Neutron Scattering Studies of Hybrid Perovskites for Photovoltaic Applications

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DuPont CR&D
40 Years of Neutron Scattering Symposium
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  – And I hope you continue to do so in retirement
My One DCS Experiment: Spin Waves in GeNi$_2$O$_4$

- **GeNi$_2$O$_4$**
  - Antiferromagnetic cubic spinel
  - Two Neel transitions: 12.1 K and 11.4 K
- **DCS $S(Q,\omega)$ beautifully shows**
  - 0.3 meV spin wave gap
  - Nicely dispersing spin waves

The Rise of Hybrid Perovskites for Photovoltaics

Unprecedented rate of improvement...

- **Ambipolar conductivity**: p- or n-type semiconductor
- **Carrier diffusion lengths**: > 1 µm
- **High defect tolerance**
- **Ideal bandgap** of 1.55 eV for MAPbI₃ (tunable)
- **High Voc** (>1 V)
- **Low Voc Deficit** (69% of bandgap)

Efficiencies as high as 20.1% reported.

The Perovskite Storm

650
Perovskites

ABX₃
• Hundreds of perovskites: Properties vary and include insulating, antiferromagnetic, piezoelectric, thermoelectric, semiconducting, conducting, and superconducting materials
• (MeNH₃)PbI₃ (MAPbI₃): “Standard” composition for perovskite-based PV, including record devices, with bandgap of 1.6 eV

Structure
• 3D network of corner sharing PbI₆³⁻ octahedra with charge-compensating cations in the gaps

Bandgap of MAPbI₃ is readily tuned by chemical substitution:
• Halide substitution, e.g. MAPb(BrₓI₁₋ₓ)₃: 1.6 to 2.2 eV
• Metal substitution, e.g., MASnI₃: 1.3 eV
  ➢ Sn oxidation to Sn(IV) leads to degradation
• Cation substitution: Cs, 1.7 eV; FA, 1.5 eV
  ➢ CsPbI₃ readily decomposes
  ➢ Cation must be small enough to fit within the gap (tolerance factor)
MAPbI$_3$ Brillouin Zone and Band Structure

- Cubic perovskite Pm-3m
- Direct bandgap semiconductor
  - High optical absorption coefficient
  - Thin films harvest light effectively
- High symmetry Brillouin zone boundary points
  - R, M, X
  - Optical bandgap is located at the R point
  - R point becomes the $\Gamma$ point in the tetragonal phase
Hybrid perovskite crystal structures are complex

• Presence of organic cations generates large amounts of disorder at high temperatures where PV devices operate

• Structural phase transitions involving rotations of PbI$_6$ octahedra, coupled to organic cation reorientations through hydrogen bonds, have significant impact on physical properties such as
  – Charge carrier mobility
  – Ionic conductivity
  – Exciton binding energies
  – Optical absorption
  – Thermal conductivity
  – Heat capacity
Structures: Neutron and X-Ray Diffraction

- Neutron diffraction data collected at POWGEN/SNS
- Fully and partially deuterated samples
  - Reduce incoherent scattering
  - Measure isotope effects on phase transitions
  - C, N and H/D atom positions

- X-ray diffraction data collected at Advanced Photon Source
  - DND-CAT
  - 0.4 Å wavelength (31 keV)
  - High resolution

<table>
<thead>
<tr>
<th>Element</th>
<th>Neutron Coherent Cross-section (barn)</th>
<th>X-Ray Cross-section (barn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.76</td>
<td>0.6</td>
</tr>
<tr>
<td>D</td>
<td>5.59</td>
<td>0.6</td>
</tr>
<tr>
<td>C</td>
<td>5.56</td>
<td>5</td>
</tr>
<tr>
<td>N</td>
<td>11.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Pb</td>
<td>11.12</td>
<td>9392</td>
</tr>
<tr>
<td>I</td>
<td>3.5</td>
<td>1622</td>
</tr>
</tbody>
</table>
Orthorhombic structure: $T = 10\,\text{K}$

- **Pnma structure refinement**
  - $T = 10\,\text{K}$ to minimize diffuse background contribution
  - Scattering to high Q – some diffuse background even at 10K
  - Full un-constrained refinement carried out.
  - Same structure as MAPbBr$_3$ at 10 K (Swainson et al.)

- Three strong hydrogen bonds between D and the I(2) sites of $1 \times 2.625\,\text{Å}/179.5^\circ$ and $2 \times 2.696\,\text{Å}/150.6^\circ$

- Deuterium ADPs as expected for such a structure

- Pb and I ADPs small with little directional motion by the iodines
Tetragonal structure: T = 190K

- I4/mcm symmetry
  - C and N $\frac{1}{4}$ occupancy, D $\frac{1}{8}$ occupancy; 8 positions
- D-I distances on order of 3.0 Å: weaker H-bonds
Cubic structure: $T = 350\text{K}$

- Pm-3m symmetry
- Despite extreme disorder
  - Only 5 atomic positions so no constraints needed
  - Very significant diffuse background which was partially modelled using a $\sin(q)/q$ curve to reduce number of background parameters
  - Structure agrees with literature structure
- MA is completely disordered as a nearly free rotor.
- Iodine ADPs similar size to the deuterium atoms
- Closest centroid D-I distance 3.09 Å
  - Weak hydrogen bonds

95% ellipsoids
MAPbI$_3$ Structures

- Only showing the PbI$_6$ octahedra
- Cubic-tetragonal transition involves rotations of octahedra around a single cubic axis
  - Order parameter is rotation angle
- Tetragonal-orthorhombic transition involves tilts around additional cubic axes
### Structural phase transitions in MAPbI$_3$

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Glazer Notation for Octahedra Tilts and Rotations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pm3m</td>
<td>$a^0a^0a^0$</td>
</tr>
<tr>
<td>I4/mcm</td>
<td>$a^0a^0c^-$</td>
</tr>
<tr>
<td>Pnma</td>
<td>$a^+b^-b^-$</td>
</tr>
</tbody>
</table>

Hybrid Perovskite Phase Transitions

- **Cubic-tetragonal phase transition of MAPbI$_3$**
  - Similar to cubic-tetragonal transition in SrTiO$_3$ at 110 K
  - Driven by condensation of single triply degenerate R-point phonon (out-of-phase rotation around cubic c axis)
  - Superlattice Bragg peaks appear with cubic indices $\frac{1}{2}$ (hkl) with h, k, l odd
  - I4/mcm

- **Low temperature transition involves cubic M and X-point phonons**
  - Rotations around different cubic axes
  - But coupled to order-disorder transition of MA cations through hydrogen bonds
• Cubic-tetragonal phase transition at $T = 330 \text{ K}$
  – First-order (phase coexistence)
• (200) cubic Bragg reflection
  – Splits into (220) and (004) tetragonal Bragg peaks
  – Tetragonal strain is a secondary order parameter
• R-point $\frac{1}{2}$ (311) Bragg reflection
  – Pseudo-cubic unit cell
  – Same as (211) in tetragonal cell
  – Shows the presence of out-of-phase PbI$_6$ rotations
  – I4/mcm space group
Two structural phase transitions
- High temperature transition nearly continuous, but XRD shows phase coexistence
- Lattice parameters show discontinuities at low temperature structural transition at 160 K
• X-ray and neutron diffraction both show phase transition is close to tricritical (intersection of first and second order transitions)
  – Tetragonal distortion from x-ray diffraction
  – Distortion mode analysis from neutron diffraction
  – Order parameter scales with \((T_c - T)^{0.25}\)
• Cubic 200 Bragg peak
  – Splits into (220) and (004) Bragg peaks in tetragonal phase
  – Phase coexistence
    • Narrower region than d6-MAPbI₃

• Tetragonal (211) superlattice Bragg peak
  – ½ (311) in cubic cell
  – Pnma phase appears via first-order transition at T = 160 K
• Tetragonal distortion vs T
• Small region of cub0c-tetragonal coexistence

• Tetragonal distortion vs T
  – \((T_c - T)^{2\beta}\)
  – \(\beta = 0.248\)
  – Tricritical
d6-MAPbI$_3$ Single Crystal Diffraction on TOPAZ at SNS

- d6-MAPbI$_3$ single crystal
  - 1-2 mm in size
- Tetragonal (211) Bragg reflection
  - Superlattice $\frac{1}{2}$ (311) in pseudocubic cell
  - Power law fit again consistent with near-tricritical behavior
MAPbI$_3$ phase transitions: MA disorder grows with temperature

- Pnma $T = 10$ K
- Pnma $T = 130$ K
- I4/mcm $T = 190$ K

**Orthorhombic**
- Pm-3m $T = 350$ K

**Tetragonal**
- I4/mcm $T = 300$ K

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Hydrogen bonds play a role in structural transitions

- Hydrogen bond strengths are directly correlated with structural phase transition at 160 K
  - Low temperature orthorhombic structure has strongest H-bonds
  - Order-disorder transition of MA cations

- H-bonds decrease in strength with increasing temperature
  - Thermal expansion
  - MA cation disorder
Neutron Spectroscopy of h6-MAPbI$_3$: dispersion

- CNCS spectrometer at SNS
  - $T = 1.7$ K
- MA vibrations have little dispersion
  - Molecular vibrations
  - Intermolecular coupling is weak
- Peak assignments (from DFT)
  - 10-25 meV peaks correspond to CH$_3$ torsions, and librations and translations of MA cations
  - Peak at 38 meV is intramolecular vibration, mostly NH$_3$ torsion
**MAPbI₃: Neutron Vibrational Spectra and DFT Calculations**

- VISON spectrometer at SNS
  - \( T = 10 \text{ K} \)
- Neutron vibrational spectrum
  - Similar to IR and Raman, but no selection rules
  - MA vibrations dominate due to large incoherent neutron scattering cross-section for H
- Density functional theory
  - Vibrational eigenvectors
    - Use as input to calculate neutron spectrum
    - Provides vibrational mode assignments
    - I. Milas (DuPont) and Y.Q. Cheng (ORNL)
- Measurements of vibrations and phonons are important for understanding
  - Electron-phonon coupling (charge transport)
  - Thermal conductivity (heat capacity)

**Comparison of neutron and DFT spectra provides a demanding test of accuracy of DFT calculation**
MAPbI$_3$ neutron vibrational spectra vs DFT

- Partially and fully deuterated samples
  - Establish vibrational mode assignments
    - “NH$_3$ torsion” at 37.7 meV shifts significantly upon deuteration
      - $\nu_H/\nu_D = 1.26$ (vs 1.41)
    - “CH$_3$ torsion” at 11.5 meV shifts to 9 meV upon deuteration
      - $\nu_H/\nu_D = 1.26$ (vs 1.41)
  - Test accuracy of vibrational eigenvectors from DFT calculations
QENS: Structural transitions affect dielectric properties

Mean square displacement (MSD) measured using HFBS at NIST Center for Neutron Research

- Calculated from elastic peak intensity vs T
- Measure of mobility of methylammonium (MA) cations

Dielectric constant tracks mobility of the MA cations at structural phase transitions

- **T < 160 K** – Low dielectric constant
  - MA cations are fully ordered, dipoles no longer reorient in response to electric field
  - Dynamics due to rotations around C-N bond
- **T > 160 K** – High dielectric constant
  - Nearly free rotation of MA cations above transition leads to large dielectric constant
  - Cubic-tetragonal transition at 330 K does not affect MA cation dynamics or dielectric properties

High dielectric constant in cubic and tetragonal phases reduces exciton binding energy → increases charge separation efficiency

Dielectric constant and low T phase transitions: other halides

\[ \text{CH}_3\text{NH}_3\text{PbBr}_3 \]

\[ \text{CH}_3\text{NH}_3\text{PbCl}_3 \]

\[ \varepsilon(1 \text{ kHz}) \]

**CH\(_3\)NH\(_3\)PbBr\(_3\)**

**CH\(_3\)NH\(_3\)PbCl\(_3\)**

- **MSD (A\(^2\))**
  - **warming**
  - **cooling**

**T (K)**

- **0**
- **50**
- **100**
- **150**
- **200**
- **250**
- **300**
- **350**

- **0.0**
- **0.5**
- **1.0**
- **1.5**
- **2.0**

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MAPbI$_3$: QENS and Partial Deuteration

- MSD is characteristic of H atoms of MA cations: rotations around the C-N bond at low T and rotations of the bond at high T.
- No significant isotope effect on phase transition or MSD values.
Structural transitions affect electronic properties

- Photoluminescence measured as a function of temperature
- PL is sensitive to electronic structure of PbI$_3$ sublattice
  - PbI$_6$ octahedra undergo additional tilts/distortions at the 160 K tetragonal $\rightarrow$ orthorhombic phase transition
  - Tilts change Pb-I-Pb bond angles, and this affects electronic structure
  - PL shifts to higher energy in orthorhombic phase

Sargent group, U. Toronto
MAPbI$_3$: high temperature transition affects ionic conductivity

- Electrical conductivity vs temperature
  - Cubic $\rightarrow$ tetragonal phase transition occurs at 327 K
  - Conductivity is sensitive to Pb-I-Pb bond angles and lengths

- Activation energy for conduction in cubic phase is 0.38 eV
  - Consistent with ionic conductivity in other halides
  - Detailed understanding is still lacking

Does high temperature phase transition affect electronic properties?

- PL shifts with temperature
  - Associated with change of electronic band structure
  - Band gap should shift due to lattice expansion
  - Separating thermal effect from structural effect is difficult

- Short-range cubic structure could be tetragonal?
  - Single crystal diffraction shows R-point Bragg reflections in cubic phase, but broadened
  - Electronic structure would not change significantly across phase transition
Some remaining questions

- **Lead-halogen phonons**
  - Nature of phase transitions: displacive vs order-disorder
    - How do energies of PbI$_6$ rotational modes change with temperature? Are the modes overdamped?
  - Anharmonicity and ultralow thermal conductivity
  - What is magnitude of electron-phonon coupling?
  - Is tricritical nature of cubic-tetragonal transition important for PV properties?

- **Electronic properties**
  - Why are these materials so efficient for PV?
    - High dielectric constants? Defect and exciton screening?
    - Is Pb necessary for high efficiency?
  - Reason(s) for high carrier mobilities?
  - Can these materials be doped with electrons or holes?
  - Understand the effects of phase transitions on electronic properties?
Conclusions

• Hybrid perovskites are complex
  – Static and dynamic disorder due to organic cations
  – Structural phase transitions
  – Hydrogen bonds

• Structural complexity impacts properties important for photovoltaic applications
  – Dielectric constants
  – Optical properties
  – Thermal conductivity
  – Heat capacity
  – Thermal stability

• Neutron (and x-ray) scattering studies can provide a detailed microscopic understanding of the structures and dynamics of hybrid perovskites and other advanced materials
Thanks! Questions?