

<u>PHOnon Excitation by Nuclear Inelastic X-ray scattering</u>

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

Wolfgang Sturhahn

wolfgang@nrixs.net

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

- \Rightarrow 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

 \Rightarrow inverse construction (DOS to spectrum), version 2.1.0 (2012)

 \Rightarrow 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
 - \Rightarrow 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
- \clubsuit 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

• • •	~/Library/NRIXS/PHOENIX/projects/bccFe.prc (edited)	
S 🖆 🖽 📉 🔎 🛄		
Add Spectra Extract PDOS Sound Velocities PDOS Contraction		Project directory
iox input parameters		
	<pre>peak : 1.00E+00 valid range (meV) : -9.90 to 9.90</pre>	IX/projects/bccFe.prc
Nuclear resonant isotope	fit range (meV): -2.99 to 2.99 centered at 0.11 Ch1A2 peak FWHM pos. %bgr. asm. start: 334.90 9.03E+03 1.20 0.107 3.107 1.08 final: 2.94 9.50E+03 1.00 0.013 1.833 1.08 errors: 0.46 3.21E+02 0.04 0.031 0.863 0.11	/ Data/ Fe_cvm.bin Fe_dos.dat Fe_ite.csv
column assignment energy 1 counts 2 error 3	smoothing range (meV) : -2.897 to 3.084	Fe_nrm.dat
Autput file prefix Fe amount minimal more everything	Quantities derived directly from the data>	Fe_padd_ptLtxt Fe_phox_ptLtxt
format	Lamb-Moessbauer factor : 0.7995 +- 0.0019 kinetic energy : 14.0707 +- 0.0823 meV/atom quantum excess energy : 1.2739 +- 0.0823 meV/atom	Fe_shf.dat Fe_sum.dat
Sample temperature (K) 297	mean force constal t: 175.5276 +- 3.7350 N/m	
Data background 1	Quantities derived after refinement> Lamb-Moessbauer factor : 0.7996 +- 0.0019	
Data corrections < use with care	kinetic energy : 14.0804 +- 0.0824 meV/atom quantum excess energy : 1.2837 +- 0.0824 meV/atom	
normalization 0 %/100meV	mean force constant : 177.1053 +- 3.7686 N/m	
energy, linear 0 1E-3	<pre>isotope fractionation : 1.5047 +- 0.0966 perMille/% high T isotope frac. : 1.5469 +- 0.0329 perMille/%</pre>	
energy, quadratic 0 1E-6/meV	Consistency tests using the data>	
Elastic peak built-in from file	tested quantity %deviation norm.dev. status	
ranges (meV) for fitting 6.0 smoothing 6.0		
inelastic background 1 %	Consistency tests using the phonon DOS>	-Directory-
left/right asymmetry 1	tested quantity %deviation norm.dev. status norm of DOS 0.04 +- 0.43 0.10 ok	>
resolution file Data/mono.res	Lamb-Mossbauer factor 0.01 +- 0.26 0.02 ok kinetic energy per atom 0.13 +- 0.75 0.17 ok	RIXS/PHOENIX/projects
column assignment energy 1 intensity 2	mean force constant $0.81 + 2.51$ 0.32 ok	/ bccFe.prc/
processing noneautomanual	deviator = quadr. mean of norm.dev> 0.68 ok	hcpFe.prc/
Additional filter FWHM 0 meV	Quantities calculated from the partial DOS>	
Fit control steps 20 damping 0.1	Lamb-Moessbauer factor : 0.7997 +- 0.0008 kinetic energy : 14.0982 +- 0.0656 meV/atom	
Mphox engine enable	mean force constant : 178.5330 +- 2.3673 N/m	
mpnox engine enaole	isotope fractionation : 1.525 ↔ 0.0769 perMille/% high T isotope frac. : 1.5594 ↔ 0.0207 perMille/% Lamb-Moesbauer factor at T=0 : 0.9235 ↔ 0.0003 kinetic energy vibrational specific heat : 2.7103 ↔ 0.0111 k.B/atom	
Phox output files	vibrational entropy : 3.0726 +- 0.0118 k_B/atom resilience : 104.3601 +- 0.5060 N/m	
M	Lamb-Moessbauer temperature : 1416.9 +- 6.87 K CPU time : user 0.77 s system 0.01 s	
	CHO CTIME : USER 0.77 S System 0.01 S PHOENIX module PHOX finished	
dos		



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
- \succ 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

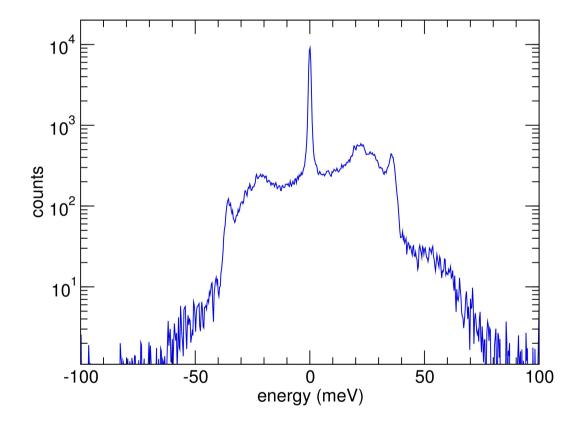
psth (GUI "PDOS Contractions")

- ☆ generates NRIXS spectrum from phonon DOS
- ☆ calculates temperature dependent contractions of phonon DOS



<u>example bccFe – spectrum:</u>

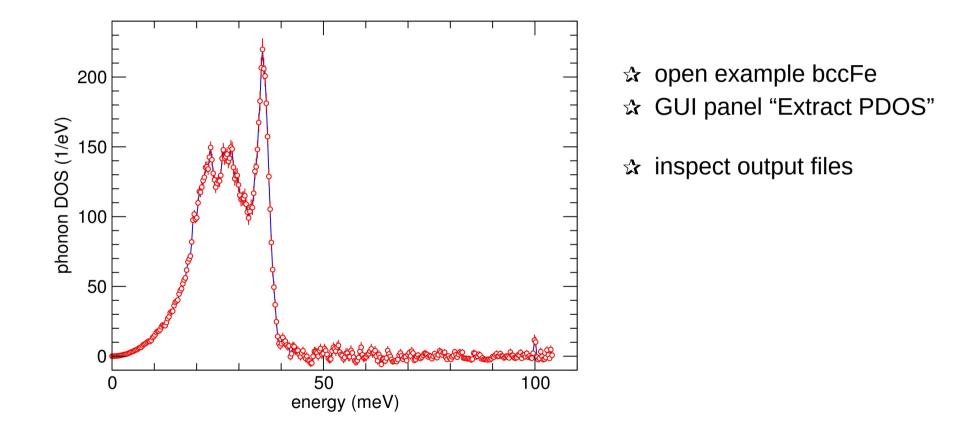
add data of several NRIXS scans on bcc-Fe, ASCII input format



- ☆ open example bccFe
- ☆ GUI panel "Add spectra"
- ☆ inspect output files

<u>example bccFe – DOS:</u>

extract phonon DOS from bcc-Fe spectrum created before





The "deviator" definition:

 \succ 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
- \Rightarrow 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
$$\int \left\{ \frac{S(\omega) - S(-\omega)}{S(\omega) + S(-\omega)} - \tanh[A_2 \frac{\beta \omega}{2}] \right\}^2 d\omega \longrightarrow \min \qquad B_2 = 1$$

> normalization $A_3 = \int D(\omega) d\omega$ $B_3 = 1$

> LM factor
$$A_4 = 1 - \int \{S(\omega) - S(0)\} d\omega$$
 $\ln B_4 = -\int \frac{\omega_R}{\omega} \coth \frac{\beta \omega}{2} D(\omega) d\omega$

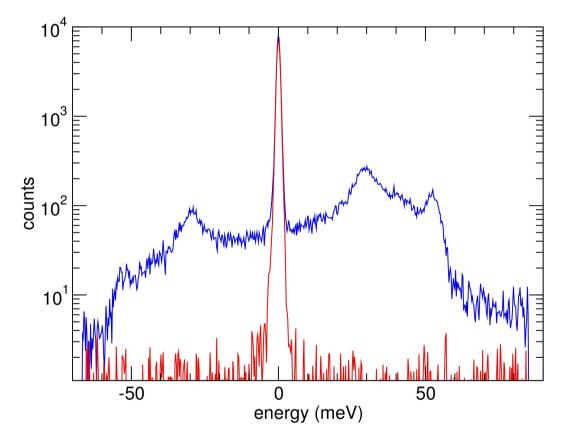
$$\blacktriangleright \text{ kinetic energy } A_5 = \frac{1}{4\omega_R} \int (\omega - \omega_R)^2 S(\omega) \, d\omega \qquad B_5 = \frac{1}{2} \int \omega \, \coth \frac{\beta \omega}{2} \, D(\omega) \, d\omega$$

> force constant
$$A_6 = \frac{k^2}{2\omega_R^2} \int (\omega - \omega_R)^3 S(\omega) \, d\omega \quad B_6 = \frac{k^2}{2\omega_R} \int \omega^2 D(\omega) \, d\omega$$



<u>example hcpFe – spectrum:</u>

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



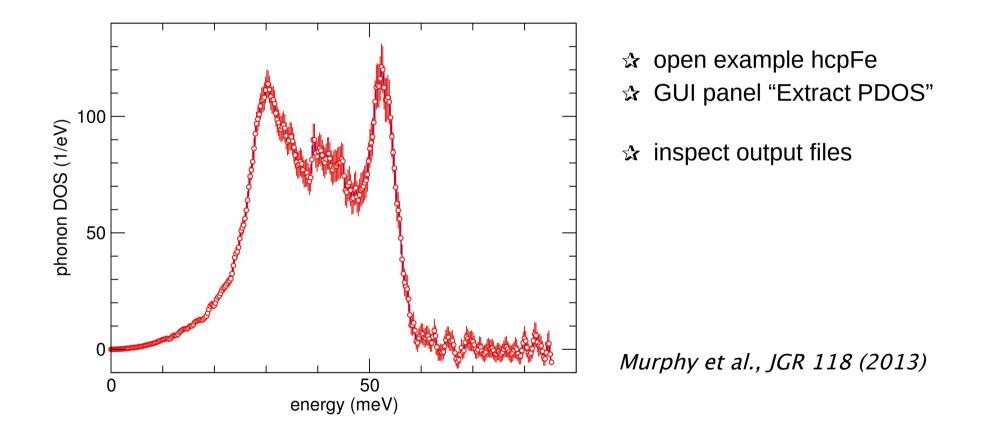
- \Rightarrow open example hcpFe
- ☆ GUI panel "Add spectra"
- ☆ inspect output directories & files

Murphy et al., JGR 118 (2013)



example hcpFe - DOS:

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





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



<u>example σ-FeCr:</u>

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

valuate problems in the experiment



The Debye sound velocity:

The phonon DOS behaves Debye-like at low energies

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

 \succ The Debye sound velocity v_{D} is an average over all sound velocities



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

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

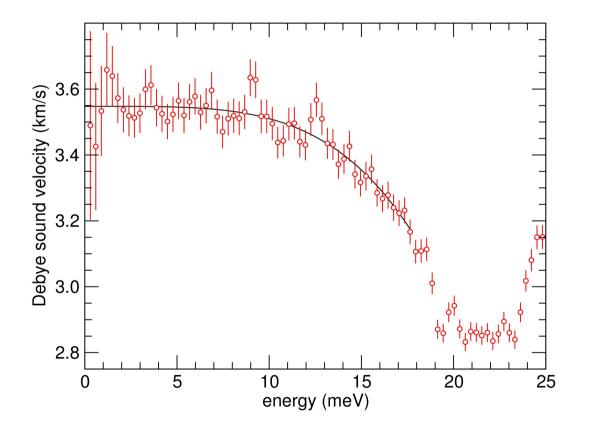
An excellent approximation for the solution is

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



example bccFe:

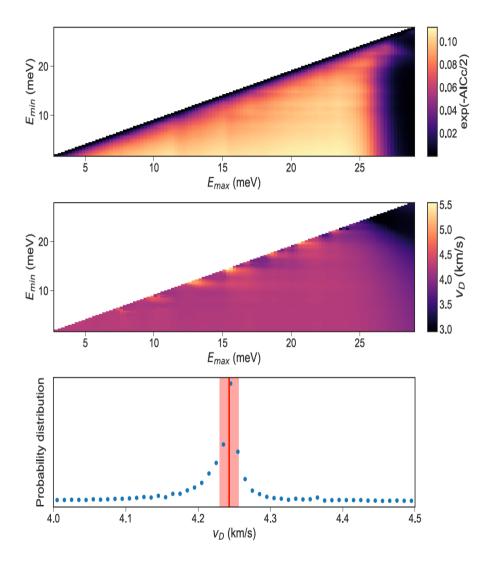
extract sound velocities from phonon DOS created earlier



- \Rightarrow 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

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

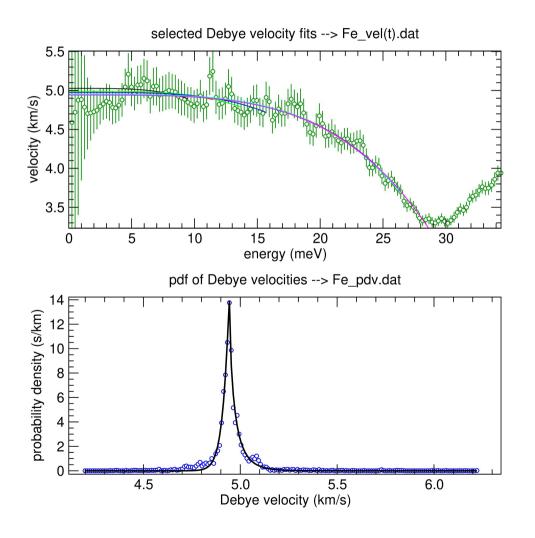
M = nr. of fit parameters, N = nr. data points

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

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example hcpFe:

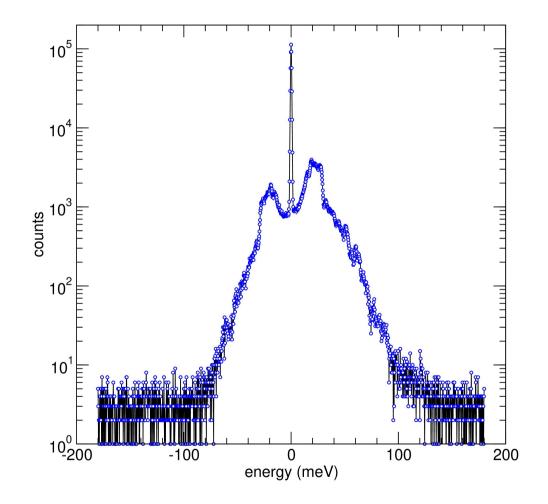
extract sound velocities from phonon DOS created earlier



- \Rightarrow open example hcpFe
- ☆ GUI panel "Sound Velocities"
- $\mbox{$\stackrel{\hfill}{\sim}$}$ focus on the pdf

example oxide:

determine an appropriate energy range for data collection

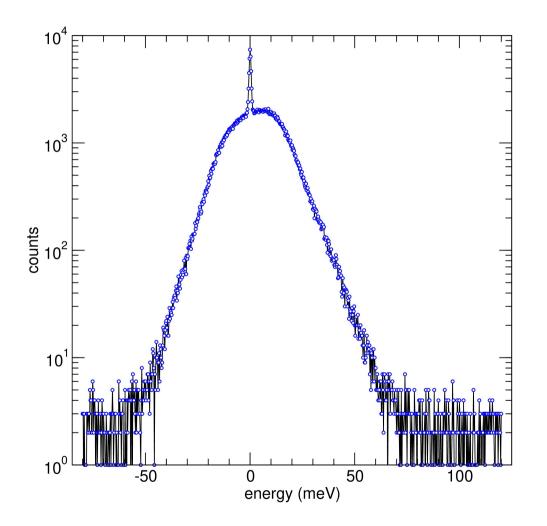


- ☆ create new project
- ☆ use NRXIS spectrum "oxide.dat"
- ☆ extract PDOS temperature around 300 K
- \Rightarrow use mphox option
- ☆ use phoxalyzer to evaluate choice of energy range



example glass:

difficult materials may torpedo your experimental plan

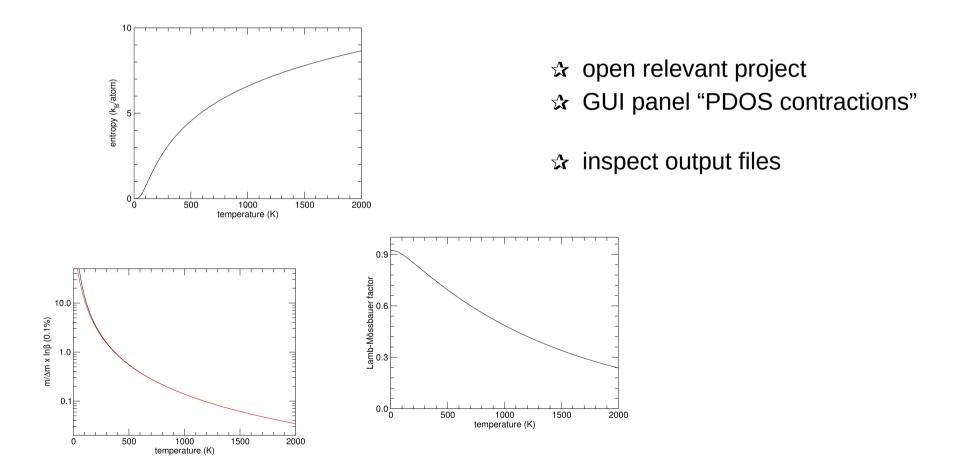


- ☆ create new project(s)
- ☆ use NRIXS spectra in folders "glass1" and "glass2"
- ☆ extract PDOS temperature around 300 K
- use phoxalyzer to evaluate results
 f-factor, force constant etc.



example temperature dependence:

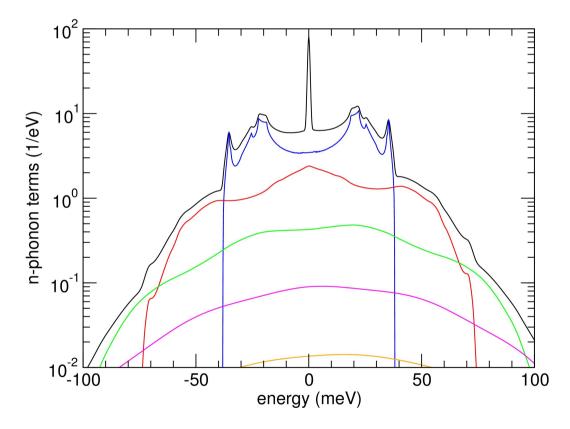
calculate temperature dependent functions from phonon DOS extracted earlier





example theory:

calculate NRIXS spectrum from a theoretical phonon DOS "theory.dos"



- ☆ create new project
- ☆ GUI panel "PDOS contractions"
- ☆ inspect output files

