Inelastic X-Ray Scattering & Lattice Dynamics

Esen Ercan Alp
Advanced Photon Source, Argonne National Laboratory

alp@anl.gov

NX School 2019
June 24, 2019, Argonne National Laboratory, Argonne, IL

Lattice dynamics for beginners
Inelastic X-Ray Scattering & Spectroscopy @ APS

- Nuclear Resonant Inelastic X-Ray scattering, NRIXS: Sectors 3, 16, 30
- Momentum Resolved High Energy Resolution IXS (HERIX) Sectors 3, 30
- Resonant Inelastic X-Ray Scattering, RIXS: Sector 27
- X-Ray Raman Scattering, XRS: Sectors 13, 16, 20
- X-Ray Emission Spectroscopy, XES: Sectors 6, 13, 16, 17
The cause and magnitude of inelastic scattering determines which method to use.

The change in energy could be as little as nano-eV or as high as keV.

X-rays are quite different than other probes because:

i) large and small energy transfers are possible  
ii) large momentum transfers at low energy is possible  
iii) avoid multiple scattering by being a gentle probe  
iv) polarization sensitivity  
  v) large energy tunability  
  vi) small beam size
Compton Scattered X-rays

Fluorescent X-rays

CeRh$_3$B$_2$

Elastic Peak

175 keV incident photons

Courtesy: Y. Sakurai, Spring-8
Incident beam energy
Lattice dynamics for beginners

Lattice dynamics describes vibrations of atoms in condensed matter:

- crystalline solids
- glasses, and
- liquids

However, some of the convenience gained by symmetry or periodic lattice is lost for glasses and liquids. Also, effect of surfaces and defects are glowing short-comings of the classical model.

Lattice dynamics is a reflection of forces acting upon atoms and leads to

- sound velocity: $V_s$, $V_p$
- vibrational entropy, $S_v$
- specific heat, $C_p$
- force constant, $<F>$
- compression tensor, $c_{11}$, $c_{12}$, $c_{44}$
- Young’s modulus, $E$
- Shear modulus, $G$
- stiffness and resilience
- Gruneisen constant, $\gamma$
- viscosity, $\nu$

Many experimental techniques exist to study lattice dynamics

- sound velocity, deformation, thermal expansion, heat capacity….
- spectroscopic methods using light, x-rays and neutrons, and electrons
- point contact spectroscopy

Imagine that you can measure all that for a micron sized sample, at 3 Mbar at 4000 K, in a way that is element selective, or even better isotope selective.
Two main approximations should be noticed:

- **Born-Oppenheimer (adiabatic) approximation**
  - Motion of atoms are independent and decoupled from the electrons.
  - All electrons follow the nuclei. This can be justified by considering the time scales involved: $10^{-15}$ s (femto) for electrons, $10^{-12}$ s (pico) for nuclei.

- **Harmonic approximation**
  - At equilibrium, attractive and repulsive forces are balanced.
  - When atoms move away from the equilibrium positions, they are forced to come back by restoring forces.
  - Magnitude of atomic displacements are small compared to interatomic distance.
  - All atoms in equivalent positions in every unit cell move together.
Figure 1. Traditional potential energy curve for two atoms, showing a minimum at a separation of $r_0$ that might correspond to the bond length, the steep rise for shorter distances that reflects the repulsion due to overlap of electron density of the two atoms, and the more gentle rise towards zero for larger separations reflecting the attractive interaction. This plot is however somewhat of a simplification of the situation within a crystal, because typically the atoms within a crystal are held in place by a large number of interactions, including the long-range Coulomb interaction, and the position of the minimum of any pair of atoms may not reflect actual equilibrium contact distances.

More recently we have seen a number of key developments in the study of lattice dynamics. In terms of experiments, we are seeing a new generation of instruments at neutron scattering facilities, particularly with the ability to collect data over wide ranges of scattering vector and energy simultaneously. The new instrumentation is matched by software for simulating the outputs of experiments, coupled with new capabilities to calculate quantum mechanics.

These capabilities coincide with the emergence of investigations concerned with new phenomena such as negative thermal expansion, which directly need calculations and measurements of lattice dynamics for a clear understanding (see Section 6.5 for example). All these developments have led to renewed interest in lattice dynamics.

1.3 The harmonic approximation

The key approximation in the theory of lattice dynamics is the harmonic approximation. This is illustrated by considering the potential energy between two atoms, as shown in Figure 1. We can write the energy as a Taylor expansion around the minimum point $r_0$:

$$E(r) = E_0 + \frac{1}{2} \left. \frac{\partial^2 E}{\partial r^2} \right|_{r_0} (r - r_0)^2 + \frac{1}{3!} \left. \frac{\partial^3 E}{\partial r^3} \right|_{r_0} (r - r_0)^3 + \frac{1}{4!} \left. \frac{\partial^4 E}{\partial r^4} \right|_{r_0} (r - r_0)^4 + \cdots$$

ignoring these terms is the harmonic approximation

There should be no thermal expansion in the harmonic model.

The fact that there is thermal expansion is an indication that the potential under which the atoms move is not harmonic.

However, harmonic model has so many convenient features that we adopt it to explain many features of atomic vibrations.
Diatomic infinite 1-D chain

\[ E = \frac{1}{2} J \sum_n (u_{1,n} - u_{2,n})^2 + \frac{1}{2} J \sum_n (u_{2,n} - u_{1,n+1})^2 \]

\[ J = \frac{\partial^2 E}{\partial u_{1,n} \partial u_{2,n}} \]  
Force constant (spring constant)

\[ u_{1,n}(t) = \tilde{u}_1 \exp(i(kna - \omega t)) \]
\[ u_{2,n}(t) = \tilde{u}_2 \exp(i(kna - \omega t)) \]

Time dependent displacement of two atoms in terms of relative displacement of each atom
\[ E_{1,n} = \frac{1}{2} J(u_{1,n} - u_{2,n})^2 + \frac{1}{2} J(u_{1,n} - u_{2,n-1})^2 \]

\[ E_{2,n} = \frac{1}{2} J(u_{2,n} - u_{1,n})^2 + \frac{1}{2} J(u_{2,n} - u_{1,n+1})^2 \]

\[ f_{1,n} = -\frac{\partial E_{1,n}}{\partial u_{1,n}} = -J(u_{1,n} - u_{2,n}) - J(u_{1,n} - u_{2,n-1}) \]

\[ f_{2,n} = -\frac{\partial E_{2,n}}{\partial u_{2,n}} = -J(u_{2,n} - u_{1,n}) - J(u_{2,n} - u_{1,n+1}) \]

\[ \ddot{u}_{1,n}(t) = -\omega^2 \tilde{u}_1 \exp i (kna - \omega t) = -\omega^2 u_{1,n}(t) \]

\[ \ddot{u}_{2,n}(t) = -\omega^2 \tilde{u}_2 \exp i (kna - \omega t) = -\omega^2 u_{2,n}(t) \]

\[ m_1 \ddot{u}_{1,n}(t) = -m_1 \omega^2 u_{1,n}(t) = -J(2u_{1,n}(t) - u_{2,n}(t) - u_{2,n-1}(t)) \]

\[ m_2 \ddot{u}_{2,n}(t) = -m_2 \omega^2 u_{2,n}(t) = -J(2u_{2,n}(t) - u_{1,n}(t) - u_{1,n+1}(t)) \]
Mass normalized displacements (real)

\[ e_1 = m_1^{1/2} \tilde{u}_1; \quad e_2 = m_2^{1/2} \tilde{u}_2 \]

Matrix form of Newton’s eq\(^n\) of motion

\[ \omega^2 \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = D(k) \cdot \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} \]

\[
D(k) = \begin{pmatrix} 2J/m_1 & -J (1 + \exp(-ika)) / \sqrt{m_1 m_2} \\ -J (1 + \exp(+ika)) / \sqrt{m_1 m_2} & 2J/m_2 \end{pmatrix}
\]

Eigen solutions

\[ \omega^2(k) = 2J \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \]

\[ \omega^2(k) = \frac{J^2 a^2}{2(m_1 + m_2) k^2} \]

out-of-phase

\[ m_1^{1/2} e_1 = -m_2^{1/2} e_2 \]

in-phase

\[ m_1^{-1/2} e_1 = m_2^{-1/2} e_2 \]

Optic mode

Acoustic mode
Inelastic X-Ray Scattering: A plethora of different techniques

IXS

Non-Resonant

ΔE \sim \text{meV}

IXS

Resonant

ΔE \sim 1 \text{meV}

Nuclear resonant
HERIX-3 and HERIX-30

HERIX-3

2.2 meV

HERIX-30

1.4 meV

High-resolution monochromator

E = 21-24 keV
ΔE ~ 2 eV

Undulator, High-heat Load mono

ΔE ~ 1 meV

High-resolution monochromator
CdTe detector

Bimorph focusing mirror
Beam size (VXH)=15X35 μm²

High-resolution monochromator
ΔE=1.1 meV
working at T=123 K

High-heat-load monochromator C(111)
ΔE~1.6 eV

Be compound refractive lens
## Choice of energy

<table>
<thead>
<tr>
<th>Si Reflection at 90°</th>
<th>Energy (keV)</th>
<th>Resolution (meV)</th>
<th>Reflectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 6 0</td>
<td>21.657</td>
<td>1.23</td>
<td>78</td>
</tr>
<tr>
<td>11 11 11</td>
<td>21.747</td>
<td>0.83</td>
<td>70</td>
</tr>
<tr>
<td>13 11 9</td>
<td>21.985</td>
<td>0.81</td>
<td>69</td>
</tr>
<tr>
<td>15 11 7</td>
<td>22.685</td>
<td>0.70</td>
<td>68</td>
</tr>
<tr>
<td>20 4 0</td>
<td>23.280</td>
<td>0.87</td>
<td>76</td>
</tr>
<tr>
<td>12 12 12</td>
<td>23.724</td>
<td>0.80</td>
<td>75</td>
</tr>
<tr>
<td>14 14 8</td>
<td>24.374</td>
<td>0.69</td>
<td>74</td>
</tr>
<tr>
<td>22 2 0</td>
<td>25.215</td>
<td>0.576</td>
<td>71</td>
</tr>
<tr>
<td>13 13 13</td>
<td>25.701</td>
<td>0.37</td>
<td>60</td>
</tr>
</tbody>
</table>
Bent-diced IXS analyzers

Si  Ge  LiNbO$_3$
Generations of high-resolution monochromators

1992:
- Angle encoder
- Coupling
- Rotation stage
- Goniometer

1999:
- Piezo
- Picomotor
- 1st crystal
- 2nd crystal
- 3rd crystal
- Beam
- 4th crystal

2002:
- Silicon (18 12 6) c.c.
- Mounted on cryostage

2004:
- 2x silicon (2 2 0)
- W/ weak-link ass’y

T. Toellner, D. Shu
What is being measured?

\[
\frac{d^2 \sigma}{d\Omega \ d\omega} = r_0^2 \frac{\omega_f}{\omega_i} |\mathbf{e}_i \cdot \mathbf{e}_f| N \sum_{i,f} \left| \langle i \sum e^{iQr_j} | f \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)
\]

Thomson cross section

Dynamical structure factor \( S(Q,\omega) \)

\[
S(Q,\omega) = \frac{1}{2\pi} \int dt \ e^{-i\omega t} \left\langle \phi_i \left| \sum_{ll'} f_l(Q) e^{-iQ \cdot r_l(t)} f_{l'}(Q) e^{iQ \cdot r_{l'}(0)} \right| \phi_i \right\rangle
\]

Density-density correlations

\[
f(Q) = f_{ion}(Q) + f_{valence}(Q)
\]

Atomic form factor
Dynamic structure factor

Sum over phonon branch $j$ at reduced momentum transfer, $q$

Sum over different atoms in the unit cell

Atomic form factor for each atom

scaling with square root of mass

Debye-Waller factor to account for bond strength

phonon occupation probability

Phase of the scattering amplitude

Polarization factor between momentum transfer and phonon’s polarization vector

External probe-photon

$$S(Q, \omega) = \sum_{q,j} \sum_{s} f_s(Q) \frac{\hbar}{\sqrt{2m_s}} e^{-W_s} e^{i\mathbf{Q} \cdot \mathbf{R}_s} \left[ \mathbf{Q} \cdot \mathbf{e} (q, s, j) \right] \frac{2}{\left( e^{\frac{1}{\hbar\omega/kT}} - 1 \right) + \frac{1}{2} \pm \frac{1}{2}} \delta(\omega - \omega_{q,j})$$

phonon frequency

delta-function in $\omega$
Entropy fluctuations,
\[ \Delta \omega_R \sim \alpha q^2 \]
Concentration fluctuations
\[ \Delta \omega_R \sim Dq^2 \]
Pressure fluctuations
\[ \Delta \omega_B \sim Vq^2 \]
\[ \omega_B(q) = V \cdot q \]
Hot Solid Silicon
$T=1300 \, ^\circ C$

Supercooled Silicon
$T=1300 \, ^\circ C$
Hot Solid Si

\[ T = 1300 \, ^\circ C \]

\[ c_s = 7300 \, \text{m/s} \]

Supercooled Si

\[ T = 1300 \, ^\circ C \]

\[ c_s = 4566 \, \text{m/s} \]
• Phonons are periodic oscillations in condensed systems.

• They are inherently involved in thermal and electrical conductivity.

• They can show anomalous (non-linear) behavior near a phase transition.

• They can carry sound (acoustic modes) or couple to electromagnetic radiation or neutrons (acoustical and optical).

• Have energy of $\hbar \omega$ as quanta of excitation of the lattice vibration mode of angular frequency $\omega$. Since momentum, $\hbar k$, is exact, they are delocalized, collective excitations.

• Phonons are bosons, and they are not conserved. They can be created or annihilated during interactions with neutrons or photons.

• They can be detected by Brillouin scattering (acoustic), Raman scattering, FTIR (optical).

• Their dispersion throughout the BZ can ONLY be monitored with x-rays (IXS), or neutrons (INS).

• Accurate prediction of phonon dispersion require correct knowledge about the force constants: COMPUTATIONAL TECHNIQUES ARE ESSENTIAL.
\( \omega^2 e = D(k) \cdot e \quad \Rightarrow \quad \omega^2 = e^T \cdot D(k) \cdot e \)

Eigenvalue eqn.

\[
D_{j,j'}(k) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{n'} \Phi_{0,n'}^{j,j'} \exp(i k \cdot (r_{j,0} - r_{j',n'}))
\]

Dynamical matrix

\[
e_{\lambda}^T \cdot e_{\lambda} = 1; \quad e_{\lambda'}^T \cdot e_{\lambda} = \delta_{\lambda',\lambda}
\]

Eigenvalues are orthonormal..

349.7 cm\(^{-1}\)
symmetrical stretching

asymmetrical stretching

scissoring

rocking

wagging

twisting
**PHONONS (cont’d)**

\[ E_n = \left(n + \frac{1}{2}\right) \hbar \omega \]

Energy of a single oscillation as a function of number of phonons. The second term +1/2 is the “zero-point” energy.

\[ E = \sum_{\mathbf{k}, \lambda} \omega_{\mathbf{k}, \lambda}^2 |Q(\mathbf{k}, \lambda)|^2 = \sum_{\mathbf{k}, \lambda} \left(n_{\mathbf{k}, \lambda} + \frac{1}{2}\right) \hbar \omega_{\mathbf{k}, \lambda}. \]

Total energy, in terms of normal mode coordinates

\[ \langle n(\omega_{\mathbf{k}, \lambda}) \rangle = \frac{1}{\exp(\hbar \omega_{\mathbf{k}, \lambda} / k_B T) - 1} \]

Bose-Einstein statistics for average number of modes at a given temperature

\[ \mathcal{H} = \frac{1}{2} \sum_{j, \ell} m_j |\dot{u}_{j \ell}|^2 + \frac{1}{2} \sum_{j, j', \ell, \ell'} u^T_{j \ell} \cdot \Phi_{\ell, \ell'}^{j, j'} \cdot u_{j' \ell'} \]

Hamiltonian of the system:

\[ \mathcal{H} = \text{Kin. En.} + \text{Pot. En} \]
Many thermodynamic functions like free energy, specific heat, and entropy are additive functions of phonon density of states.

This stems from the notion that the normal modes do not interact in the harmonic approximation.

Phonon density of states is the number of modes in a unit energy interval.

\[ c_v(T) = 3Nk \int \frac{\hbar^2 \omega^2 e^{\hbar \omega / kT}}{(kT)^2 (1 - e^{\hbar \omega / kT})^2} \cdot g(\omega) \cdot d\omega \]

Vibrational specific heat
Phonon density of states is a key ingredient for many thermodynamic properties.

If we choose to write in terms of energy, \( E = \hbar \omega, \quad \beta = 1/k_B T \)

\[
c_v(T) = 3k_B \int (\beta E / 2)^2 \csc h(\beta E) \cdot g(E) \cdot dE
\]

Vibrational specific heat

\[
S_v(T) = 3k_B \int_0^\infty \{ \beta E/2 \cdot \cot h(\beta E) - \ln[2 \sin h(\beta E)] \} \cdot g(E) \cdot dE
\]

Vibrational entropy

\[
f_{LM} = e^{-E_R} \int_0^\infty \{ g(E)/2 \} \cdot \coth(\beta E/2) \cdot dE
\]

Lamb-Mössbauer factor

\[
g(E) = \frac{3m}{2\pi^2 \hbar^3 \rho v_D^3} E^2
\]

Debye Sound velocity

\[
\langle F \rangle = \frac{M}{\hbar^2} \int_0^\infty E^2 g(E) dE
\]

Average restoring force constant
And, some thermodynamics

\[
\mathcal{Z} = \frac{1}{1 - \exp(-\beta \hbar \omega)}
\]

Partition function

\[
F = -k_B T \ln \mathcal{Z}
\]

Free energy

\[
C = -T \frac{\partial^2 F}{\partial T^2}
\]

Heat capacity

\[
E = \sum_{\mathbf{k}, \lambda} \left( \langle n(\omega_{\mathbf{k}, \lambda}) \rangle + \frac{1}{2} \right) \hbar \omega_{\mathbf{k}, \lambda} \equiv \int \left( \langle n(\omega) \rangle + \frac{1}{2} \right) \hbar \omega \, g(\omega) \, d\omega.
\]

Energy in terms of phonon density of states

![Phonon density of states graph](image)
Why x-rays instead of neutrons or visible light?

Limited momentum transfer capability of neutrons at low energies favor x-rays to study collective excitations with large dispersion, like sound modes.

When the sound velocity exceeds that of neutrons in the liquid, x-rays become unique. The low-momentum/high-energy transfer region is only accessible by x-rays.
Inelastic X-Ray Scattering: two approaches

IXS: Momentum resolved
- High resolution monochromator

NRIXS: Momentum integrated
- High resolution monochromator

10 cm
6 m horizontal arm
~11 cm
3 mm

APD
Sample
Nuclear Resonant Scattering
Kernresonanzabsorption von $\gamma$-Strahlung in Ir$^{191}$

Von Rudolf L. Mössbauer

Aus dem Laboratorium für technische Physik der Technischen Hochschule in München und dem Institut für Physik im Max-Planck-Institut für medizinische Forschung in Heidelberg

Bei der Emission und Selbstabsorption von weicher $\gamma$-Strahlung in Kernen treten bei tiefen Temperaturen in Festkörpern sehr starke Linien mit der natürlichen Linienbreite auf. Diese Linien erscheinen als Folge davon, daß bei tiefen Temperaturen bei einem Teil der Quantenübergänge der $\gamma$-Rückstoßimpuls nicht mehr vom einzelnen Kern aufgenommen wird, sondern von dem Kristall als Ganzes. Da die scharfen Emissions- und Absorptionslinien energetisch an der gleichen Stelle liegen, tritt ein sehr starker Resonanzfluoreszenzeffekt auf. Durch eine „Zentrifugen“-Methode, bei der die Emissions- und Absorptionslinien gegeneinander verschoben werden, läßt sich der Fluoreszenzeffekt unterdrücken und so eine unmittelbare Bestimmung der natürlichen Linienbreite von Resonanzlinien vornehmen. Erste Messungen nach dieser Methode ergeben für die Lebenszeit $\tau$ des 129 keV-Niveaus in Ir$^{191}$: $\tau = (1,4^{+0,2}_{-0,1}) \cdot 10^{-10}$ sec.

Abb. 2. Versuchsgeometrie. A Absorber-Kryostat; Q rotierende Kryostat mit Quelle; D Szintillationsdetektor. M ist der bei der Messung ausgenützte Teil des Rotationskreises der Quelle.
absorption-emission & recoil

\[ E_\gamma - R \quad E_\gamma + R \]

low temperature

intuitive expectation: large resonance absorption at high temperature

Mossbauer’s observation: less absorption at high temperature
Mg$_{2.25}$Fe$^{+2}_{0.75}$(Si$_2$O$_5$)(OH)$_4$

Antigorite

% transmission

Velocity (mm/sec)
Fe$^{2+}$, cubic
Fe$^{2+}$, octahedral
Fe$^{2+}$, tetrahedral
Fe$^{3+}$, octahedral
Fe$^{3+}$, tetrahedral
How isomer shift & quadrupole splitting are used for valence identification in Mössbauer Spectroscopy?

After 50 years of research and more than 10,000 papers, approximately 800 iron compounds have been classified, and the results are disseminated by the Mössbauer Effect Data Center (MEDC).

Given the fact that measured Mössbauer linewidths are typically 0.3 mm/sec, it is common to determine IS and QS with an accuracy of 0.1 mm/sec.

Hence, in many circumstances, this combination of IS-QS values provide valuable guidance into valence issues in minerals, lunar rocks, and meteorite studies.

Ref: Mossbauer Effect Reference and Data Journal, vol 33, No;1 (January 2010)
identifications of iron-bearing phases...128). Subgroup B (13...paramagnetic results because the oxide undergoes a...analyzed more than 100 ta...meteorites [1,2]. The lunar samples also provide a way...compositions that are comparable to basaltic martian...Meteorit. Planet. Sci. 33, 183. [2] Lofgren and Lofgren (1981), Cat.

![Fig. 1a](image1.png)

![Fig. 1b](image2.png)

![Fig. 2a](image3.png)

![Fig. 2b](image4.png)
1 revolution = 3.68 µsec => 1296 buckets

60% of the time @ the APS
Nuclear Resonance and Fallout in $^{57}\text{Fe}$-decay

- Conversion electrons, Auger electrons
- K fluorescence induced by nuclear decay
- 14.413 incoherent nuclear fluorescence
- 14.413 coherent nuclear fluorescence
- Photoelectrons, Auger electrons
- K fluorescence
- 14.413 Rayleigh photons
- Compton scattered photons

14.413 keV
Undulator

White beam slits

High Heat Load Monochromator

High resolution Monochromator

Sample

ΔE~500 keV

ΔE~150 eV

ΔE~1 eV

ΔE~1 meV

ΔE~10 neV

APD detector

10^13 Hz

5x10^9 Hz

1 Hz - 10^5 Hz
Detection of nuclear decay

- Prompt photons
- Delayed photons

- **log I**
- **time (nsec)**
- **153 nsec**

- **57 Fe**
- **spin, I**
- **Energy**
  - 136 keV
  - 14.41256 keV

- **exponential decay**
\( \alpha \) (bcc-Fe) to \( \varepsilon \) (fcc-Fe) transition under pressure by synchrotron Mössbauer spectroscopy
mixed alpha & epsilon phase of pure iron at 15.3 GPa pressure

B = 321.66 ± 0.026 kG
% hcp = 0.6629 ± 0.013

B = 320.23 ± 0.0044 kG
% hcp = 0.6365 ± 0.0047
Early dreamers...

Visualized by W. Vischer at Los Alamos & K. S. Singwi at Argonne (1960), but only properly observed after synchrotron radiation based tunable monochromators are realized.


Zero phonon “Mössbauer pip”

5 neV + mono. resolution

Phonon annihilation

Phonon creation

Energy ( ~ meV)
Phonon Density of States Measured by Inelastic Nuclear Resonant Scattering

W. Sturhahn, T. S. Toellner, and E. E. Alp

Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439

X. Zhang and M. Ando

Photon Factory, National Laboratory for High Energy Physics, Oho 1-1, Tsukuba, Ibaraki 305, Japan

Y. Yoda and S. Kikuta

Department of Applied Physics, Faculty of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

M. Seto

Research Reactor Institute, Kyoto University, Sennan-gun, Osaka 590-04, Japan

C. W. Kimball and B. Dabrowski

Department of Physics, Northern Illinois University, De Kalb, Illinois 60115

(Received 16 December 1994)
Multi-phonon decomposition

phonon creation

phonon annihilation

Energy (meV) \( (E_0=14.41256 \text{ keV}) \)
Lipkin’s sum rules related to phonon excitation probability

\[ \langle E_{\gamma}^1 \rangle = E_R = \frac{E_{\gamma}^2}{2Mc^2} \]

Recoil energy

\[ \langle E_{\gamma}^2 \rangle = 4E_R \bar{T} \]

Kinetic energy

\[ \langle E_{\gamma}^3 \rangle = \left( \frac{2\hbar^2 E_R}{M} \right) \frac{\partial^2 U}{\partial z^2} \]

Force constant

\[ E_R = \frac{\left( \frac{\hbar k}{2} \right)^2}{2M} = 1.96 \text{ meV} \]

Detailed Balance

\[
I(-E) = I(E)e^{-E/kT}
\]

\[
T = \frac{E(eV)}{k_B \ln[I(E)/I(-E)]}
\]

(-22.6 meV, 1158)

(22.6 meV, 2762)
\[ I(-E) = I(E)e^{-E/kT} \]

\[ k_B = 8.6173 \cdot 10^{-2} \text{meV}/K \]

\[ E = 22.6 \text{meV} \]

\[ I(-E) = 1158, \quad I(E) = 2762 \]

\[ T = \frac{E(\text{eV})}{k_B \ln[I(E)/I(-E)]} = 297.03K \]
Temperature dependence of phonon excitation probability

Figure 6. Energy spectra of inelastic nuclear absorption of synchrotron radiation by $^{57}$Fe at various temperatures. Solid lines are calculations according to eqs. (5.1)–(5.3), based on the results of neutron scattering at room temperature \cite{15} and convoluted with the instrumental function of the monochromator. From \cite{14}.

At low temperatures, besides vanishing in the phonon-annihilation part, the energy spectrum of inelastic absorption also vanishes at the low energy transfer region in the Chumakov, et al, Phys. Rev. B 54 (1996) 9596.
The Fe phonon density of states for bcc-Fe is shown in the graph. The formula for the phonon density of states is:

\[ g(E) = \frac{\tilde{m}}{2\pi^2 \hbar^3 \rho \nu_D^3} E^2 \]
Measurement of $v_D$, Debye sound velocity allows to resolve longitudinal and shear sound velocity, provided that bulk modulus and density, is independently and simultaneously measured by x-ray diffraction.

\[
g(E) = \frac{\tilde{m}}{2\pi^2 \hbar^3 \rho v_D^3} E^2
\]

\[
\begin{align*}
K_S &= \frac{V_P^2}{\rho} - \frac{4}{3} \frac{V_S^2}{\rho} \\
\frac{G}{\rho} &= \frac{V_S^2}{V_P} \\
\frac{3}{V_D^3} &= \frac{1}{V_P^3} + \frac{2}{V_S^3}
\end{align*}
\]

$K_S$: adiabatic bulk modulus
$G$: shear modulus
$V_P$: compression wave velocity
$V_S$: shear wave velocity
$V_D$: Debye sound velocity
$\rho$: density

<table>
<thead>
<tr>
<th>$K$ (GPa)</th>
<th>$\rho$ (g/cc)</th>
<th>$V_D$ (m/s)</th>
<th>$V_P$ (m/s)</th>
<th>$V_S$ (m/s)</th>
<th>$G$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>165 ± 1</td>
<td>8.01</td>
<td>3510 ± 12</td>
<td>5813 ± 13</td>
<td>3146 ± 11</td>
<td>79.3 ± 0.6</td>
</tr>
</tbody>
</table>
Fe phonon density of states (1/eV-atomic vol)

\[ c_v(T) = 3Nk \int \frac{\hbar^2 \omega^3 e^{\hbar \omega / kT}}{(kT)^2 (1 - e^{\hbar \omega / kT})^2} \cdot g(\omega) \cdot d\omega \]

\[ S_v(T) = 3k_B \int_{0}^{\infty} \left\{ \frac{\beta E}{2} \cdot \cot h(\beta E) - \ln\left[ 2 \sinh(\beta E) \right] \right\} \cdot g(E) \cdot dE \]

\[ \langle F \rangle = \frac{M}{\hbar^2} \int_{0}^{\infty} E^2 g(E) dE \]

\[ g(E) = \frac{3m}{2\pi^2 \hbar^3 \rho v_D^3} E^2 \]

Energy (meV)

TA-1, TA-2, LA, \[ \theta_D \]
Thermodynamic properties as an additive function of phonon density of states

Lamb-Mössbauer factor

$$f_{LM} = \exp\left[ E_R \int \frac{1}{E} \coth\left( \frac{\beta E}{2} \right) g(E) \, dE \right]$$

Vibrational entropy

$$S_V = 3k_B \int_0^\infty \left\{ \frac{\beta E}{2} \coth(\beta E) - \ln[\sinh(\beta E)] \right\} g(E) \, dE$$

Specific heat

$$C_V = k \int \frac{e^{\beta E}}{(e^{\beta E} - 1)^2} \left( e^{\beta E} \right)^2 g(E) \, dE$$

Helmholtz free energy

$$E_{\text{Helmholtz}} = k_B T \int \ln(1 - e^{-\beta E}) g(E) \, dE$$

Kinetic energy

$$E_{KE} = \frac{1}{E_R} \int (E - E_R)^2 S(E) \, dE$$

Isotope fractionation

$$\ln \beta = \frac{-\Delta m}{m} \frac{1}{8(k_B T)^2} \int E^2 g(E) \, dE$$
Information from NRIXS spectra:

- directly from the data, $S(E)$
  - temperature
    \[ T = -\frac{E}{k_B \ln \left[ \frac{S(-E)}{S(E)} \right]} \]
  - mean square displacement
    \[ \langle u^2 \rangle = -\frac{1}{k^2} \ln \left[ 1 - \int \{ S(E) - S(0) \} \, dE \right] \]
  - kinetic energy
    \[ E_{\text{kin}} = \frac{1}{4E_R} \int (E - E_R)^2 S(E) \, dE \]
  - average force constant
    \[ D = \frac{k^2}{2E_R^2} \int (E - E_R)^3 S(E) \, dE \]

- quasi-harmonic lattice model
  - partial phonon density of states
    \[ \mathcal{D}(E) \]
  - Debye sound velocity
    \[ v_D = \left( \frac{M}{2\rho \pi^2 h^3} \frac{E^2}{\mathcal{D}(E \to 0)} \right)^{1/3} \]
  - Grüneisen parameter
    \[ \gamma_D = \frac{1}{3} + \frac{\rho}{v_D} \left( \frac{\partial v_D}{\partial \rho} \right)_T \]
  - isotope fractionation
    \[ \ln \beta = -\frac{\Delta m}{M} \frac{1}{8(k_B T)^2} \int E^2 \mathcal{D}(E) \, dE \]

$\text{k} \sim \text{wave number of nuclear transition}$
$E_R \sim \text{recoil energy}$
$\rho \sim \text{mass density}$

$M \sim \text{mass of resonant isotope}$
$\Delta m \sim \text{isotope mass difference}$
$k_B \sim \text{Boltzmann's constant}$
$T \sim \text{temperature}$

Courtesy: W. Sturhahn
**Phonon density of states**

\[ g(k) dk = \frac{V}{(2\pi)^3} 4\pi k^2 \, dk. \]

Number of wave vectors in a spherical shell of radius \( k \) per unit volume of reciprocal space.

\[ g(\omega) = \frac{3V}{2\pi^2 c^3} \omega^2 \]

Phonon density of states has a quadratic dependence on frequency, and inversely proportional to the cube of sound velocity.
Let's assume that the acoustic modes have a linear relationship between frequency and wave vector:
\[ \omega = c k \]
where \( c \) is average sound velocity.

**Maximum frequency cut off is at Debye energy:**
e.g. for Cu, this frequency is \( 240 \text{ cm}^{-1} \) (~30 meV).

Considering \( 1 \text{ meV} = 11.605 \text{ K} = 8.065 \text{ cm}^{-1} \), this corresponds to 348 K, which is close to 344 K.

For Fe, the measured cut-off value is ~39.5 meV, which corresponds to 458 K, very close to reported 460 K.
Phonon density of states of iron under high pressure

Fe films deposited on W(110)
Transition from the bulk to a single iron monolayer

S. Stankov, R. Röhlsberger, T. Slezak, M. Sladecek, B. Sepiol, G. Vogl, A. I. Chumakov, R. Rüffer, N. Spiridis, J. Lazewski, K. Parlinski, and J. Korecki,
ESRF Highlights 2006

Skutterudites

1. Thermoelectric materials: always something new !..

EuFe₄Sb₁₂

The loosely bound guests affect the characteristics of the vibrations, and change the thermal conductivity.

Many elements in modern thermoelectric materials include Fe, rare-earth atoms like Eu, Sm, Dy, as well as Sb, and Te. These are all proper Mössbauer resonances we can exploit, and we do.

Vibrational dynamics of the host framework in Sn clathrates

Bogdan M. Leu, Mihai Sturza, Michael Y. Hu, David Gosztola, Volodymyr Baran, Thomas F. Fässler, and E. Ercan Alp

**FIG. 1.** (Color online) Structure of type-I clathrate $K_8Zn_4Sn_{42}$. Color scheme: gray = K, yellow = Zn/Sn, red = Sn. One small (pentagonal dodecahedron) and large (tetrakaidecahedron) host framework cage are highlighted in green and blue, respectively.

**FIG. 2.** (Color online) Structure of type-VIII clathrate $Ba_8Ga_4Sn_{30}$. Color scheme: gray = Ba, red = Sn/Ga. One host framework cage (pentagonal dodecahedron) is highlighted in blue.

type-I clathrate: pentagonal dodecahedra and tetrakaidecahedra alternating in a 1:3 ratio
type VIII : pentagonal dodecahedra; however, BGS adopts the type-I clathrate structure at high-temperature
mean square displacement via phonon dos

\[
\langle z^2 \rangle_v = \frac{1}{3k^2} \int \left[ 2\bar{n}(\bar{v}) + 1 \right] \frac{\bar{v}_R}{\bar{v}} D(\bar{v}) d\bar{v},
\]

3.8 \times 10^{-5} \text{ Å}^2/K for KZS and 3.5 \times 10^{-5} \text{ Å}^2/K for BGS.
The phonon dispersion and DOS of Sn have been calculated using the all-electron projector augmented wave force method. The phonon DOS between bct-Sn and bcc-Sn are not visible. The phonon DOS increases with increasing pressure multiphonon contributions decrease, for ambient conditions the NRIXS spectrum was calculated by collecting the delayed and IV, derived from the measured NRIXS spectra by the NRIXS signal. The phonon DOS was used in the calculation providing a better description at the high-temperature Debye temperature and energies of the spectra.
FIG. 3 (color online). (a) Theoretical phonon dispersion relation of bcc-Sn at 64 GPa. The inset shows the Brillouin zone of the bcc-Sn lattice. (b) Comparison between the theoretically calculated phonon DOS (lines) and the experimentally derived phonon DOS at 64 GPa (circles).
Vibrational spectroscopy of proteins, enzymes and biomimic model porphyrins and cubanes
Some unique advantages of NRIXS

1. Low frequency motions: $\sim$ total mass
2. No selection rule except motion of atoms along x-ray propagation
3. Peak intensity $\sim$ mode participation $\sim$ actual displacement
4. No matrix effects or limitations
5. Element and isotope selective
6. No unpredictable cancellations in scattering terms

$$\phi_\alpha = \frac{1}{3} \frac{V_R}{V_\alpha} e^2 \bar{n}_\alpha (\bar{n}_\alpha + 1) f$$

**Porphyrids:**
Tetraphenylporphyrin (TPP)
Octaethylporphyrin (OEP)

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>Ethyl</td>
</tr>
</tbody>
</table>
FeTPP(1MeIm)NO

Fe partial phonon dos (1/meV/at.vol)

Energy (meV)
The figure shows the vibrational excitation probabilities for a series of iron nitrosyl porphyrins, measured by NRVS. The excitation probabilities are displayed as a function of frequency, with the x-axis representing frequency in cm\(^{-1}\) and the y-axis representing excitation probability in 10\(^{-4}\) cm\(^{-1}\).

- **Fe(OEP)**: octaethylporphyrin
- **Fe(OEP)(Cl)**
- **Fe(OEP)(NO)**
- **Fe(TPP)(NO)**: Tetraphenylporphyrin
- **Fe(DPIXDME)(NO)**: Deuteroporphyrin IX dimethyl ester
- **Fe(PPIXDME)(NO)**: Protoporphyrin IX dimethyl ester
- **Fe(MPIXDME)(NO)**: Mesoporphyrin IX dimethyl ester

The figure illustrates the vibrational modes of these complexes, with peaks at different frequencies. The modes are labeled with letters a through g, corresponding to the specific complexes.

In particular, all five ferrous nitrosyl porphyrins (Figure 2) have an Fe mode in the 520 cm\(^{-1}\) region. Comparison among the nitrosyl complexes suggests a significant motion of the Fe NO stretch/bend mode in Fe(OEP)(NO), with Fe excitation probabilities for a series of iron nitrosyl porphyrins in solution have assigned Fe NO frequencies in the range 514 cm\(^{-1}\) to 560 cm\(^{-1}\), as well as 1349 cm\(^{-1}\) and 1370 cm\(^{-1}\). This suggests an FeNO photolysis. The difference between this and the Fe frequency shift expected for Fe oxidation state, peripheral ligand, and Fe enrichment NRVS and natural isotopic abundance, was also reported at 527 cm\(^{-1}\), which corresponds to the Fe NO oscillator.
Some unique advantages of NRIXS

1. Low frequency motions: ~ total mass
2. No selection rule except motion of atoms along x-ray propagation
3. Peak intensity ~ mode participation ~ actual displacement
4. No matrix effects or limitations
5. Element and isotope selective
6. No unpredictable cancellations in scattering terms

\[ \phi_\alpha = \frac{1}{3} \frac{\overline{V}_R}{\overline{V}_\alpha} e^2 j_{\alpha} (\overline{n}_\alpha + 1) f \]

~ 0.1 meV, all-vacuum high resolution monochromator
Protonation state of oxo-ligand in heme protein intermediates:

Synchrotron-Derived Vibrational Data Confirm Unprotonated Oxo Ligand in Myoglobin Compound II

Weiqiao Zeng, Alexander Barabanschikov, Yunbin Zhang, Jiyong Zhao, Wolfgang Sturhahn, E. Ercan Alp, and J. Timothy Sage

J. AM. CHEM. SOC. 2008, 130, 1816–1817
Figure 1. Vibrational dynamics of the heme Fe reveal an unprotonated oxo ligand in Mb(IV)=O, in contrast with the bound hydroxyl group in Mb(III)=OH. Protonation of the oxo ligand results in a downshift of the Fe—O stretching frequency from 805 cm\(^{-1}\) to 556 cm\(^{-1}\), and splits the Fe—O tilting vibrations, which are degenerate near 362 cm\(^{-1}\) in Mb(IV)=O, but are separated by 33 cm\(^{-1}\) in the asymmetrically protonated heme Mb(III)=OH complex. Error bars represent the normalized experimental signal,
The Mössbauer isotopes observed with synchrotron radiation (1985-2016)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Energy (eV)</th>
<th>Half-life (ns)</th>
<th>ΔE (neV)</th>
<th>Tabulated E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{181}$Ta</td>
<td>6215.5</td>
<td>9800.</td>
<td>0.067</td>
<td>6238</td>
</tr>
<tr>
<td>$^{169}$Tm</td>
<td>8401.3</td>
<td>4.</td>
<td>114.0</td>
<td>8409.9</td>
</tr>
<tr>
<td>$^{83}$Kr</td>
<td>9403.5</td>
<td>147.</td>
<td>3.1</td>
<td>9400</td>
</tr>
<tr>
<td>$^{187}$Os</td>
<td>9776.8</td>
<td>2.16</td>
<td>211.</td>
<td></td>
</tr>
<tr>
<td>$^{57}$Fe</td>
<td>14412.5</td>
<td>97.8</td>
<td>4.67</td>
<td>14413</td>
</tr>
<tr>
<td>$^{151}$Eu</td>
<td>21541.4</td>
<td>9.7</td>
<td>47.0</td>
<td>21532</td>
</tr>
<tr>
<td>$^{149}$Sm</td>
<td>22496.</td>
<td>7.1</td>
<td>64.1</td>
<td>22490</td>
</tr>
<tr>
<td>$^{119}$Sn</td>
<td>23879.4</td>
<td>17.8</td>
<td>25.7</td>
<td>23870</td>
</tr>
<tr>
<td>$^{161}$Dy</td>
<td>25651.4</td>
<td>28.2</td>
<td>16.2</td>
<td>25655</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>27770.</td>
<td>16.8</td>
<td>27.2</td>
<td>27800</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>29834.</td>
<td>4.25</td>
<td>107.0</td>
<td>29560</td>
</tr>
<tr>
<td>$^{125}$Te</td>
<td>35460</td>
<td>1.48</td>
<td>308.0</td>
<td>35491.9</td>
</tr>
<tr>
<td>$^{121}$Sb</td>
<td>37129.</td>
<td>4.53</td>
<td>100.0</td>
<td>37133.</td>
</tr>
<tr>
<td>$^{129}$Xe</td>
<td>39581.3</td>
<td>1.465</td>
<td>311.2</td>
<td>39578.</td>
</tr>
<tr>
<td>$^{61}$Ni</td>
<td>67419.</td>
<td>5.1</td>
<td>89.0</td>
<td>67400</td>
</tr>
<tr>
<td>$^{73}$Ge</td>
<td>68752.</td>
<td>1.86</td>
<td>245.</td>
<td>68752</td>
</tr>
<tr>
<td>$^{176}$Hf</td>
<td>88349.</td>
<td>1.43</td>
<td>319.4</td>
<td>83000</td>
</tr>
<tr>
<td>$^{99}$Ru</td>
<td>89571.</td>
<td>28.8</td>
<td>15.8</td>
<td>89651.8</td>
</tr>
<tr>
<td>$^{67}$Zn</td>
<td>93300.</td>
<td>9200.</td>
<td>0.049</td>
<td></td>
</tr>
</tbody>
</table>
Thank you ....