NRIXS studies of *Sn* halide perovskites

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In collaboration with,

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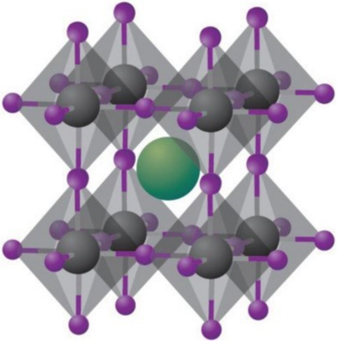
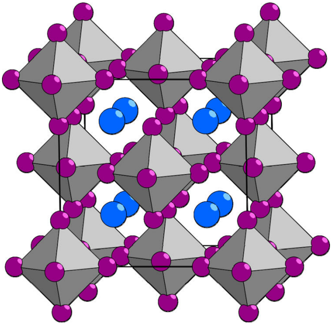
A class of interesting semiconductors

Lattice & lattice dynamics of halide perovskites
are interesting problems in CMP, and
important to understand the materials.

Structures



ABX_3



Cs_2SnX_6

(a) *Kalyanasundaram et al.* Material Matters, 2016, 11.1, 3

(b) *Kaltzoglou et al.* J. Phys. Chem. C 120, 11777 (2016)

A highly polarizable and deformable lattice

- Spin-orbit coupling
- Electron-phonon interaction & carrier mobility
- Exciton
- Polaron & mobility
- Dynamic disorder
- Phonon scattering
- Thermal conductivity
- Lattice anharmonicity

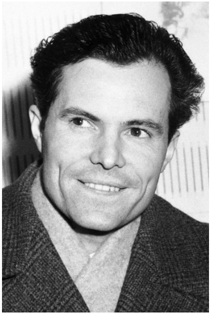
Halide perovskites: Phonons

- Raman, IR spectroscopy
- Neutron scattering
- HERIX (High energy-resolution inelastic x-ray scattering)
- NRIXS (Nuclear resonant inelastic X-ray scattering)

Rudolf Ludwig Mössbauer (1929 - 2011)

Nucleus: An embedded probe of materials

- 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***"



NRIXS cross-section

A measure of the particle autocorrelation function of the system.

$$
\begin{aligned}
\sigma(E,\boldsymbol{p}) &= \frac{\pi}{2}\,\sigma_0 \Gamma\, S(E,\boldsymbol{p}) \\
S(E,\boldsymbol{p}) &= \frac{1}{2\pi}\int dt\, d\boldsymbol{r}\; e^{i(\boldsymbol{p}\boldsymbol{r}-Et)}\; G_s(\boldsymbol{r},t) \\
G_s(\boldsymbol{r},t) &= \left\langle \sum_{\nu} \int d\boldsymbol{r}'\, \delta\Big(\boldsymbol{r}+\boldsymbol{r}_\nu(0)-\boldsymbol{r}'\Big)\, \delta\Big(\boldsymbol{r}'-\boldsymbol{r}_\nu(t)\Big) \right\rangle_T
\end{aligned}
$$

NRIXS Phonon DOS

$$\mathcal{D}(E,\hat{\boldsymbol{p}}) = \frac{1}{N}\sum_{s=1}^{3N}\left[\frac{1}{\tilde{N}}\sum_{\nu=1}^{\tilde{N}}(\hat{\boldsymbol{p}}\cdot\boldsymbol{\epsilon}_s^{\nu})^2\right]\delta\Big(E-E_s\Big)$$

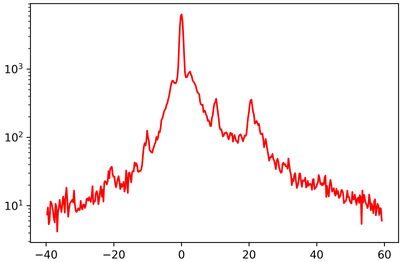
vs. the *textbook* phonon DOS,

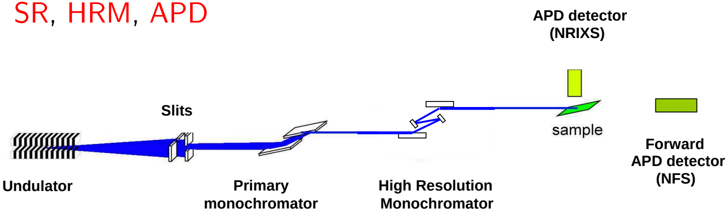
$$g(E) = \frac{1}{3N}\sum_{s=1}^{3N}\delta\Big(E-E_s\Big)$$

Thus ***partial*** *and* ***projected*** *quantities.*

NRIXS experiment

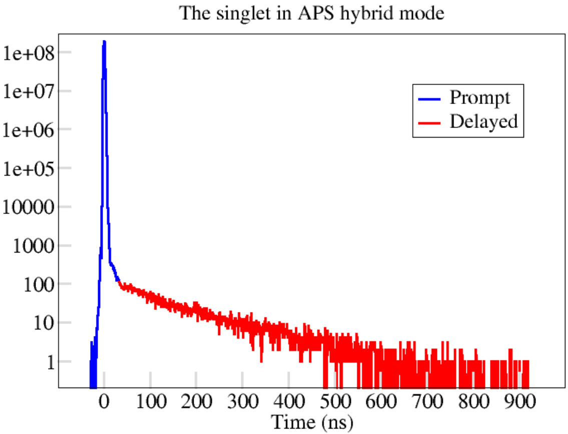
- photon in, photon out, yet measuring absorption cross section
- well defined energy and time characteristics
- low background, high SN ratio
- SR, HRM, APD





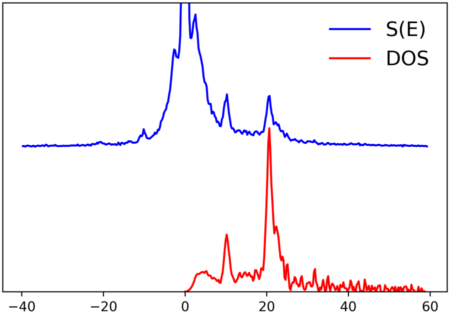
NRS (NFS & NRIXS): timing

Synchrotron radiation is a *pulsed* source



What do we learn from NRIXS

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



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
  - Internal energy
  - Vibrational entropy
  - Specific heat
  - Isotope fractionation factor
  - Grüneisen parameters

*Again, **partial** and **projected** quantities.*

Hu et al., PRB 87, 064301 (2013)

NRIXS in many disguises

What's in a name?

- NRIXS (Nuclear Resonant Inelastic X-ray Scattering)
- NIS (Nuclear Inelastic Scattering)
- NRVS (Nuclear Resonant Vibrational Spectroscopy)
- PANRA (Phonon-Assisted Nuclear Resonant Absorption)
- PAMT (Phonon-Assisted Mössbauer Transition)
- PAME (Phonon-Assisted Mössbauer Excitation)

NRS facilities at APS

- 3-ID *full time* - ^{57}Fe, ^{151}Eu, ^{161}Dy, ^{83}Kr
- 16-ID *part time* - ^{57}Fe
- 30-ID *part time* - ^{119}Sn
- Mössbauer lab

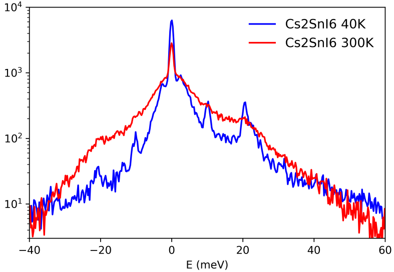
Sample environments

- LT, HT
- HP (DAC)
- Magnetic filed
- *in operando*

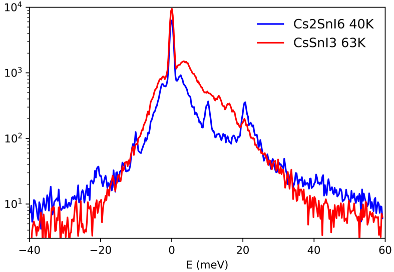
NRIXS: Sn halide perovskites

	T (K)	f-factor	K (N/m)	S (K_B)	C_v (K_B)
$CsSnI_3$(orthorhombic)					
	63	0.47(1)	95(04)	1.6	1.9
	200	0.14(1)	143(10)	4.5	2.8
$CsSnBr_3$(orthorhombic)					
	30	0.57(1)	94(20)	0.9	1.4
	100	0.26(2)	106(28)	3.0	2.6
	195	0.12(3)	138(36)	4.5	2.8
Cs_2SnI_6(cubic)					
	40	0.50(1)	210(09)	1.7	2.0
	200	0.26(2)	208(27)	3.5	2.7
	300	0.17(2)	195(13)	4.5	2.9
Cs_2SnBr_6(cubic)					
	300	0.08(7)	176(72)		
SnI_4(cubic)					
	65	0.39(1)	229(08)	1.4	1.4
	300	0.07(15)	245(35)	4.5	2.8

NRIXS: S(E)

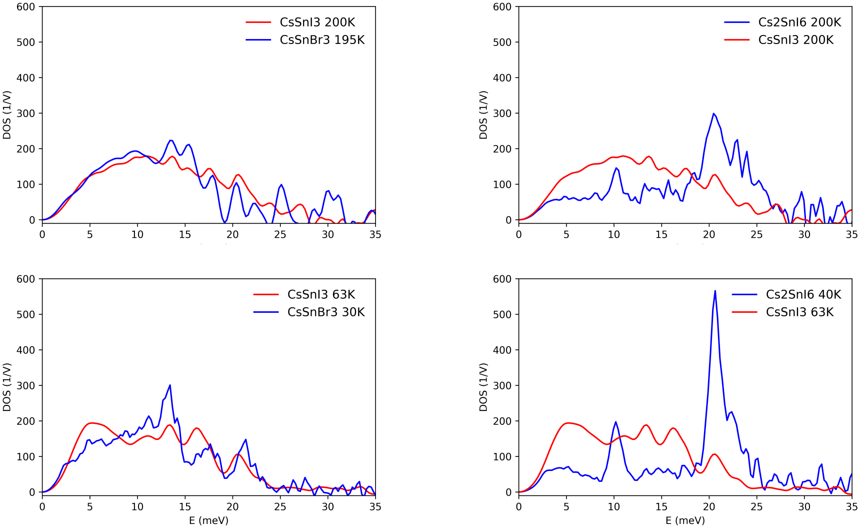


Cs2SnI6 40K
Cs2SnI6 300K
10^4
10^3
10^2
10^1
−40
−20
0
20
40
60
E (meV)

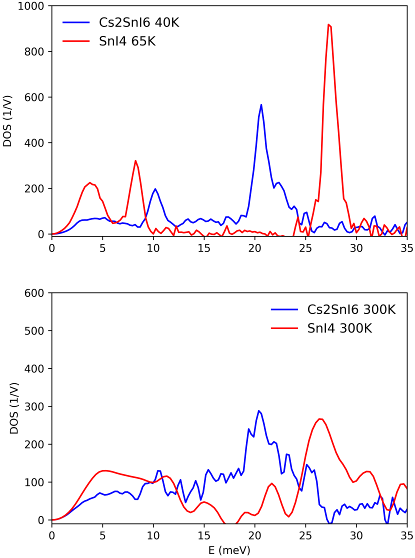


Cs2SnI6 40K
CsSnI3 63K
10^4
10^3
10^2
10^1
−40
−20
0
20
40
60
E (meV)

NRIXS


CsSnI3 200K
CsSnBr3 195K
Cs2SnI6 200K
CsSnI3 200K
CsSnI3 63K
CsSnBr3 30K
Cs2SnI6 40K
CsSnI3 63K
DOS (1/V)
E (meV)
0
100
200
300
400
500
600
5
10
15
20
25
30
35

NRIXS



Liu et al., J. Chem. Phys. 143, 164508 (2015)

Lattice potential

The Lattice Hamiltonian

$$H = \sum_{\mu} \frac{p_{\mu}^2}{2m_{\mu}} + \frac{1}{2} \sum_{\mu\mu'} V(\boldsymbol{r}_{\mu}, \boldsymbol{r}_{\mu'})$$

$$\frac{\partial^2 V}{\partial z^2} = K_{\hat{\boldsymbol{k}}} + A_{\hat{\boldsymbol{k}}} z + \frac{B_{\hat{\boldsymbol{k}}}}{2} z^2$$

Hu et al., PRB 87, 064301 (2013)

Moments of NRIXS spectrum

The central moments of S(E)

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

$$\begin{aligned} R_0 &= 1 \\ R_1 &= 0 \\ R_2 &= 4\, E_r\, T \\ R_3 &= \frac{\hbar^2 E_r}{m} \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle \end{aligned}$$

Hu et al., PRB 87, 064301 (2013)

Anharmonicity revealed by NRIXS

$$R_3 = \frac{\hbar^2 E_R}{\tilde{m}} \left[K_{\hat{\boldsymbol{k}}} + \frac{B_{\hat{\boldsymbol{k}}}}{2} \langle z^2 \rangle \right]$$

The so-called 'force constant'

$$R_3 \Big/ \left(\frac{\hbar^2 E_R}{\tilde{m}} \right)$$

Hu et al., PRB 87, 064301 (2013)

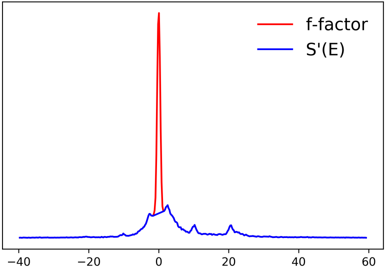
Lamb-Mössbauer factor & mean square displacement

They are related,

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

The f-factor can be calculated from the spectrum,

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



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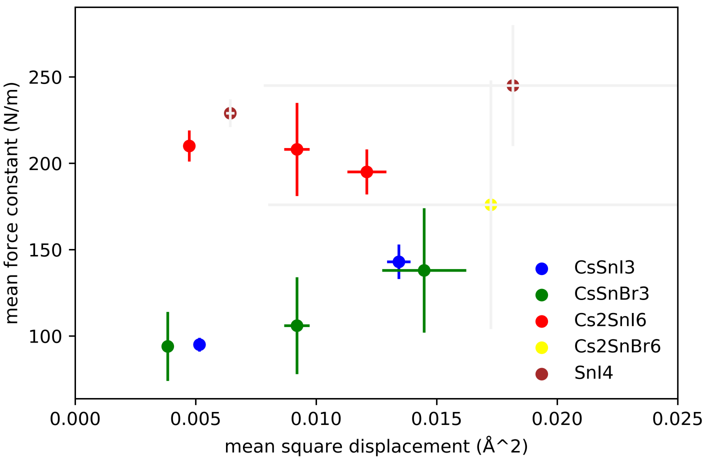
Sn halide perovskites: K vs. MSD



How to reveal anharmonicity by NRIXS

$$R_3 = \frac{\hbar^2 E_R}{\tilde{m}} \left[K_{\hat{\boldsymbol{k}}} + \frac{B_{\hat{\boldsymbol{k}}}}{2} \langle z^2 \rangle \right]$$

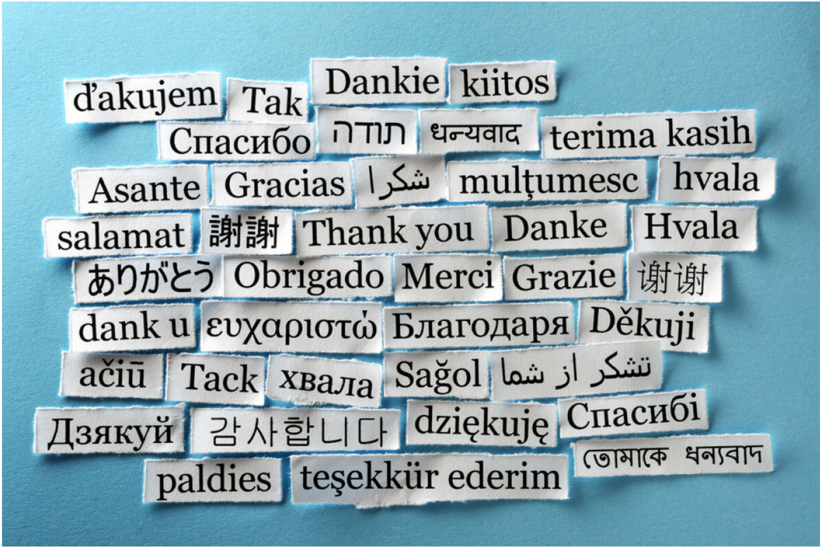
$$y = a + k\, x$$

Hu et al., PRB 87, 064301 (2013)

Summary

A simple message, or two.

- NRIXS provides $S(E)$ and DOS to check/verify material models
- NRIXS measurements can reveal lattice anharmonicity.
- It is applied to halide perovskites.
  Now we need to explain(calculate) the K *vs.* $\langle x^2 \rangle$ plot, and $S(E)$ and DOS as well.



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