer to evaluate results
  f-factor, force constant etc.

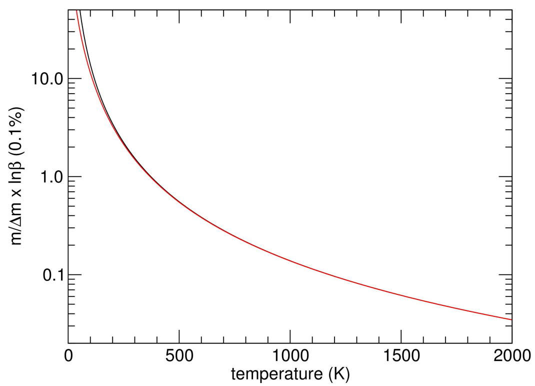
example temperature dependence:

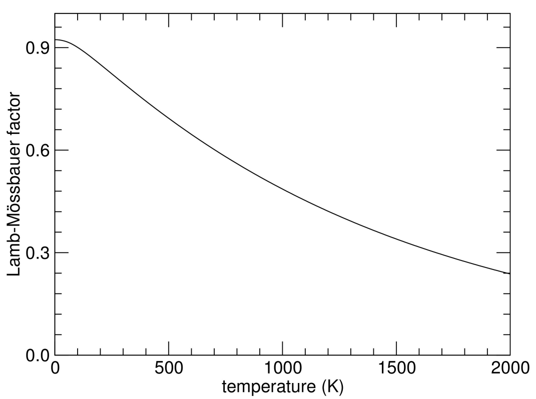
➢ calculate temperature dependent functions
from phonon DOS extracted earlier



- ✰ open relevant project
- ✰ GUI panel “PDOS contractions”

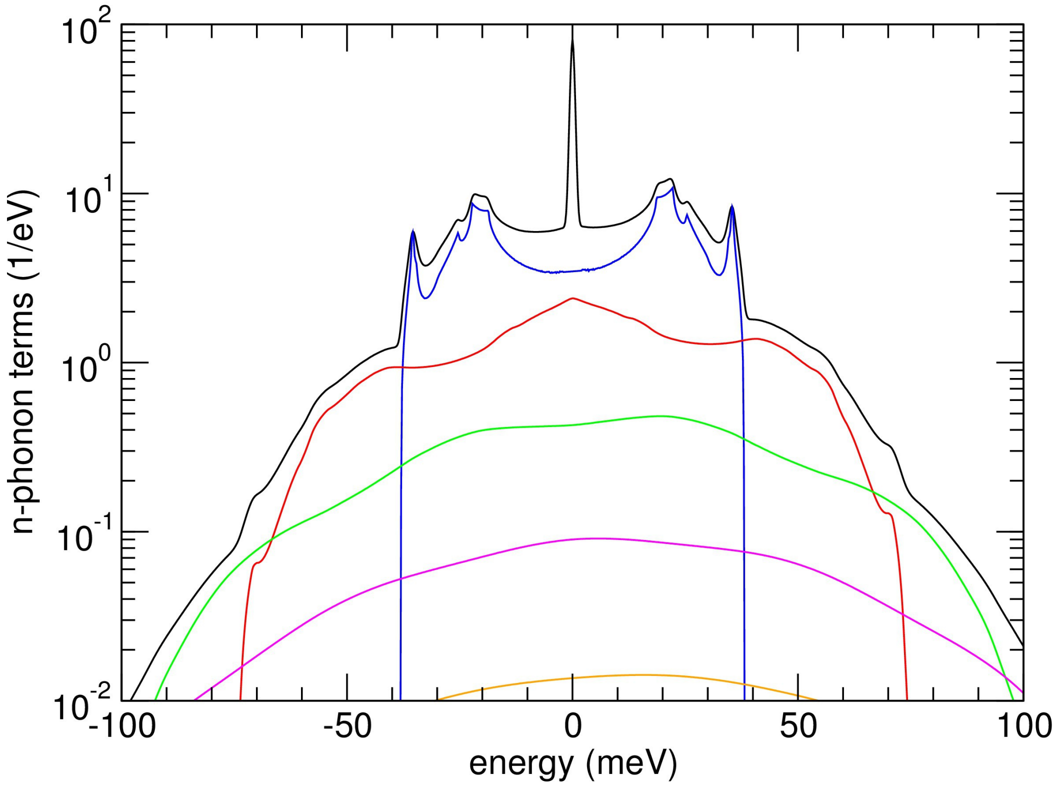
- ✰ inspect output files





example theory:

➢ calculate NRIXS spectrum
from a theoretical phonon DOS “theory.dos”



- ✰ create new project
- ✰ GUI panel “PDOS contractions”

- ✰ inspect output files