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The Power of Density Functional Theory for Materials Physics and Chemistry

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Keith Refson

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About Me

- PhD – Edinburgh Physics
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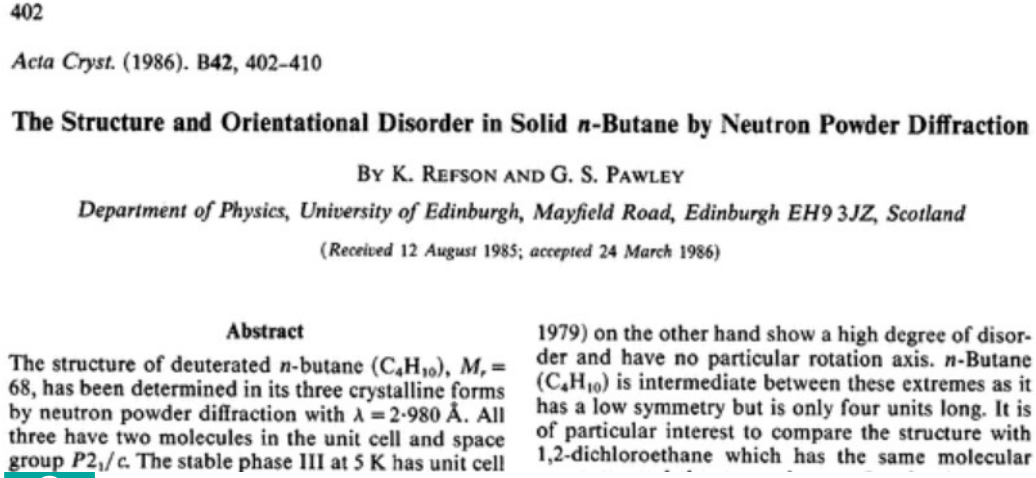

402

Acta Cryst. (1986). B**42**, 402–410

The Structure and Orientational Disorder in Solid *n*-Butane by Neutron Powder Diffraction

By K. Refson and G. S. Pawley

Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, Scotland

(*Received* 12 *August* 1985; *accepted* 24 *March* 1986)

Abstract

The structure of deuterated *n*-butane (C_4H_{10}), M_r = 68, has been determined in its three crystalline forms by neutron powder diffraction with $\lambda = 2{\cdot}980$ Å. All three have two molecules in the unit cell and space group $P2_1/c$. The stable phase III at 5 K has unit cell

1979) on the other hand show a high degree of disorder and have no particular rotation axis. *n*-Butane (C_4H_{10}) is intermediate between these extremes as it has a low symmetry but is only four units long. It is of particular interest to compare the structure with 1,2-dichloroethane which has the same molecular

The CASTEP Project

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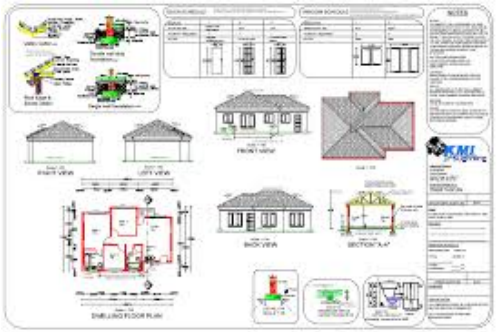
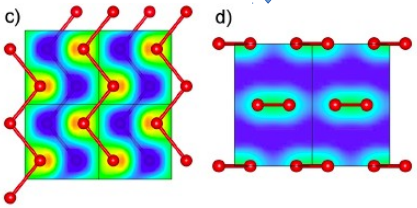


CASTEP

$$\left\{\frac{1}{2}\nabla^2+V_{\text{ext}}(\vec{r})+V_H(\vec{r})+V_{\text{xc}}([n(\vec{r})])\right\}\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r})$$



Simulation scales

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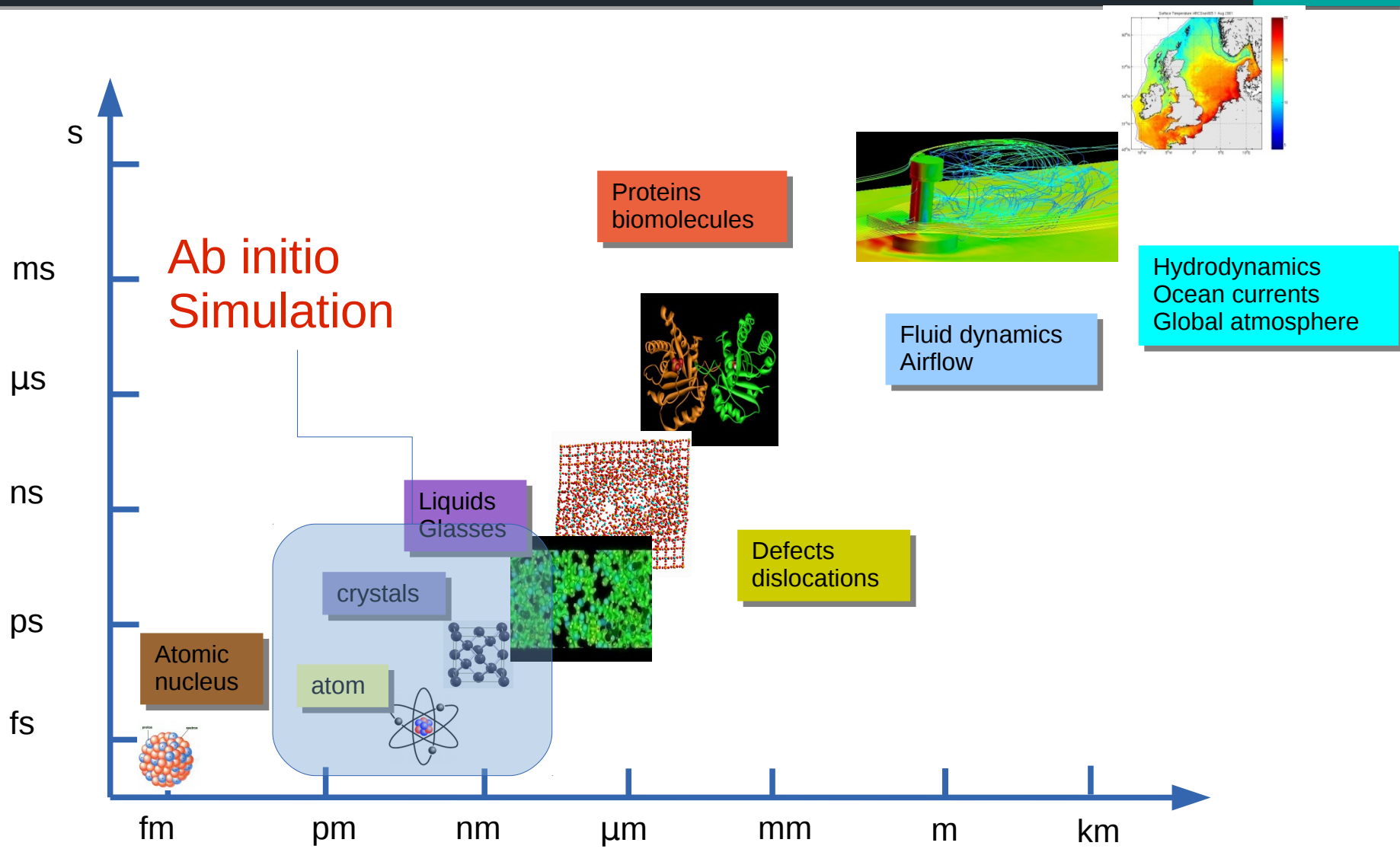

Quantum Mechanics and Density Functional Theory

The quantum Toolbox

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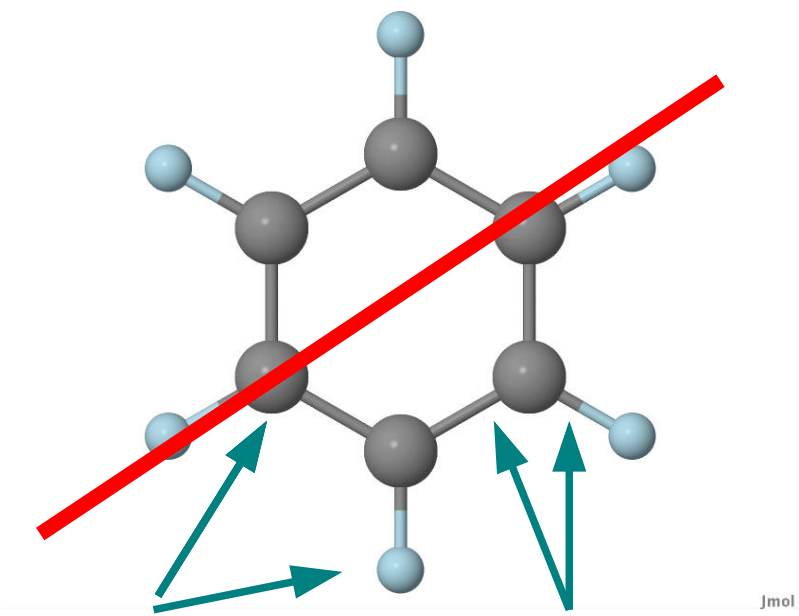
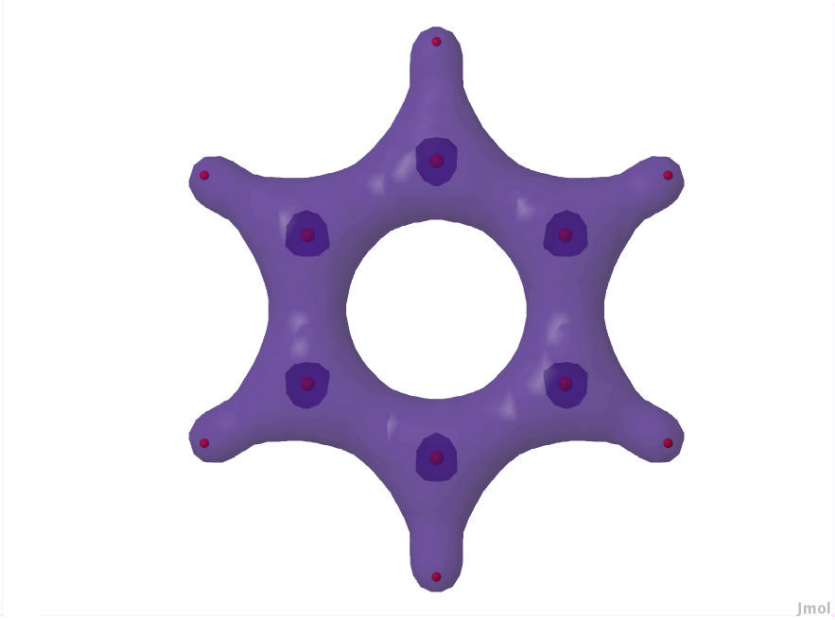


Atoms Bonds



Nuclei Electrons

F = m a

$$\frac{-\hbar^2}{2m_e}\Psi + \hat{V}\,\Psi = E\,\Psi$$

The Theory of Everything

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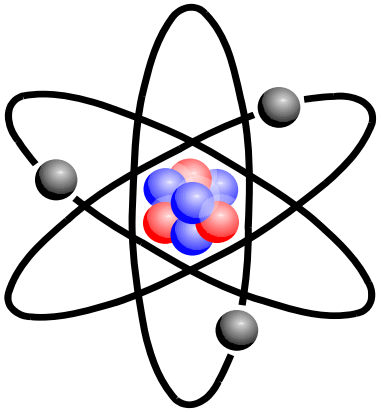
"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble."

P.A.M. Dirac, Proceedings of the Royal Society **A123**, 714 (1929)

Why?

Each electron interacts with the nucleus
Every electron also interacts with every other electron.

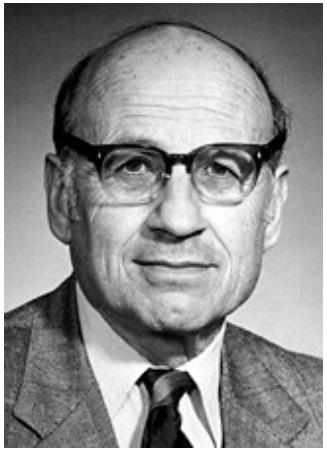


In Lithium (Z=3) there are 3 e-e interactions to consider.
In Boron (Z=5) there are 10 e-e interactions to consider.
In Iron (Z=26) there are 325 e-e interactions to consider.
In Uranium (Z=92) there are 4186 e-e interactions to consider.

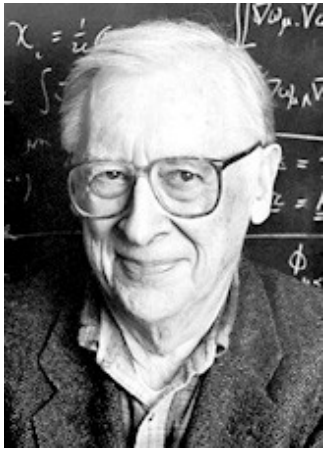
.. and that's just isolated atoms. We need to model crystals and molecules containing hundreds of atoms.

QM of multi-electron atoms still too complex to solve on Powerful supercomputers in 2016.

Approximate quantum mechanics



Walter Kohn 1923-2016



John Pople 1925-2004

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

Key developments dating back to 1960s and 70s were approximate quantum theories which were nevertheless “good enough”.

Density Functional Theory- Local Density Approximation

Hartree-Fock approximation, MP2, CI, CCSD(S,T)

Density Functional Theory

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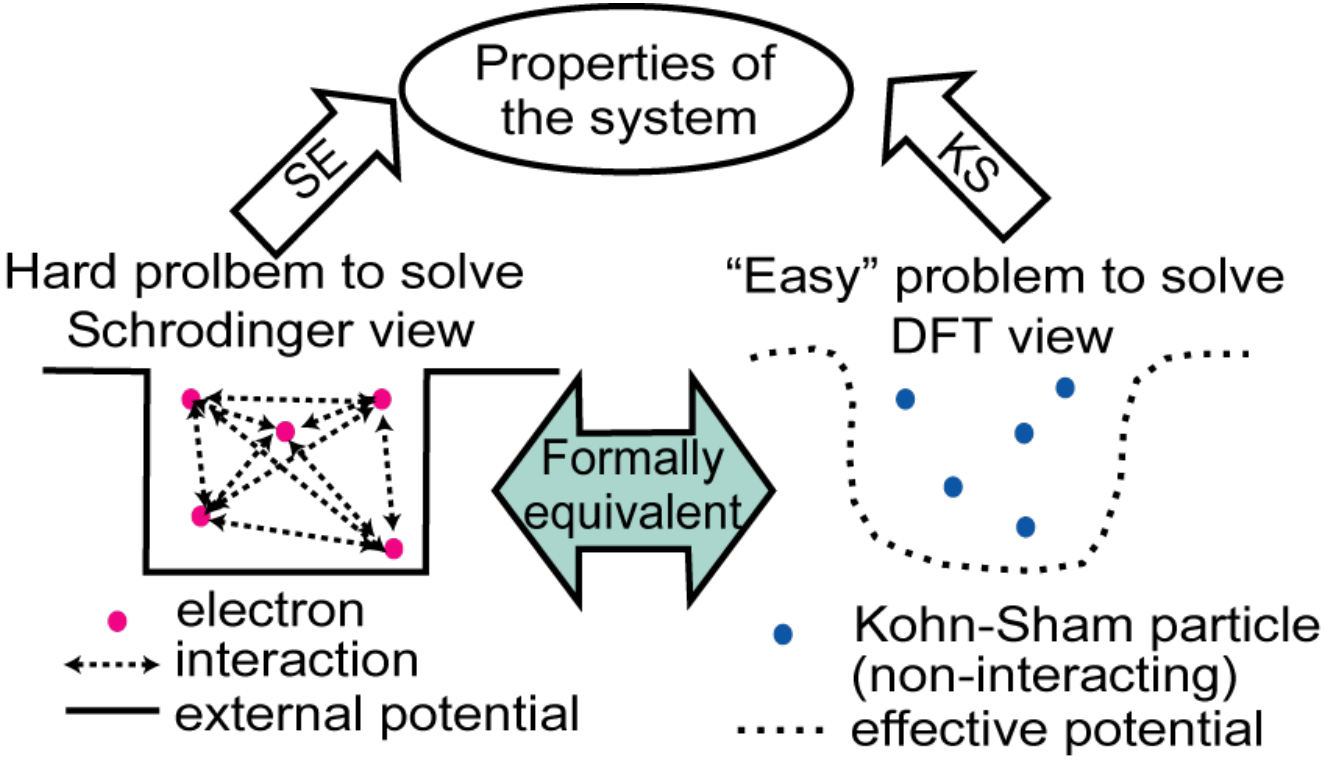

Approximate e-e interaction with

- local density approximation (LDA)
- generalized gradient approximation (GGA)
- Hybrids, DMFT, GW, …

Modified from Mattsson et al., (2005) Modeling. Simul. Mater. Sci. Eng. 13, R1.

Kohn-Sham equations

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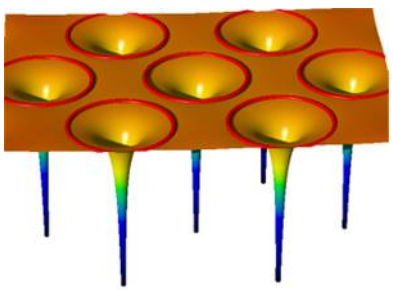
$$\left\{\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + V_{\text{xc}}([n(\vec{r})])\right\}\phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$



$$n(\vec{r}) = \sum_i^{occ} |\phi_i^2(\vec{r})|$$

LDA and GGAs

LDA

$$V_{xc}[n] \approx V_{xc}(n(\vec{r}))$$

$$V_{xc} \equiv \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$$

Parameterized from uniform electron gas

- *Cohesive energies ~ 1eV too large*
- *lattice parameters and bond lengths -1-2%*
- *Band gaps too small*
- *Hund's rule for open shells not always obeyed*
- *Van der Waals forces not included*

GGAs

$$V_{xc}[n] \approx V_{xc}(n(\vec{r}), \nabla n(\vec{r}))$$

e.g. PBE, PW91, BLYP, ...

Parameterized from non-uniform electron gas and atoms

- *Cohesive energies ~ 100 meV*
- *lattice parameters and bond lengths -1-2%*
- *Band gaps too small*
- *Hund's rule for open shells not always obeyed*
- *Van der Waals forces not included*

Plane-waves and pseudopotentials

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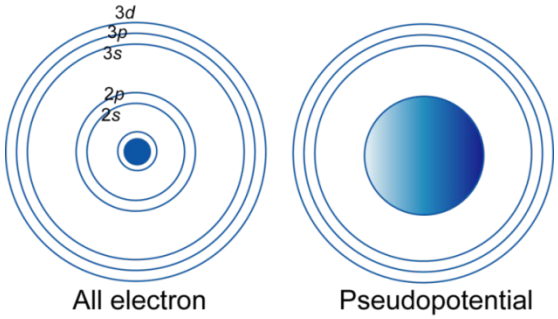
Plane-wave basis set

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}},$$

$$u_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{G}\mathbf{r}}$$

- Well-adapted for crystalline and solid/liquid modelling
- Systematic control of basis set convergence

Pseudopotential for ionic interactions



- "All electron" method but frozen core.
- Retain chemically relevant valence electrons
- Good scaling/large systems

Ionic bonding in NaCl

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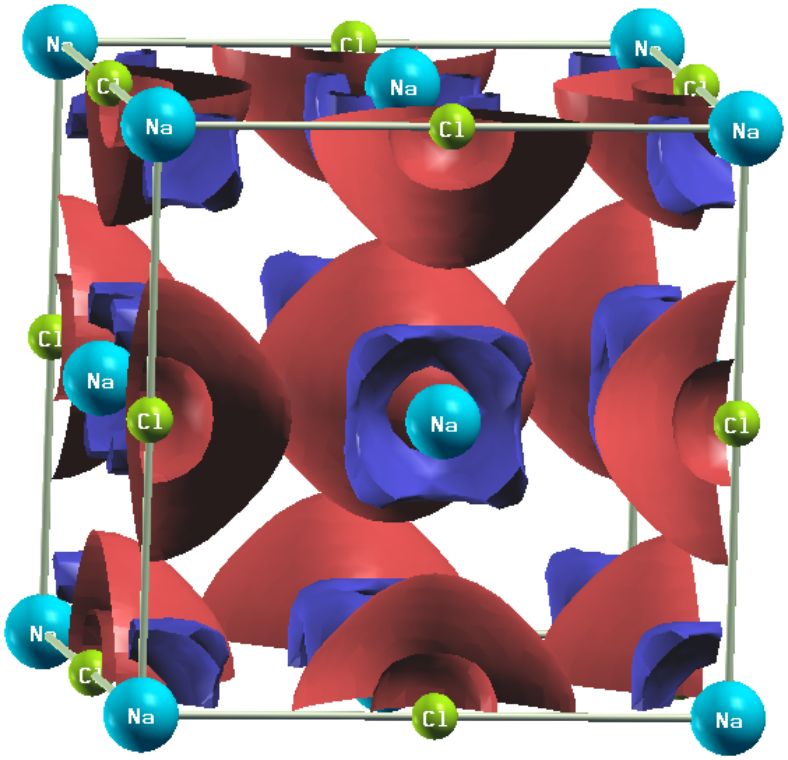
Charge transfer from Na to Cl

Unlike Si, no build up of charge between atoms



Covalent bonding in silicon

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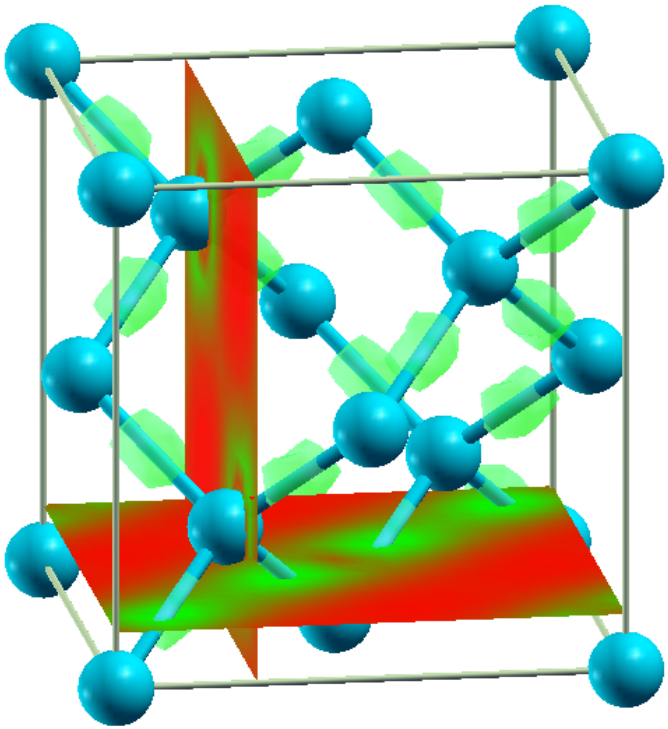
Covalent bonding arises from build up of -ve charge between +ve nuclei.

Chemical bond is emergent property of electron-ion system

Not merely qualitative description – can compute bond and cohesive energy.
(E_{coh}=5.45 eV; expt 4.62 eV)
Lattice Parameter a_0=0.549nm (0.5431nm)



Metallic bonding in aluminium

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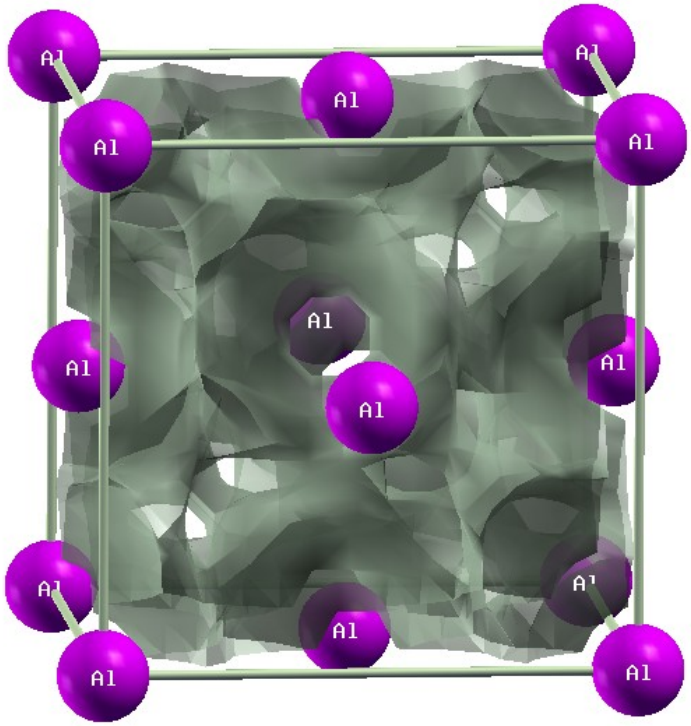
Valence electrons are spread out – metallic state.

Calculation shows no band gap; correctly predicts Al is metallic.



DFT Simulation Codes

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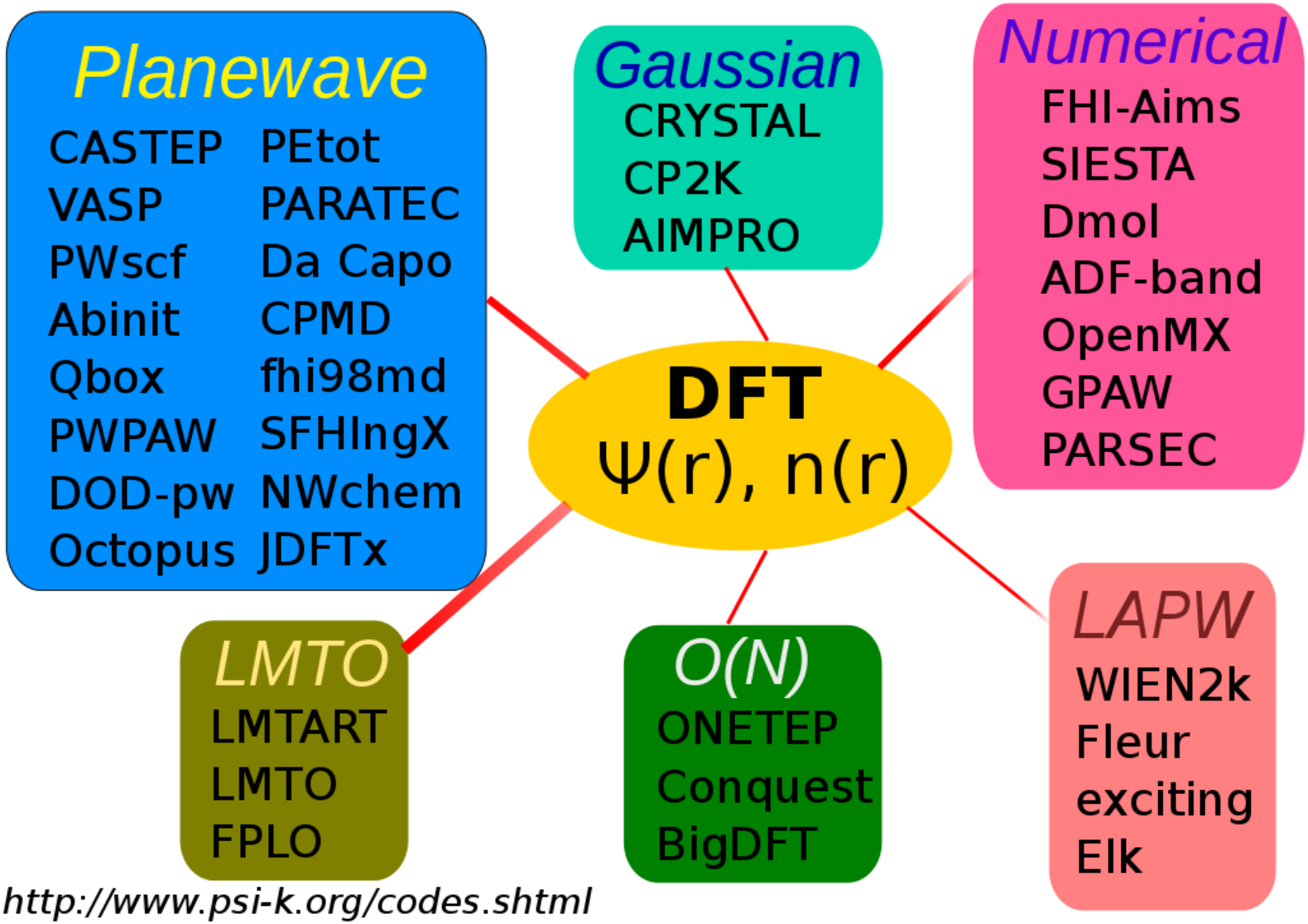

http://www.psi-k.org/codes.shtml

Popularity of DFT

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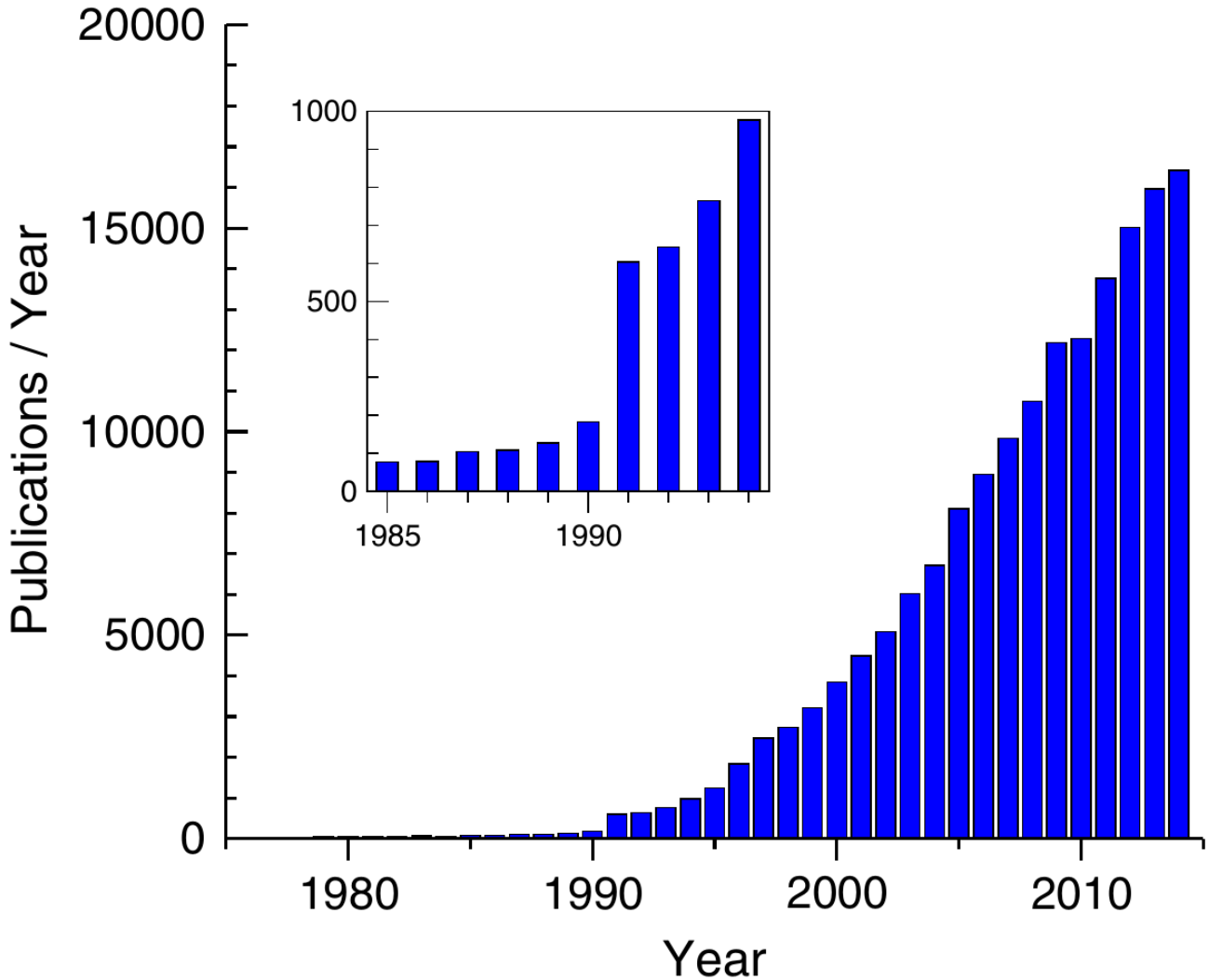

Electronic Structure

Densities of States

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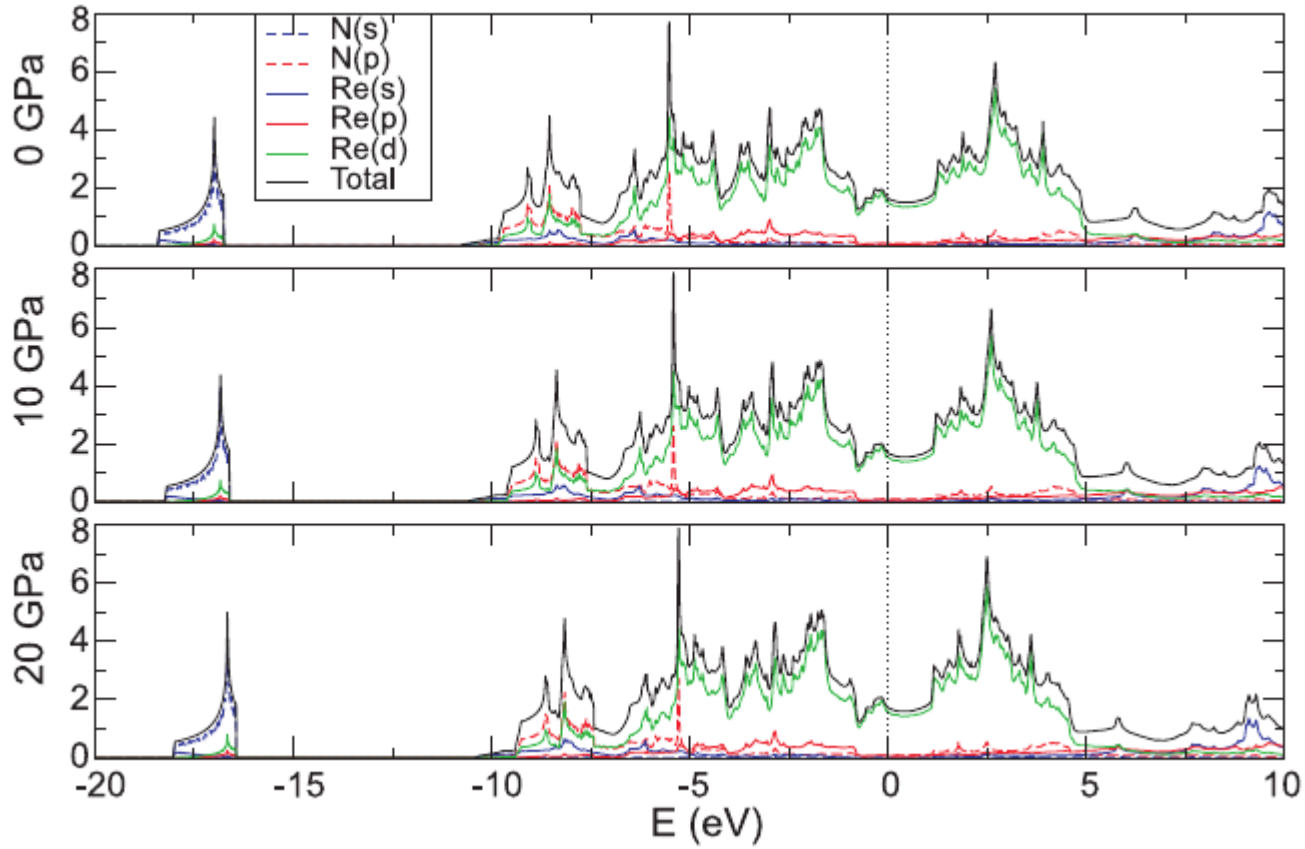

Charged Defects in ZnO

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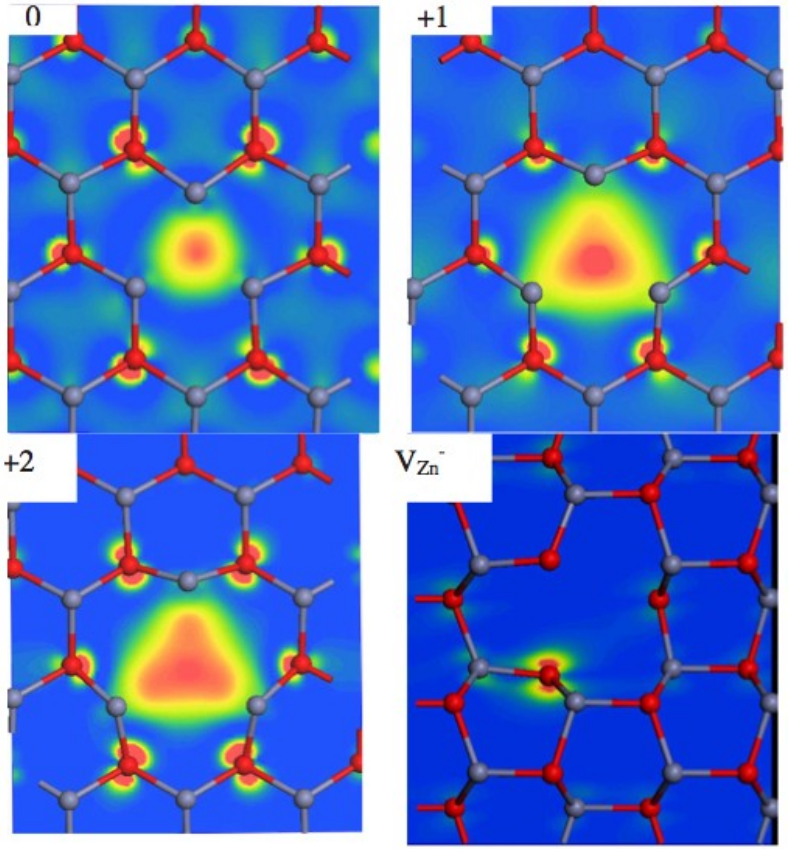

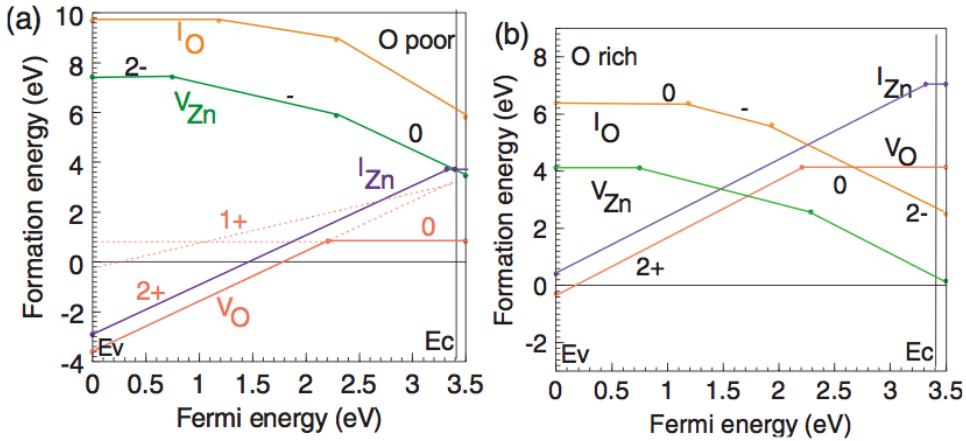

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Clark, Zunger, et al., PRB 81, 115311 (2010)

Charge ordering (with DFT+U)

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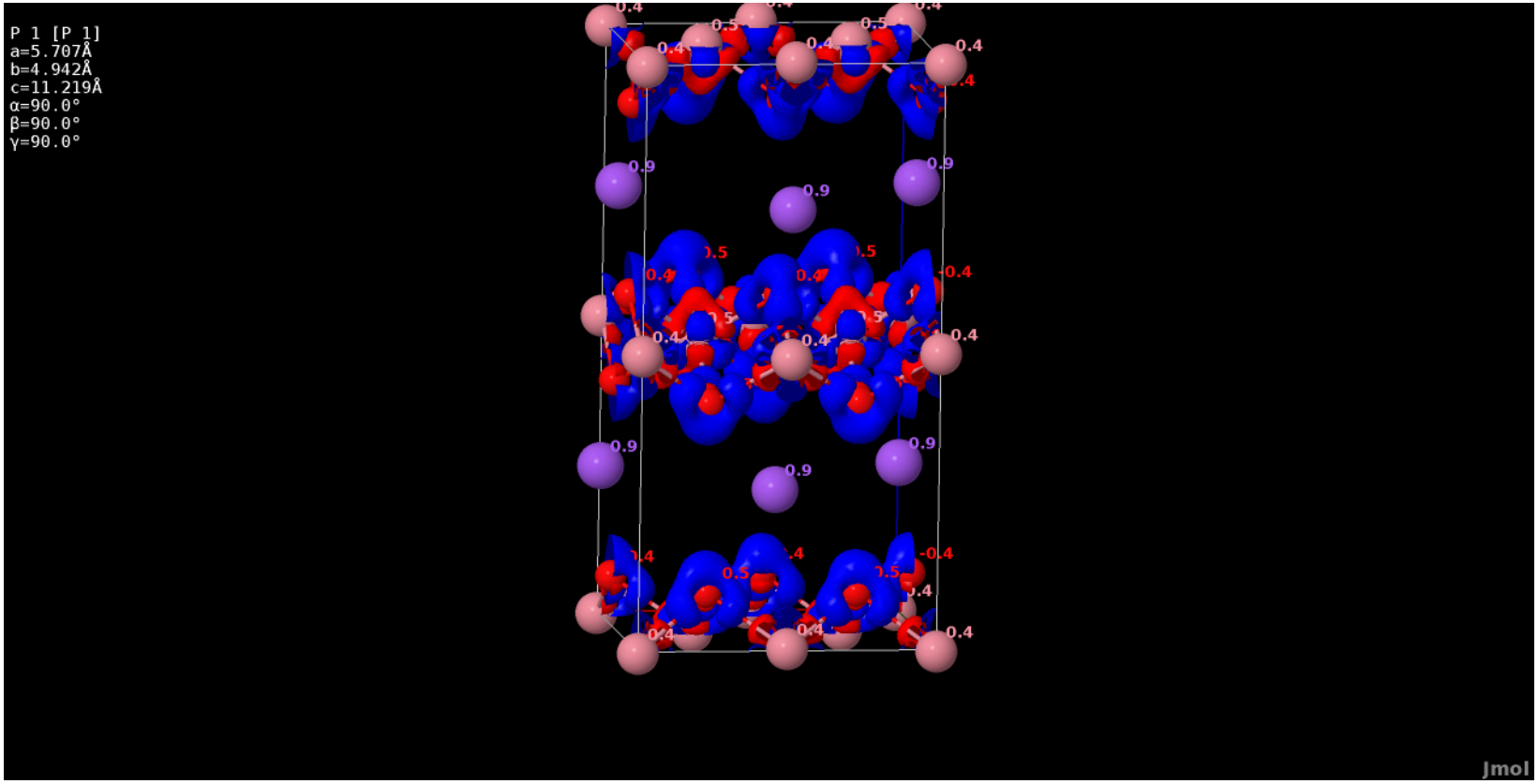

Crystal Structure

From electronic to crystal structure

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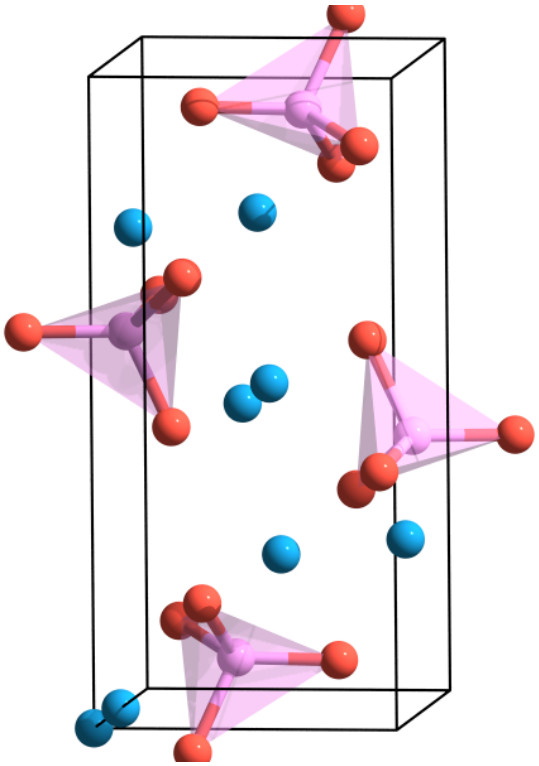
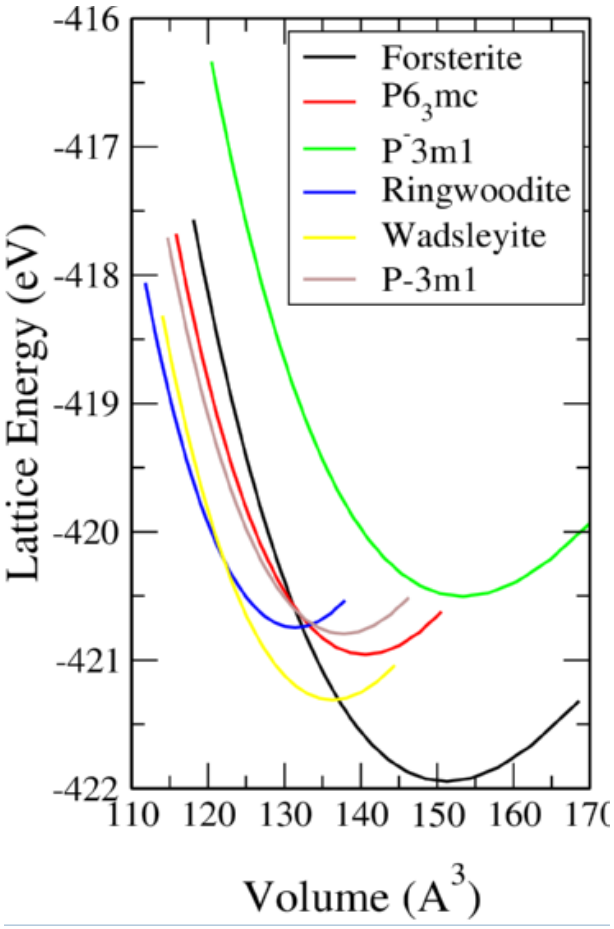
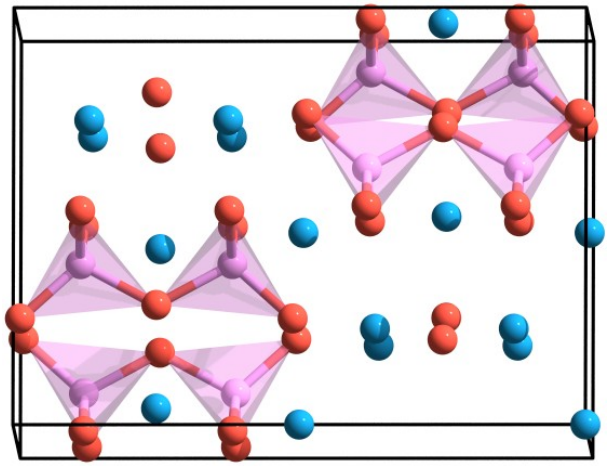
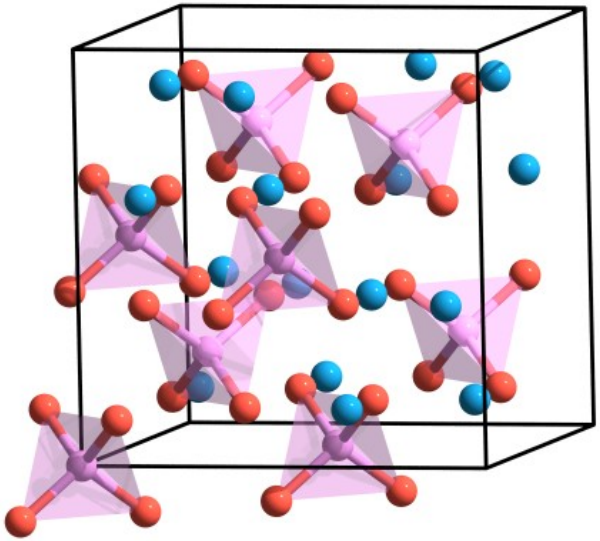
Polymorphs of Mg_2SiO_4









AIRSS: Prediction of Crystal Structures

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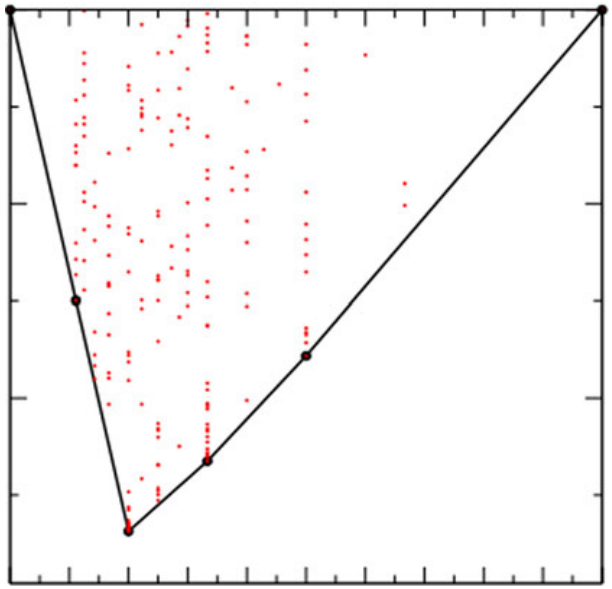
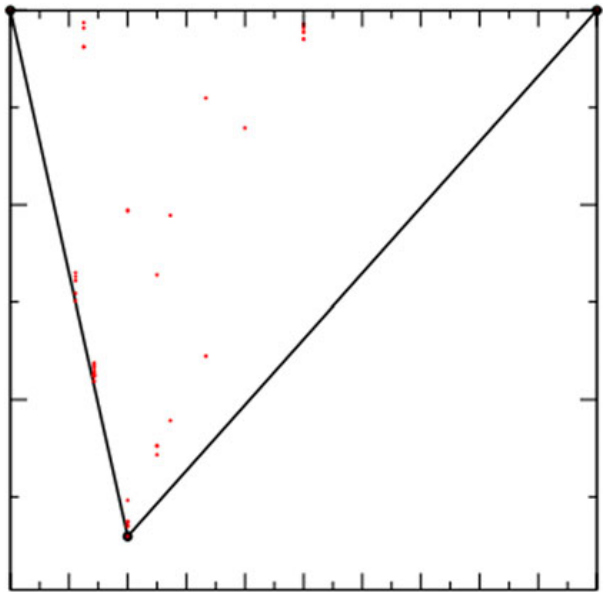
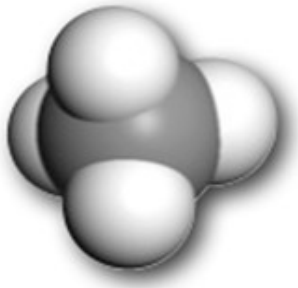
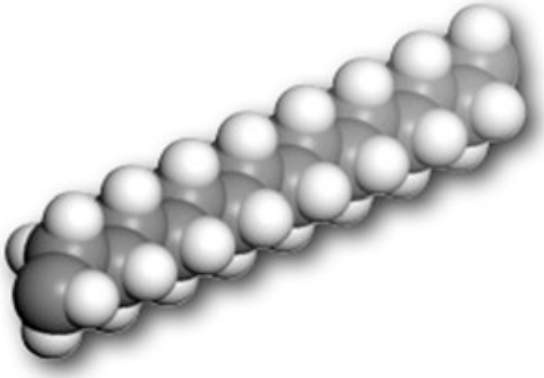


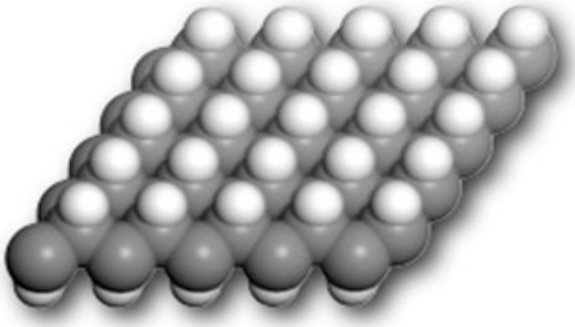




methane



polyethane



graphane

Predicting Structure

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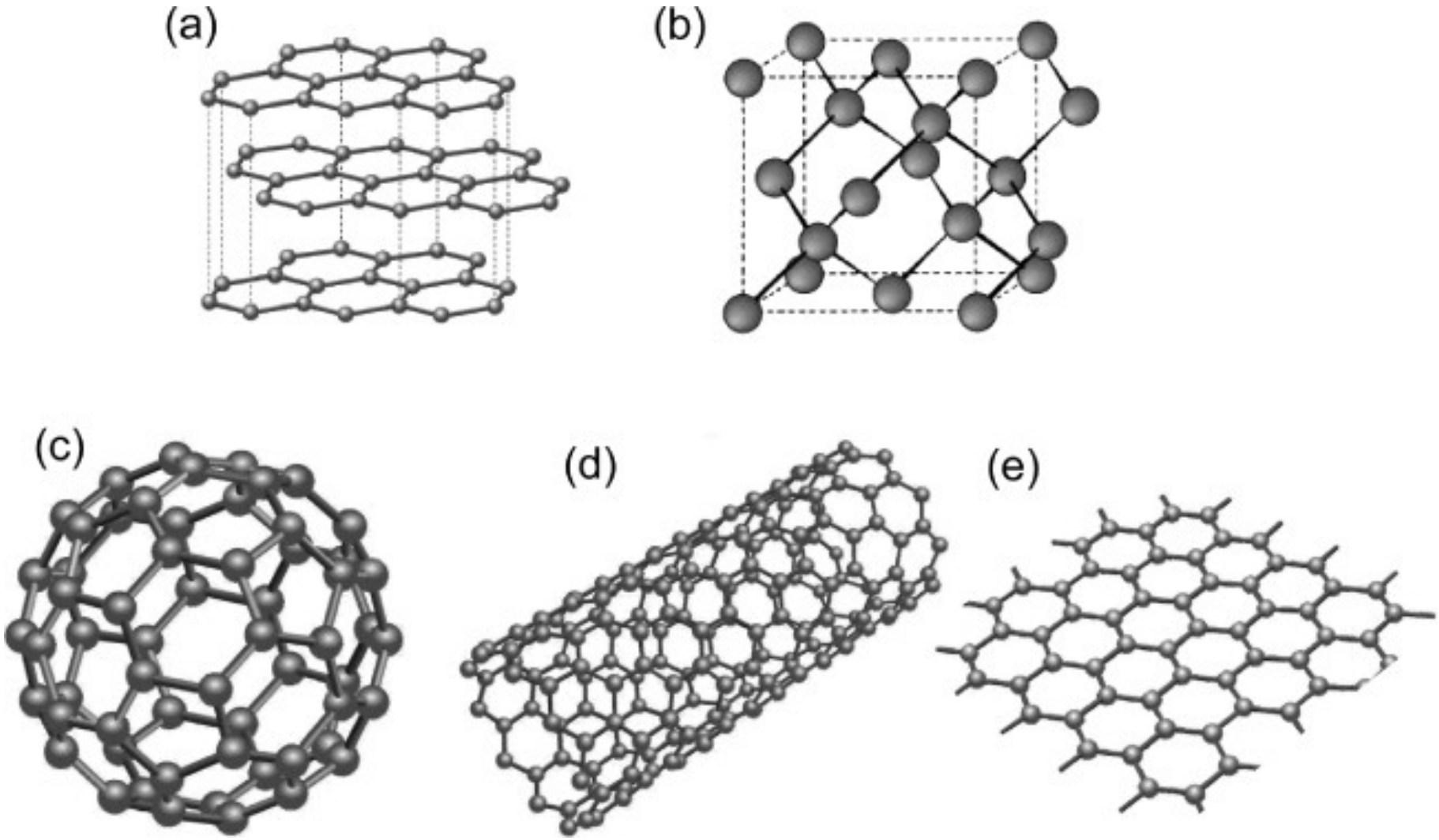

Vibrations, Phonons and Spectroscopy

Vibrational Spectroscopy

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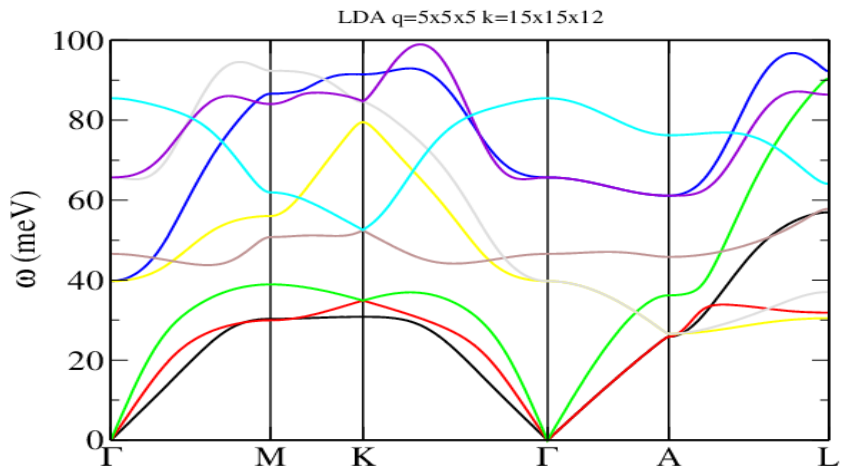
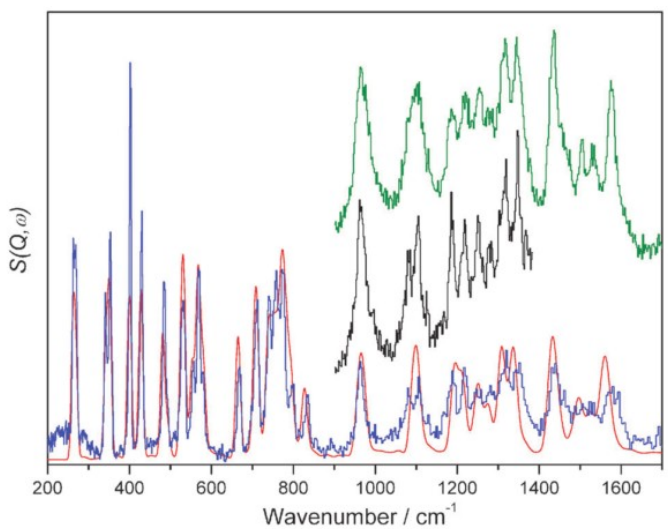
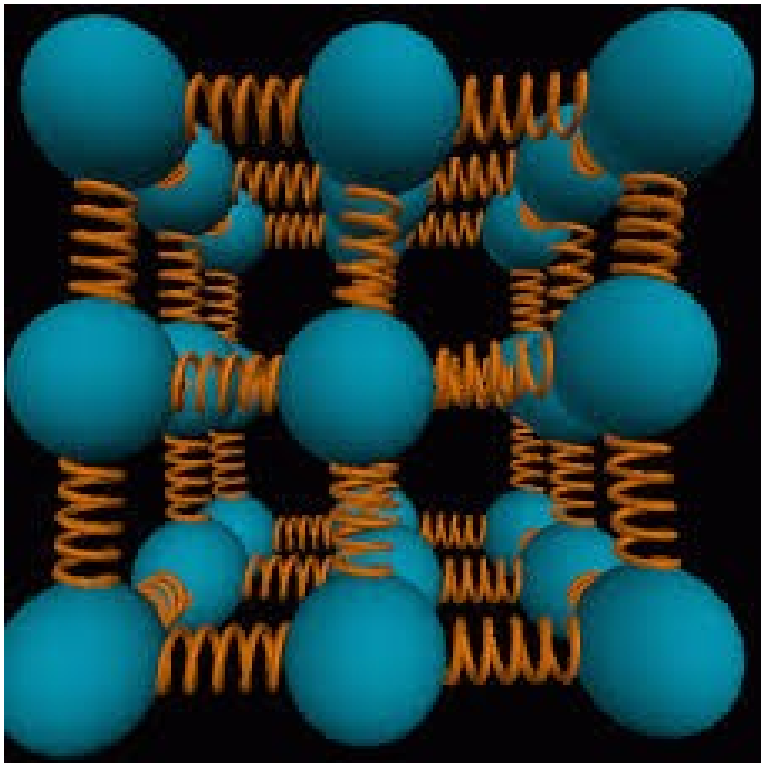


$$\Phi^{\kappa\alpha}_{\kappa'\alpha'}(\mathbf{0},\boldsymbol{R}) = \frac{\partial^2 E}{\partial r_{\kappa\alpha}\,\partial r_{\kappa'\alpha'}}$$





Modelling the spectrum

Orientationally averaged infrared absorptivity

$$I_m = \left| \sum_{\kappa,b} \frac{1}{\sqrt{(M_\kappa)}} Z^*_{\kappa,a,b} u_{m,\kappa,b} \right|^2$$

Raman cross section

$$I^m_{\text{raman}} \propto \left| \boldsymbol{e_i} \cdot \boldsymbol{A^m} \cdot \boldsymbol{e_s} \right|^2 \frac{1}{\omega_m} \left(\frac{1}{\exp(\hbar \omega_m / k_B T) - 1} + 1 \right)$$

$$A^m_{\alpha,\beta} = \sum_{\kappa,\gamma} \frac{\partial^3 E}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta \partial u_{\kappa,\gamma}} u_{m,\kappa,\gamma} = \sum_{\kappa,\gamma} \frac{\partial \epsilon_{\alpha\beta}}{\partial u_{\kappa,\gamma}} u_{m,\kappa,\gamma}$$

Inelastic neutron cross section

$$S^n(\omega_m) = \int d\boldsymbol{Q} \sum_\kappa \sigma_\kappa \left\langle \frac{(Q \cdot u_{m,\kappa})^{2n}}{n!} \exp\left(-(Q \cdot u_{m,\kappa})^2\right) \right\rangle$$

Spectral response to light depends on response of electrons; for neutrons only nuclei.

Rattler mode in thermoelectric $Na_{0.8}CoO_2$

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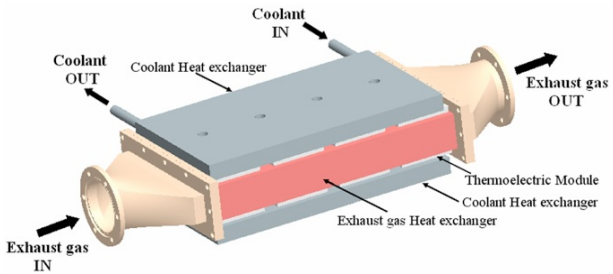
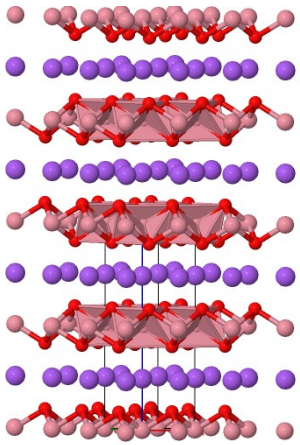
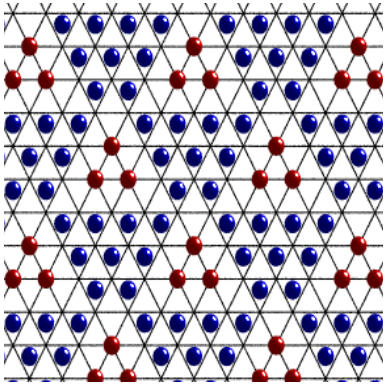


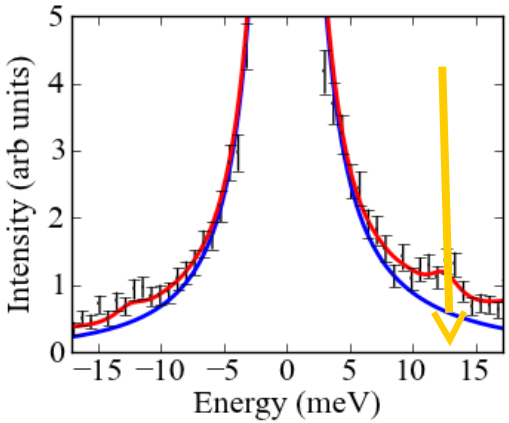




"Square Phase" Na ordering at 150K

Thermoelectric
"figure of merit"

$$zT = \frac{S^2 T \sigma}{\kappa}$$



Inelastic X-Ray spectrum measured at ESRF

Roger, M., *et al.*, *Patterning of sodium ions and control of electrons in sodium cobaltate.* Nature **445**, 631 (2007)

Ab initio Lattice Dynamics

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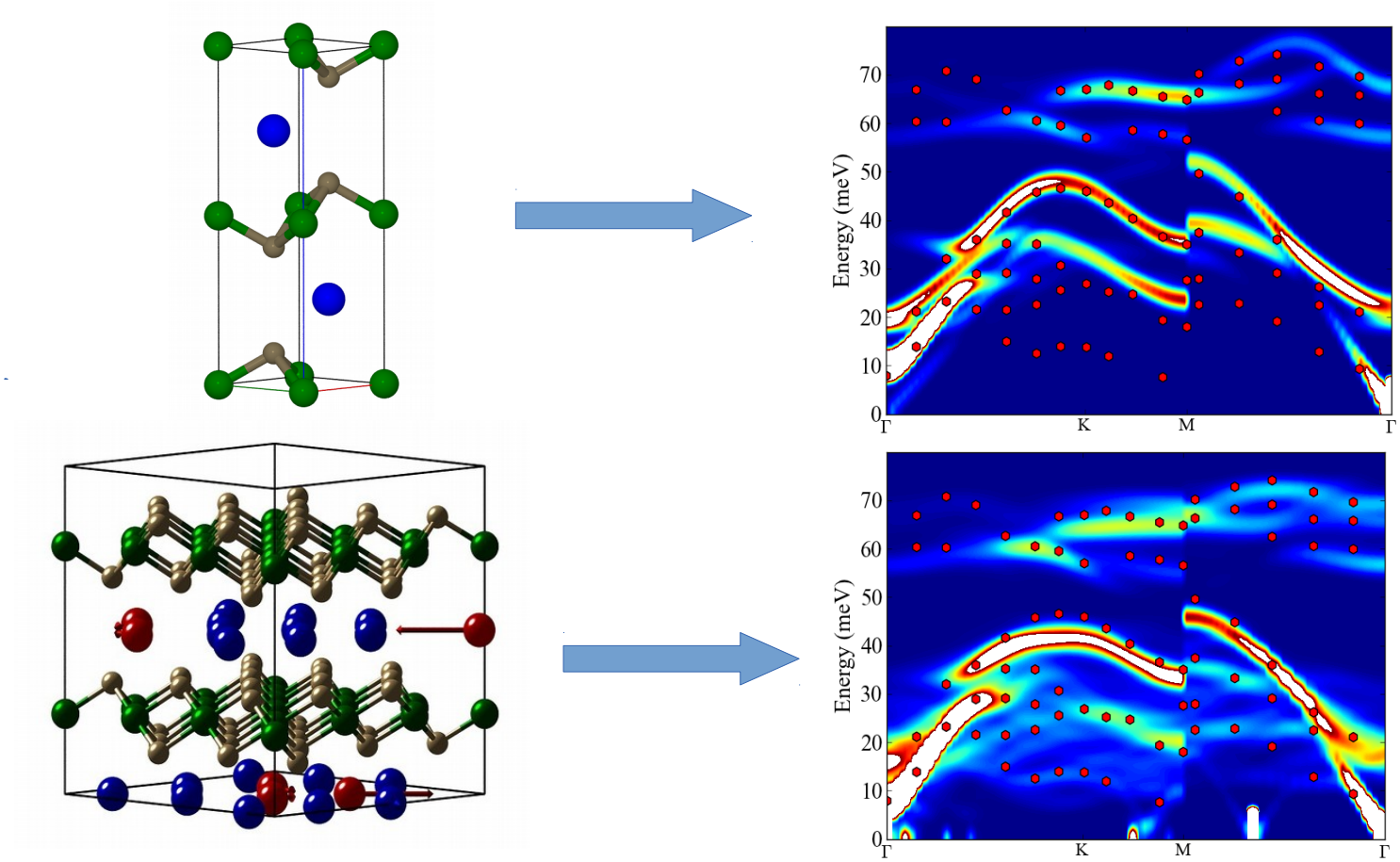

D. Voneshen et al.,*Suppression of thermal conductivity by rattling modes in thermoelectric sodium cobaltate*. Nature Materials **12**, 1028 (2013)

Vibrational spectroscopy of C_{60}

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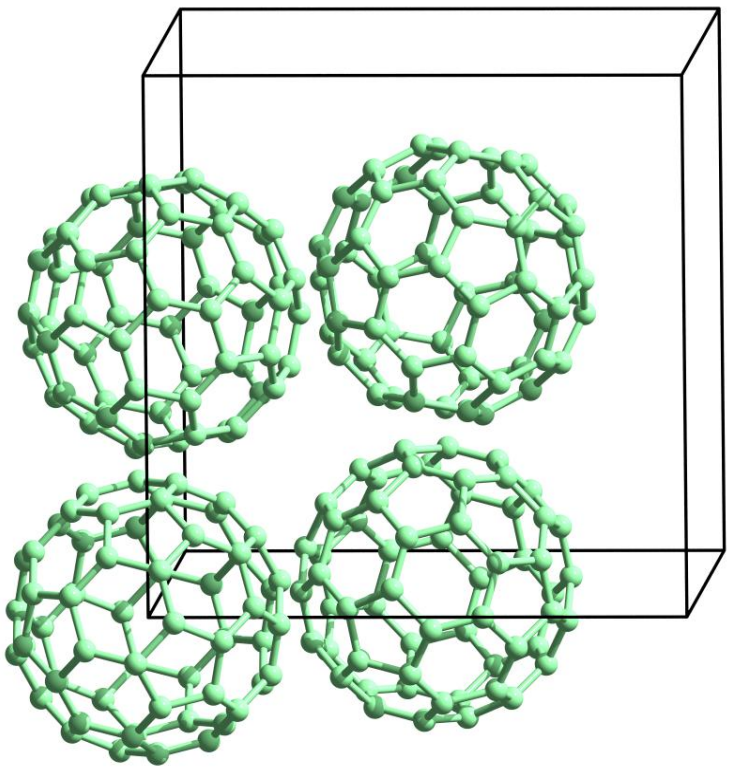

- Above 260K takes Fm3m structure with dynamical orientational disorder
- m3m point group lower than I_h molecular symmetry
- Selection rules very different from gas-phase.
- Intramolecular modes and factor group splitting seen.
- Try ordered Fm3 model for crystal spectral calculation.

Parker et al, PCCP **13**, 7780 (2011)

GGA Raman spectrum of C_{60}

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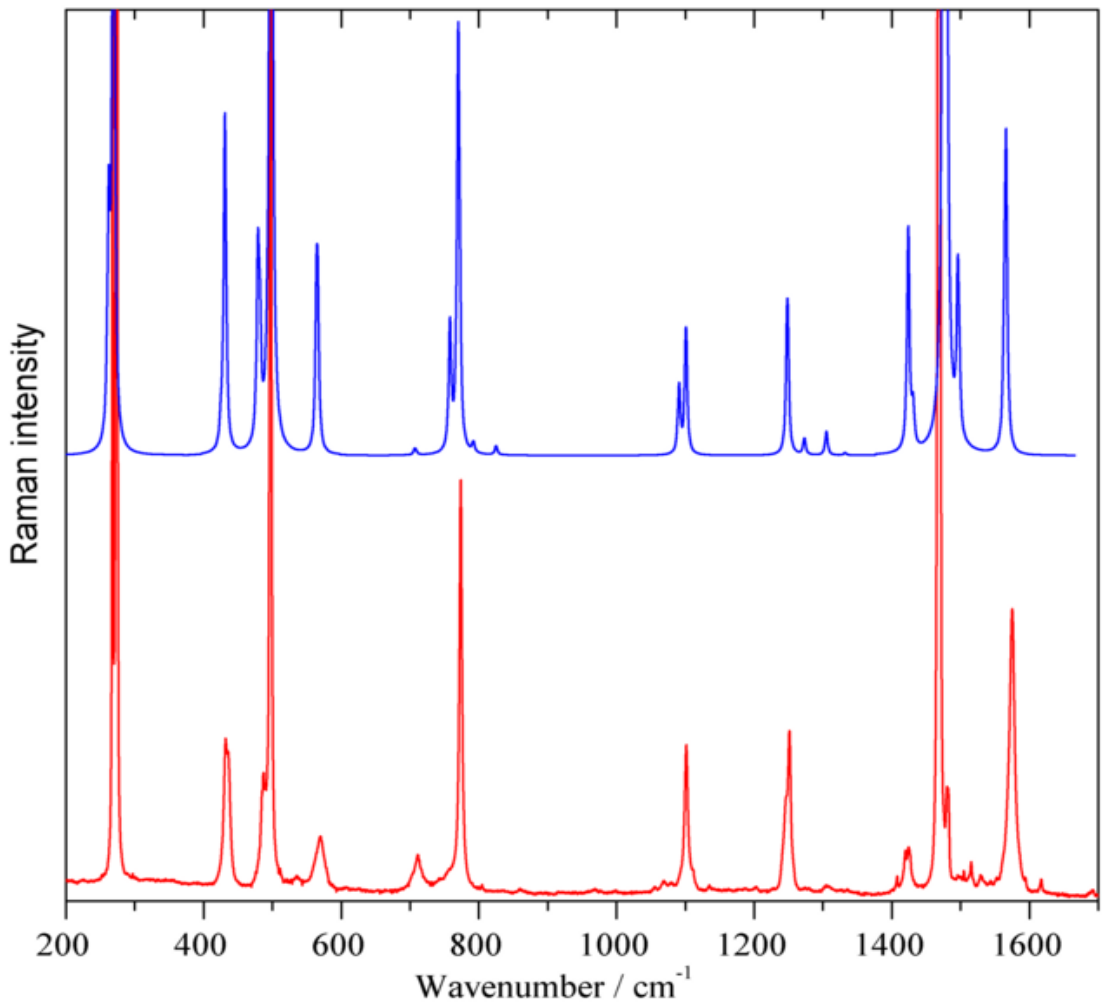

C_{60} INS -Tosca

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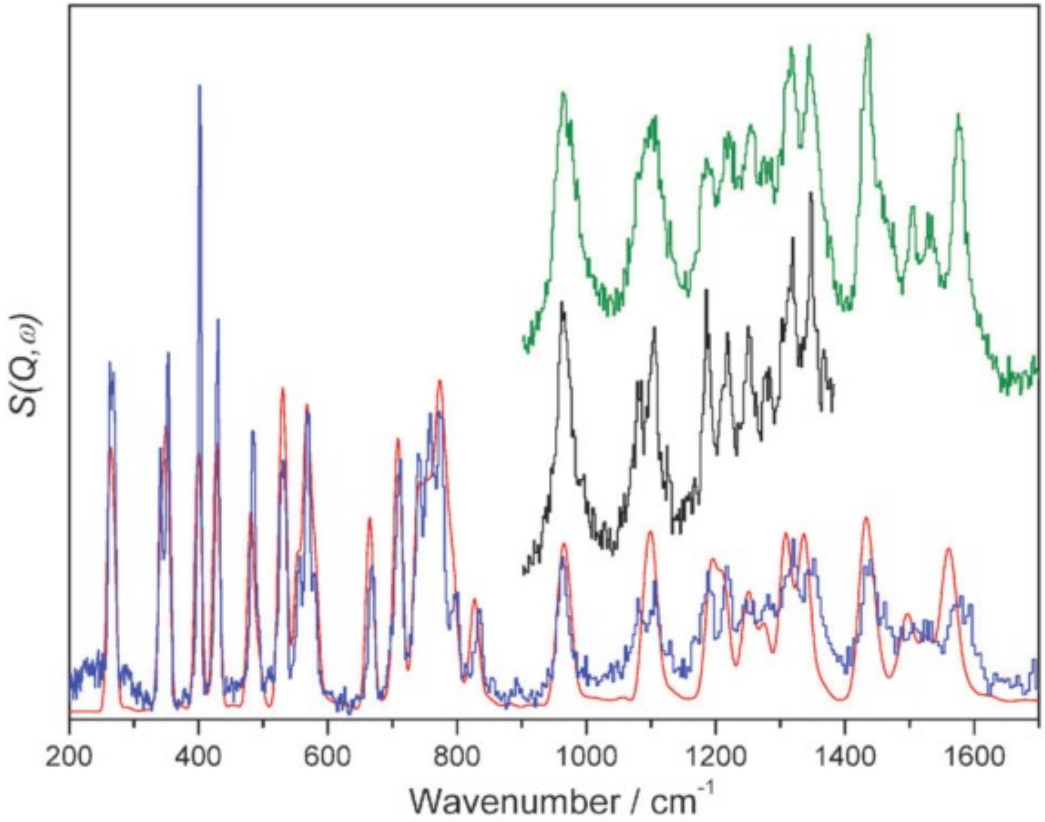

GGA infrared spectrum of C_{60}

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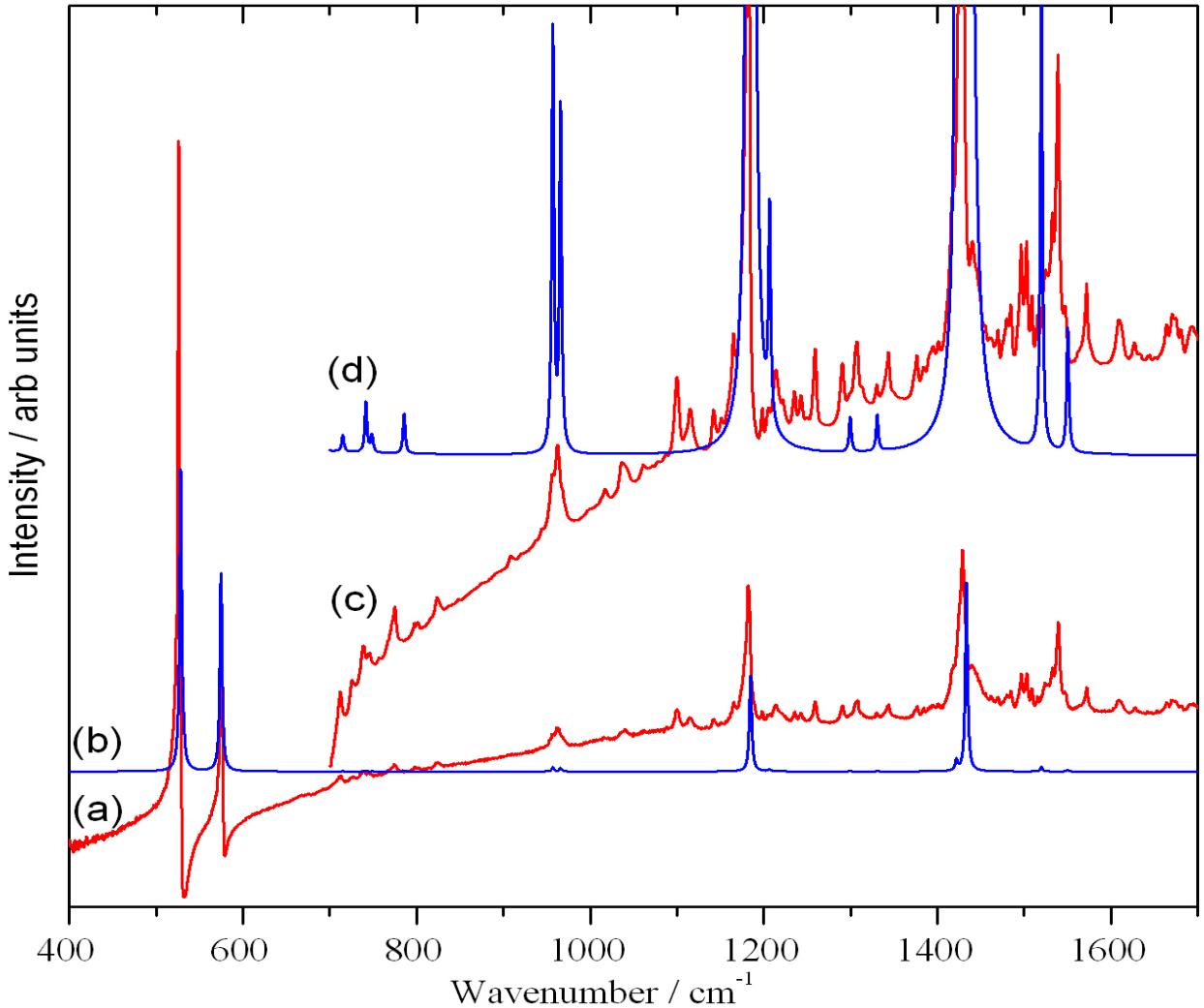

Phonons and Diffraction

Thermal Diffuse Scattering in Titanite

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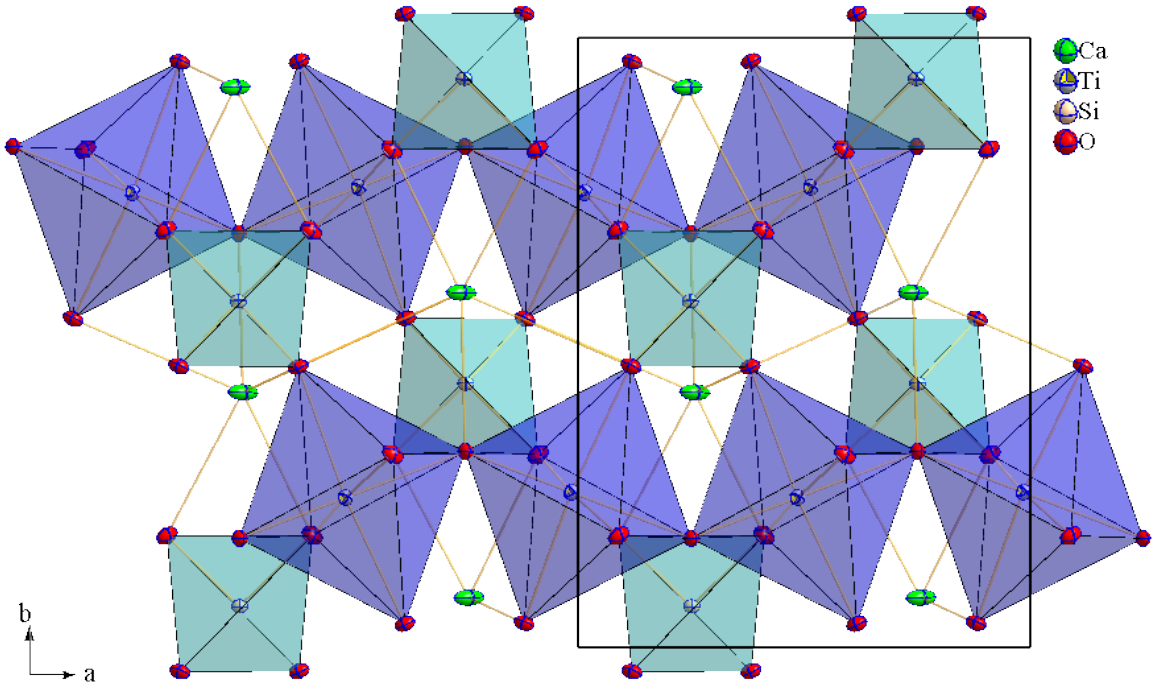

Motivation

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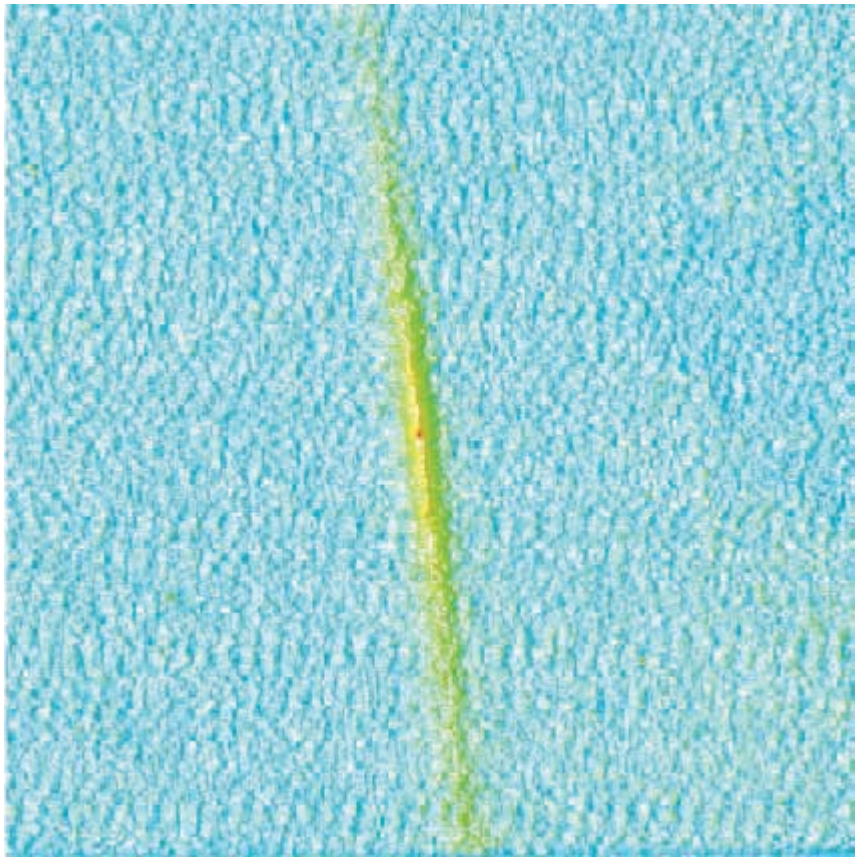

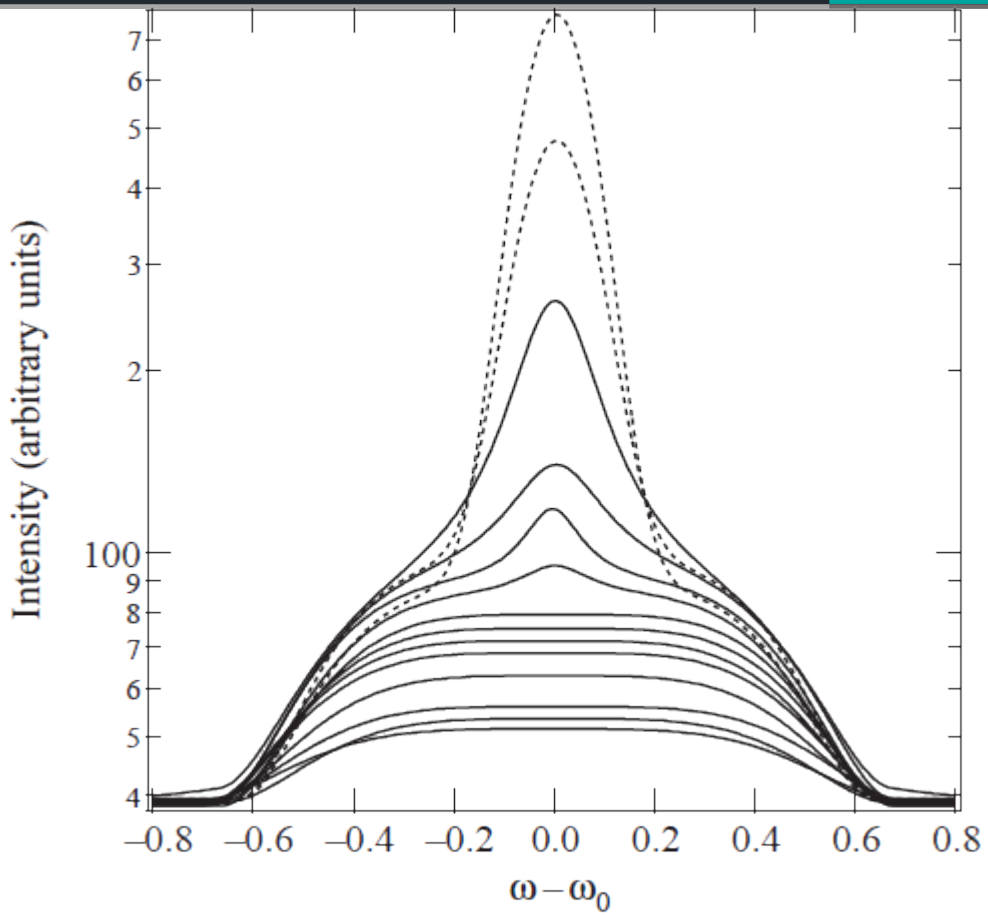

T. Malcherek *et al.*, J. Appl. Cryst. **34** (2001), 108.

Experiment

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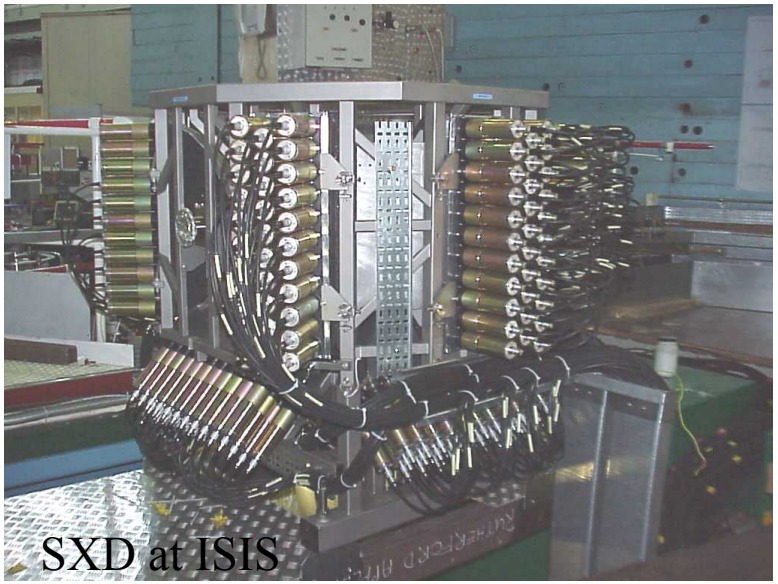

SXD at ISIS

BW5 at DESY

Diffuse scattering

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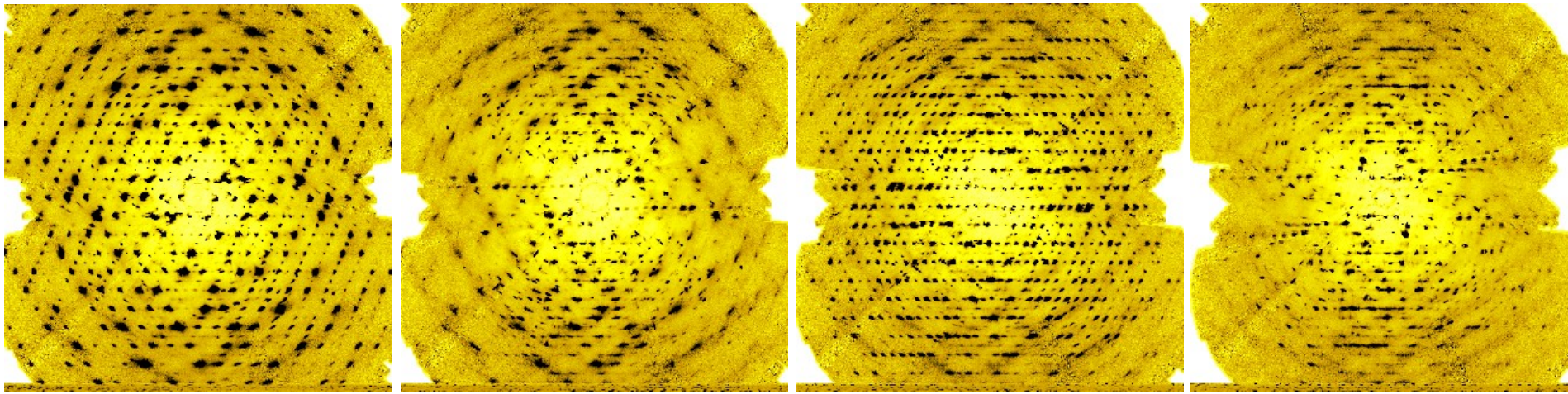
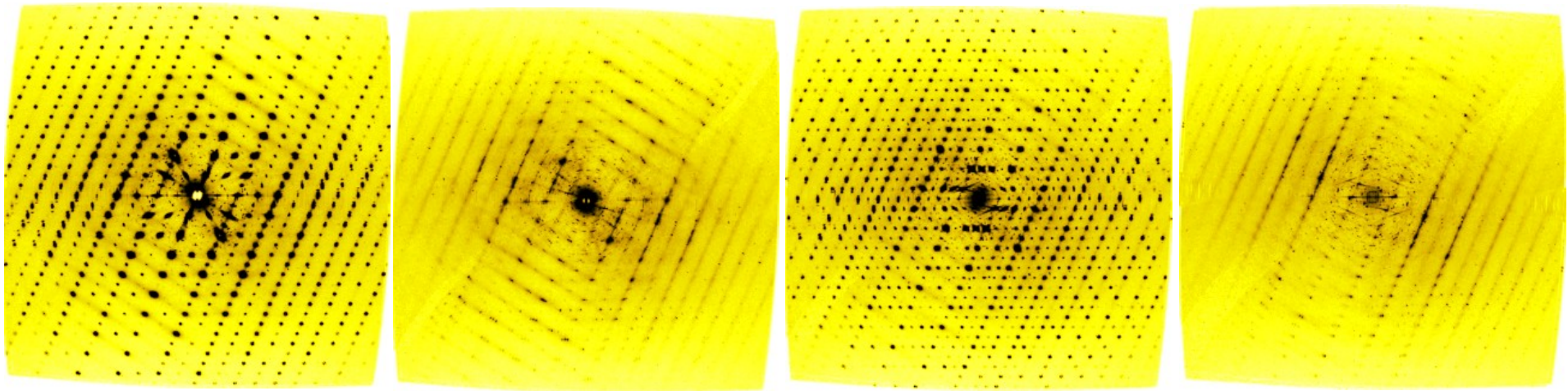


Neutron



X-Ray

Phonons and diffraction

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$$F_j(\vec{q}) = \sum_s \frac{f_s}{\sqrt{\mu_s}} \cdot e^{-M_s} \cdot (\vec{q} \cdot \vec{e}_{\vec{q},j,s}) \cdot e^{-i\vec{q}\cdot\vec{r}_s}$$

$$I_{TDS} = \frac{\hbar N I_e}{2} \sum_j \frac{1}{\omega_{\vec{q},j}} \coth\left(\frac{\hbar \omega_{\vec{q},j}}{k_B T}\right) |F_j(\vec{q})|^2$$

R. Xu and T. C. Chiang, Z. Kristallogr. **220** (2005), 1009.

Dispersion curves from DFPT

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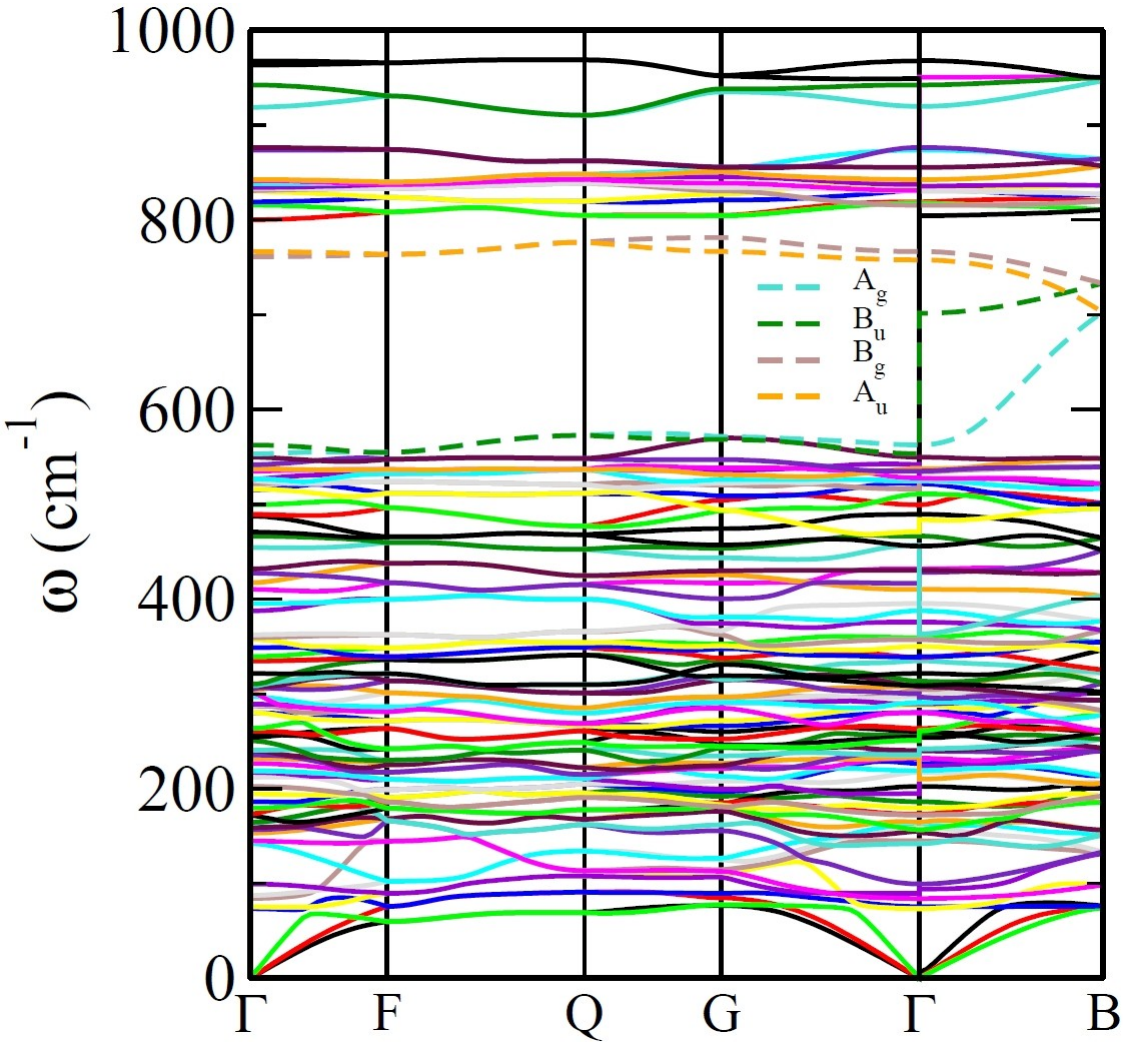

Comparison with data

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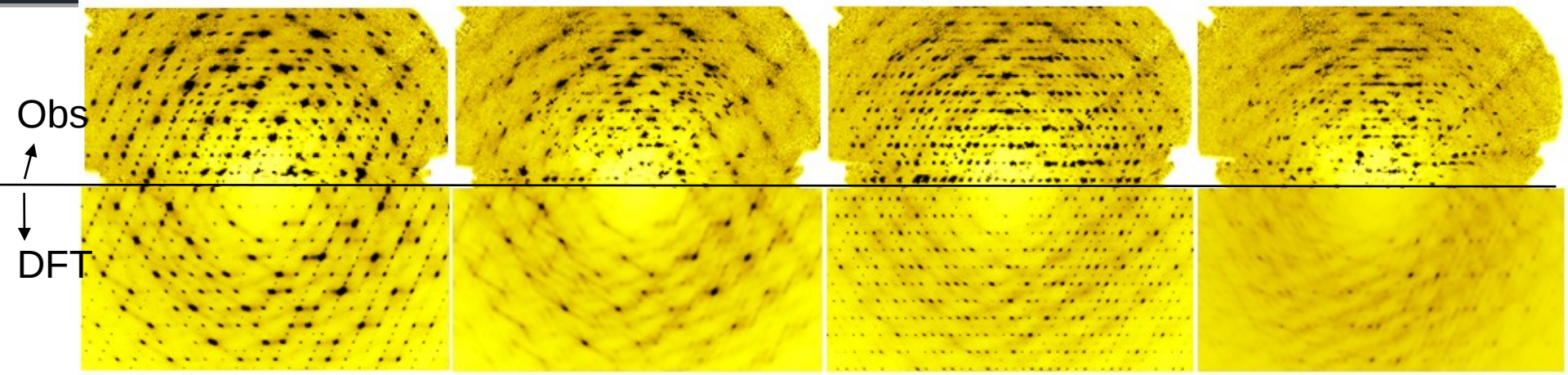
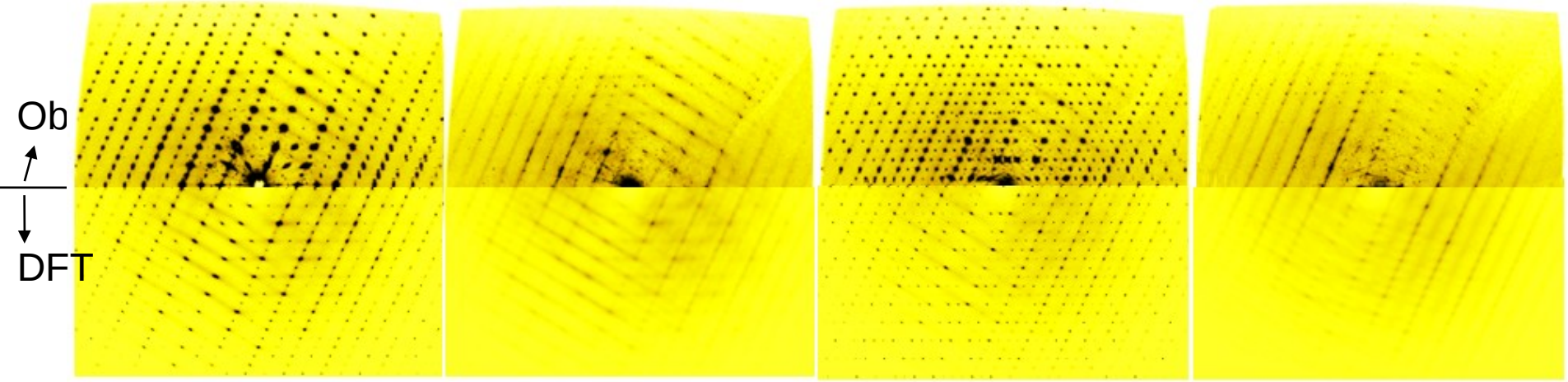


Neutron



X-Ray

Dynamics and Dynamic Structure

Dynamics of nuclei

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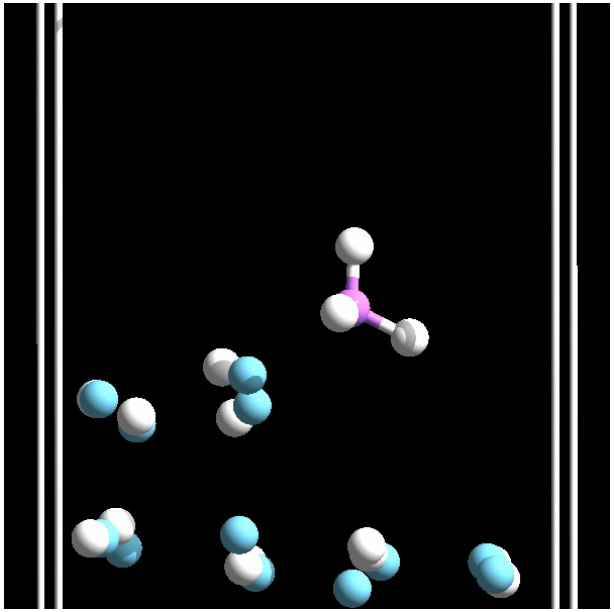
With forces calculated from DFT
Can also calculate dynamics:

- Molecular dynamics – time evolution
- Lattice dynamics - spectroscopy

$$r(t+\delta t)=r(t)+v(t)\delta t+\frac{1}{2}a(t)\delta t^2$$

$$v(t+\delta t)=v(t)+\frac{1}{2}[a(t)+a(t+\delta t)]\delta t$$

$$a(t+\delta t)=\frac{1}{m}F(t+\delta t)$$



Water on metal Surfaces

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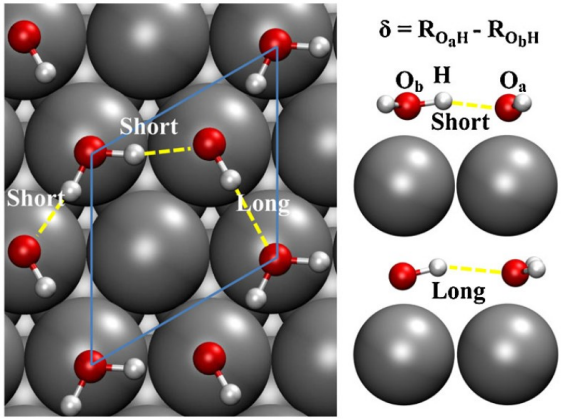

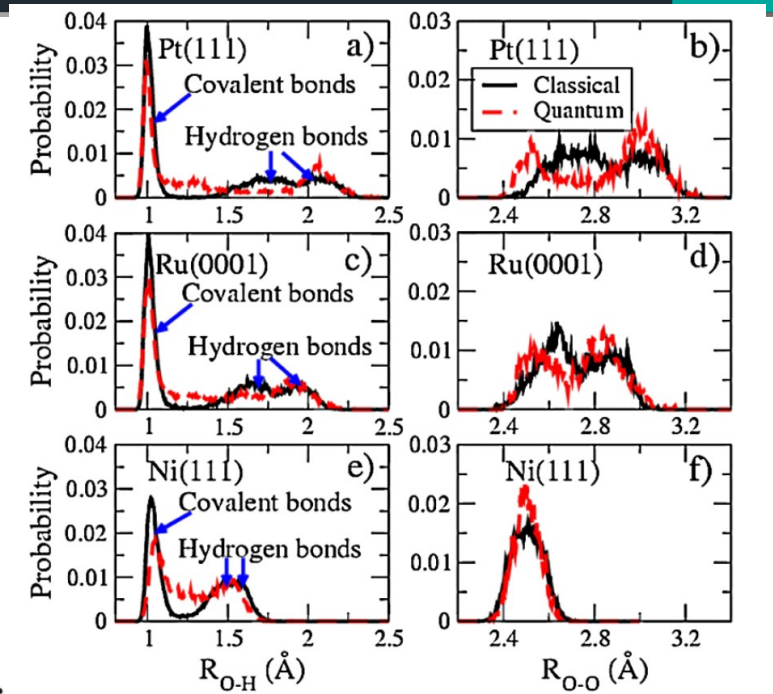

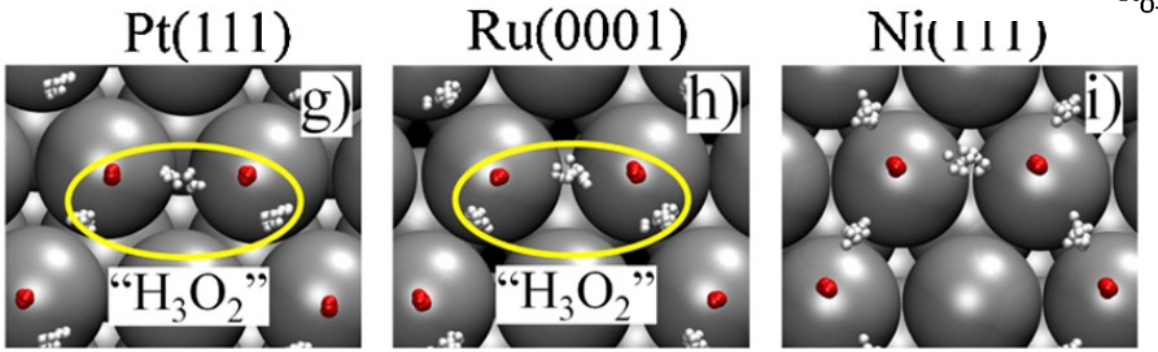

Li, Probert, Alavi, Michaelides, PRL **104**, 066102 (2010)

Superionic conductivity in $LiBH_4$

Fast-ion conduction in $LiBH_4$

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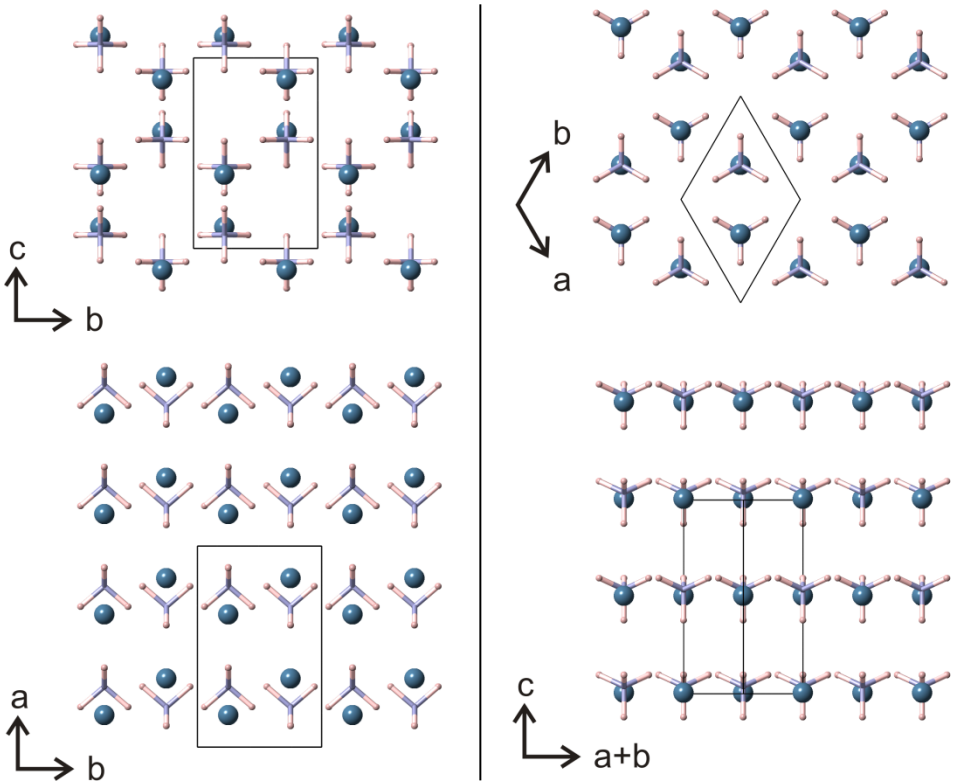

< 390 K
Orthorhombic (Pnma)

> 390 K
Hexagonal (P63/mmc)
Disordered
Superionic conductivity

> 560 K: liquid
> 650 K: decomposition

Ab Initio Molecular Dynamics

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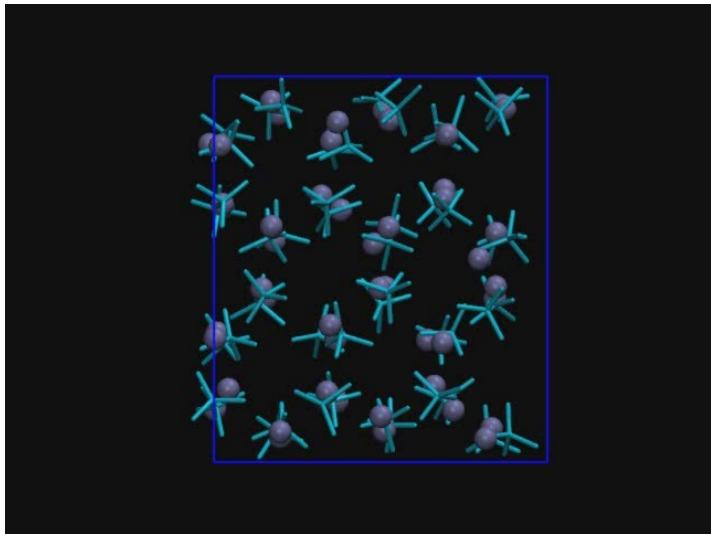
- Code: CP2K
- Born-Oppenheimer molecular dynamics in isokinetic ensemble (Gaussian thermostat)
- Forces evaluated by DFT using the QUICKSTEP method
- Supercell: 288 atoms (48 formula units)
- Time step: 0.5 fs
- Run lengths 20-30 ps after equilibration
- PBE exchange-correlation functional
- Dual basis set (Gaussian DZ orbitals & plane waves up to 280 Ry) and Goedecker pseudopotentials are used



Equilibrium MD picture

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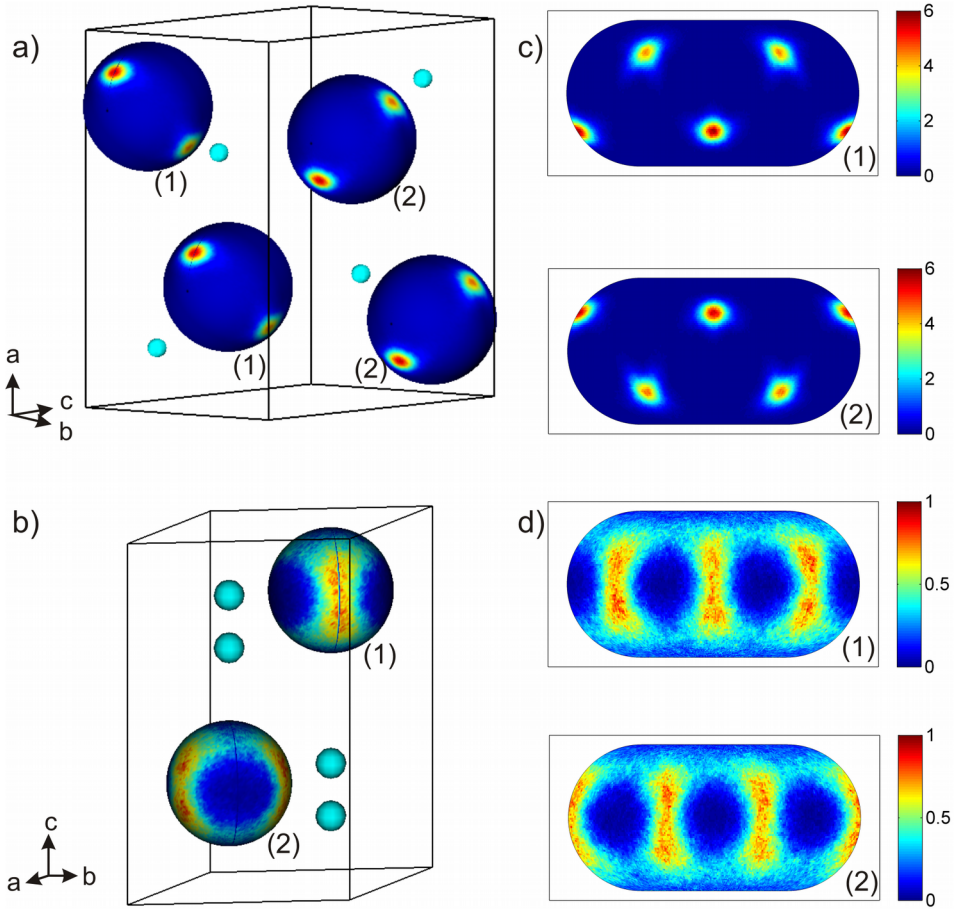
BH4 rotational disorder:



298K

473K

Equilibrium MD picture

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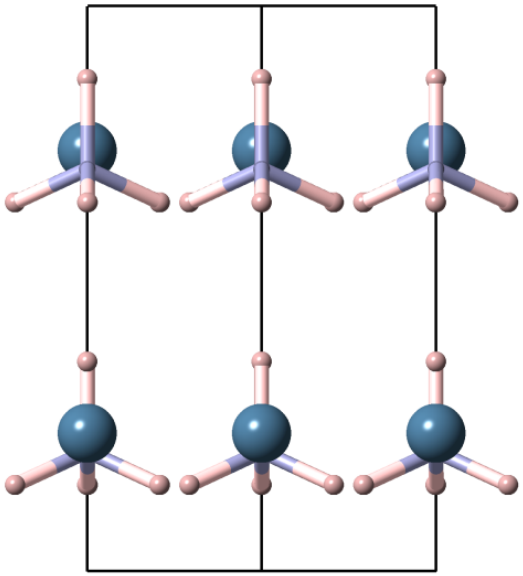
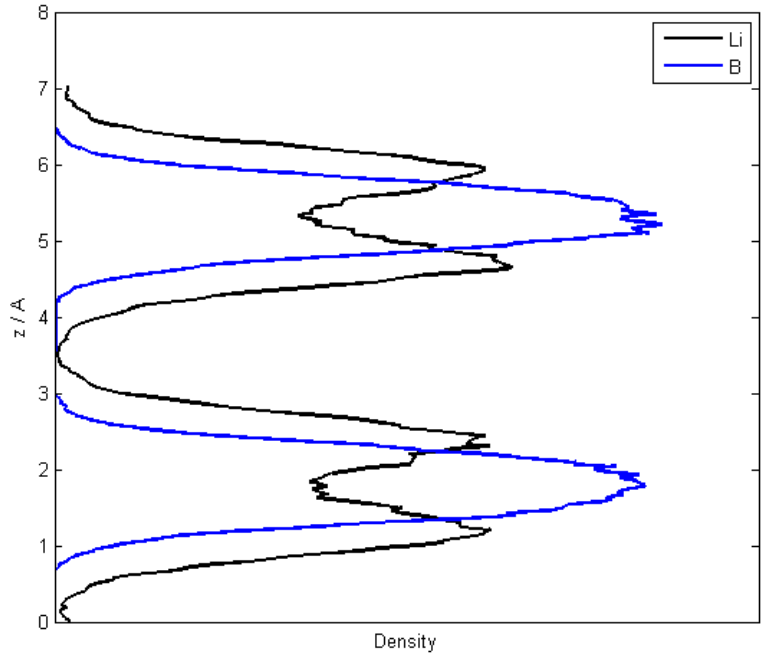
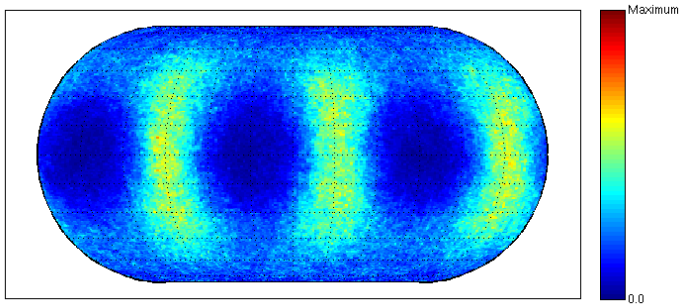
Li dynamical disorder:





BH4 rotational disorder:



Measurements of Li mobility

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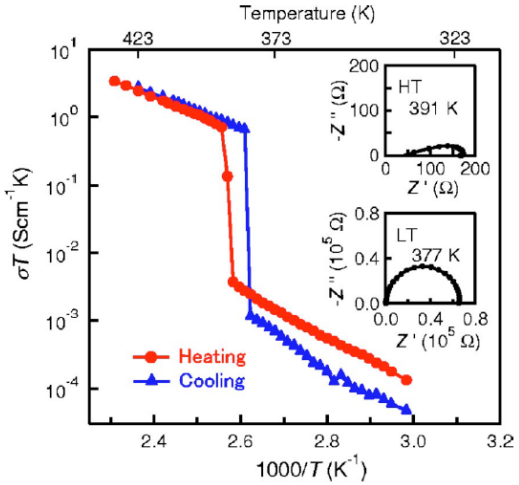
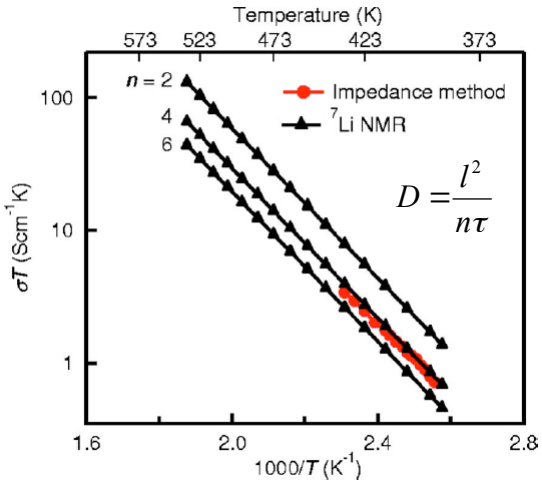
Motoaki Matsuo et al., Applied Physics Letters **91**, 224103 (2007).



A/C impedance measurements



Li-7 NMR measurements

At 535K: $\sigma = 0.139$ S/cm ⟷ $D_{Li} = 2.28 \cdot 10^{-6}$ cm^2/s

Calculating diffusion by AIMD

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Diffusion coefficient calculated by...

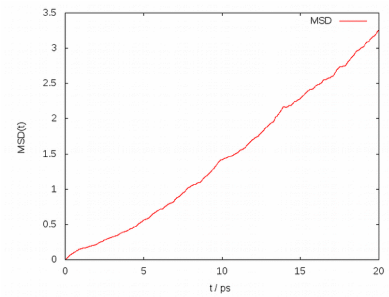
Einstein-Sutherland equation

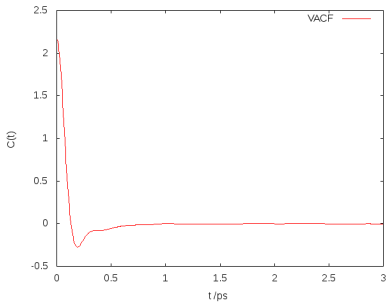
$$D = \frac{1}{n}\frac{d\langle r^2(t)\rangle}{dt}$$

Green-Kubo formula

$$D = \frac{2}{n}\int_0^\infty dt\langle v(0)\cdot v(t)\rangle$$

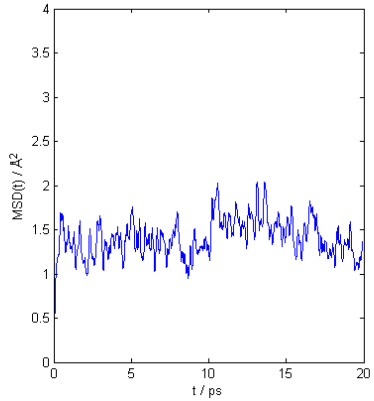
Lennard-Jonesium
(mimicking liquid Argon)

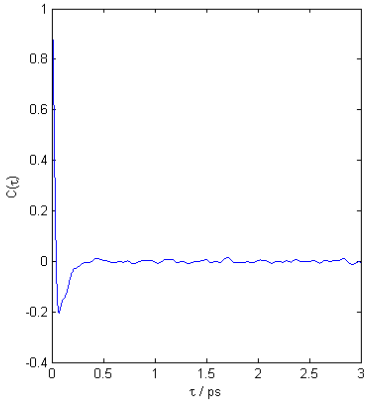




Fast diffusion

LiBH4 at 535 K





Diffusion by ion jumps
(rare events)
which are often
followed by a jump back
to the original position

Limits of AIMD: diffusion in fluids with $D > 10^{-5}$ cm^2/s

Nonequilibrium Molecular Dynamics

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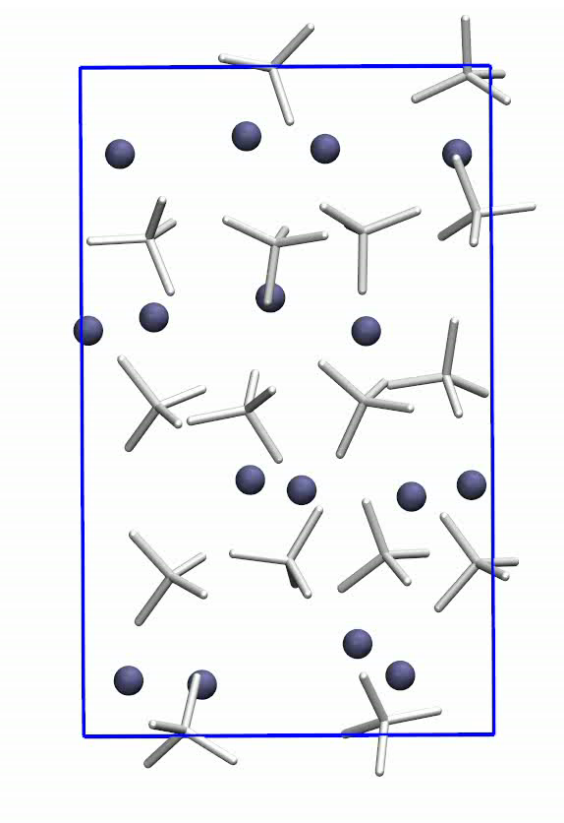

- An external field ***Fe*** is applied that couples to a fictitious atomic property ("colour", *ci*):

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + c_i \mathbf{F}_e$$

- The (fictitious) field and its induced response are related by (real) transport coefficients:

$$D = \frac{k_B T}{\rho_c} \lim_{t \to \infty} \lim_{F_e \to 0} \frac{\langle J_c(t) \rangle}{F_e}$$

- NEMD functionality implemented in CASTEP and CP2K
- *ab initio* nature of the method allows mechanism discovery

Results – F_e = 0.05 eV/Å

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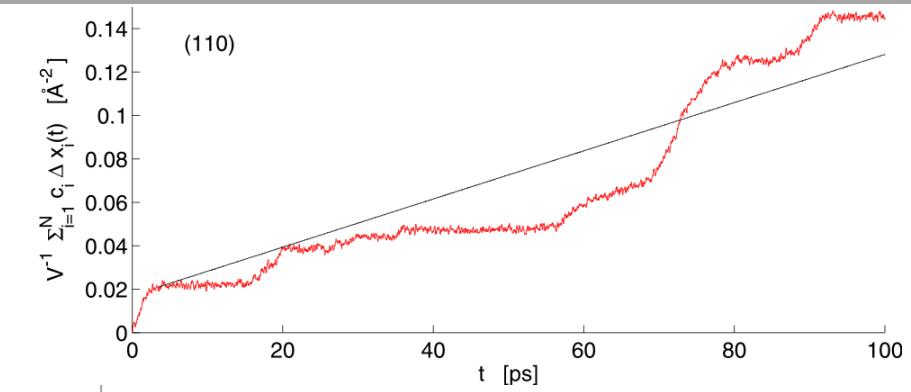
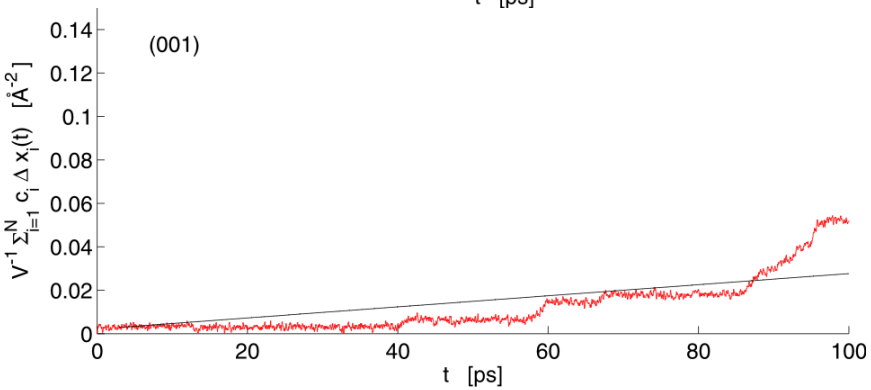
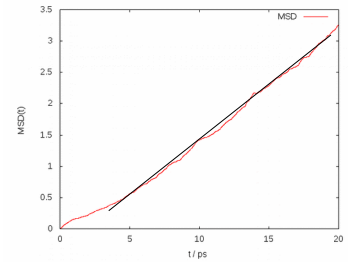


$D_{Li} = 5.82 \cdot 10^{-6}$ cm²/s



$D_{Li} = 1.34 \cdot 10^{-6}$ cm²/s

(Measured: $D_{Li} = 2.28 \cdot 10^{-6}$ cm²/s)



Compare: $D = \frac{1}{n} \frac{d\langle r^2(t) \rangle}{dt}$ vs $D = \frac{k_B T}{\rho_c} \lim_{t \to \infty} \lim_{F_e \to 0} \frac{\langle J_c(t) \rangle}{F_e}$

Diffusion Pathway

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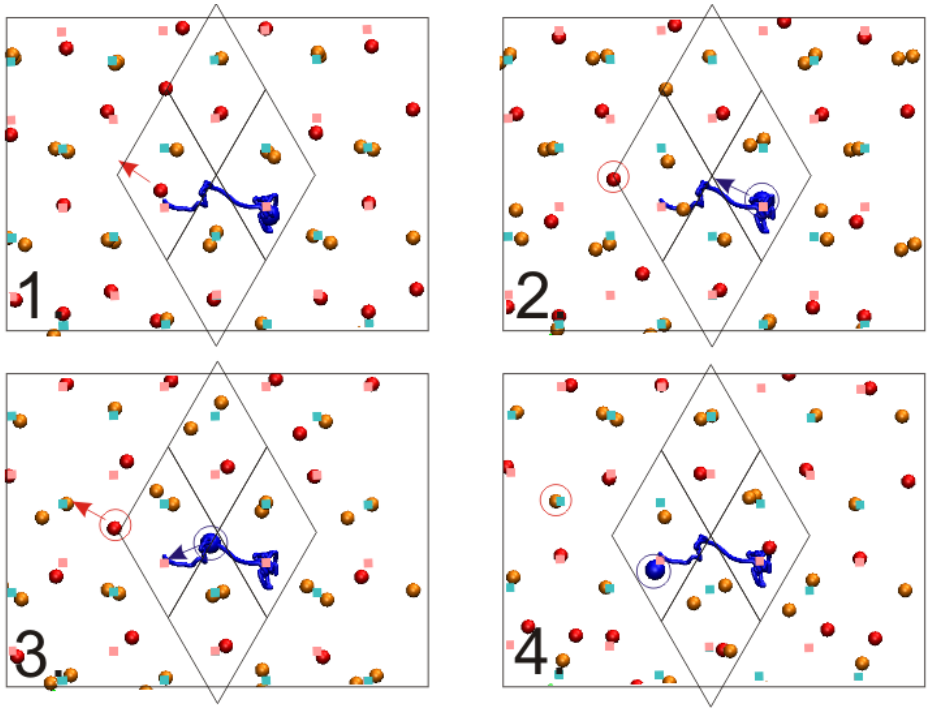
Inspection of the NEMD trajectory:



hopping is via jumps from a lattice site into an empty interstitial site (2 & 3), and from there on to another lattice site (4).

P.C. Aeberhard, S. Williams, D. Evans, K. Refson, and W.I.F. David, Physical Review Letters 108, 095901 (2012).

THE JOURNAL OF
PHYSICAL CHEMISTRY C

ARTICLE

pubs.acs.org/JPCC

The Nature of BH_4^- Reorientations in Hexagonal $LiBH_4$

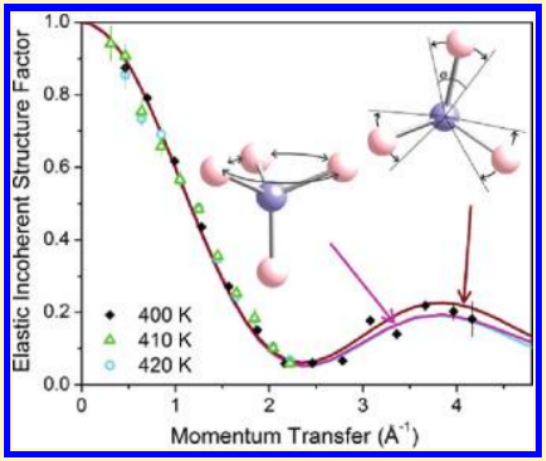
Nina Verdal,*[,†] Terrence J. Udovic,[†] and John J. Rush[†,‡]

[†]NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Dr., MS 6102, Gaithersburg, Maryland 20899-6102, United States

[‡]Department of Materials Science and Engineering, University of Maryland, 2135 Chemical & Nuclear Engineering Bldg., College Park, Maryland 20742-2115, United States

S *Supporting Information*

ABSTRACT: Lithium borohydride ($LiBH_4$) has lately been the subject of intense inquiry within the hydrogen storage community. Quasi-elastic neutron scattering spectra were measured for $LiBH_4$ in the high-temperature hexagonal crystal phase. The elastic incoherent structure factor associated with the rapid BH_4^- anion reorientations was determined at 400, 410, and 420 K for momentum transfers as high as 4.2 $Å^{-1}$. The results strongly suggest a BH_4^- reorientational mechanism approaching quasi-free, trigonal-axis rotation of three borohydride H atoms, combined with reorientational jump exchanges between these delocalized "orbiting" H atoms and the remaining axial borohydride H atom. This mechanism is consistent with previously reported diffraction and spectroscopy studies.



Na_xCoO2 again- Na-ion Batteries

Na-ion batteries

- Expanding use of Li-ion batteries into new areas of energy storage:
- High-capacity and large-scale deployment?
  - Automotive
  - Load-levelling for renewable energy
- Problem Li is *scarce* and *expensive*
- *Large-scale deployment for high-capacity poses significant challenge to world's Li resources.*
- Can we replace Li by other cheaper, more abundant elements?
- Na is obvious choice: Na-analogues exist, esp. Na_xCoO_2

Na_xCoO_2

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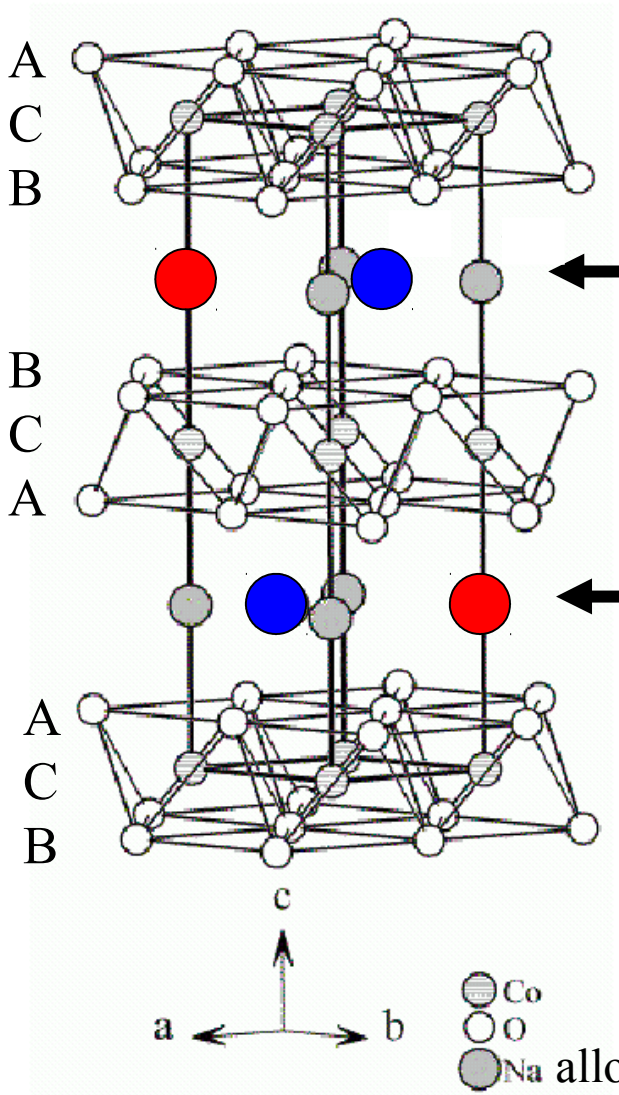

CoO_2 layer

Na can occupy A or C position

CoO_2 layer

Na can occupy B or C position

CoO_2 layer

allowed positions

- Tunable number of Na^+ ions
- $x = 0$ to 1 per CoO_2

Na1 if C position

Na2 otherwise

Superstructures

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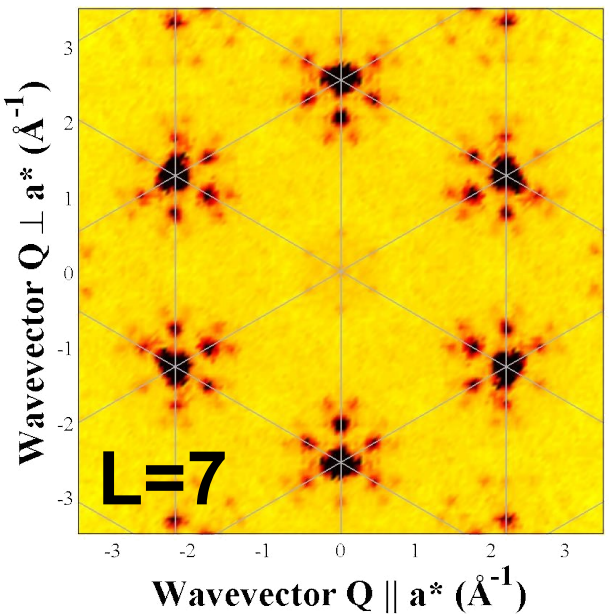
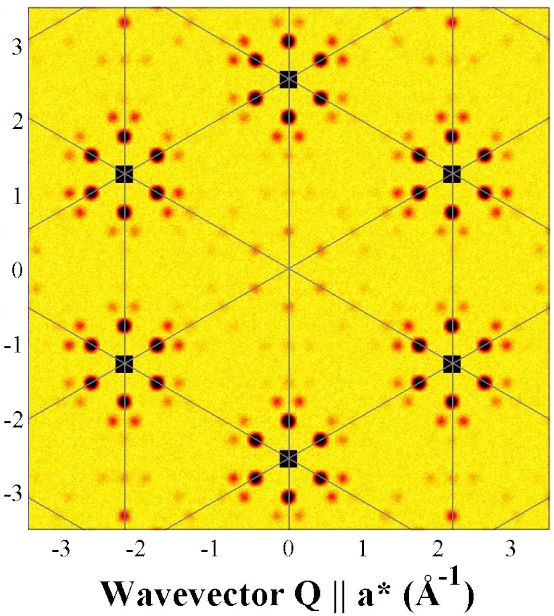
T = 250 K

Ordered Stripe Phase

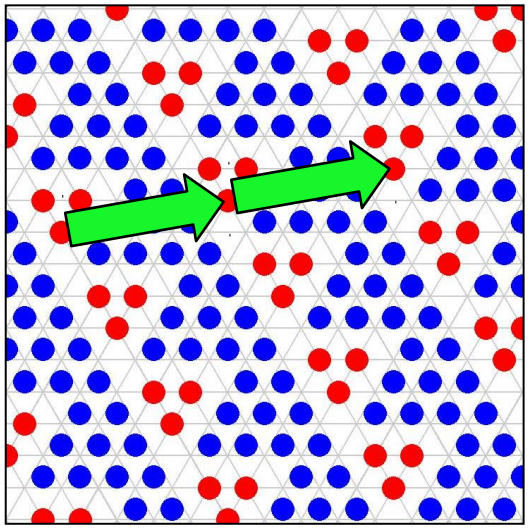
Experiment



Calculation



Model



Unable to detect superlattice reflections using powder diffraction…
Need the sensitivity of single-crystal diffraction

Superstructures

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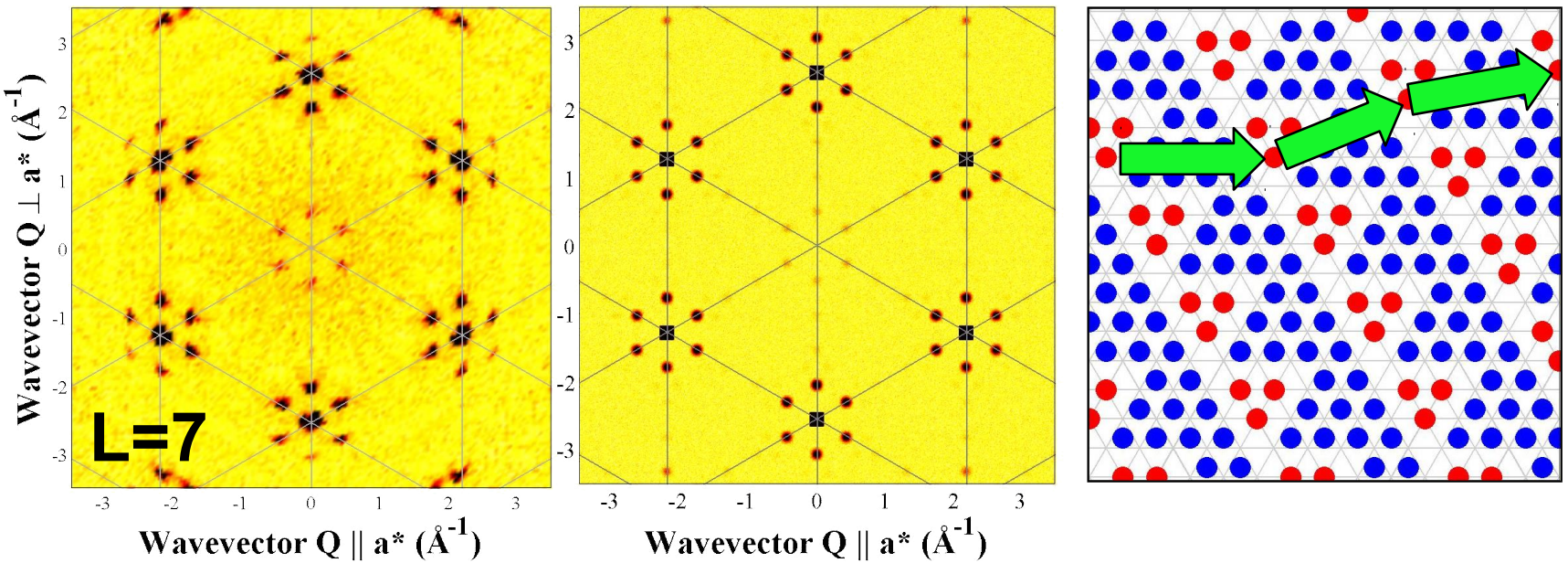
T = 350 K Disordered Stripe Phase

Experiment ***Calculation*** ***Model***



Dynamic or static disorder along the stripes?

AIMD Simulations of diffusion

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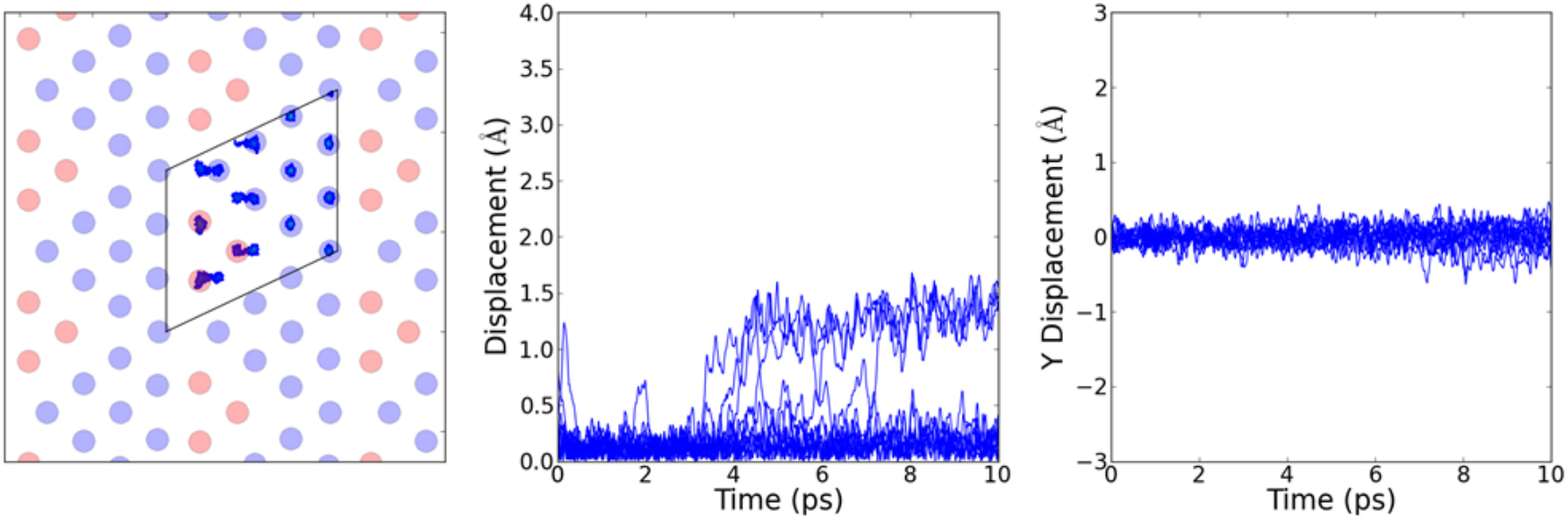
Ordered stripe phase (T = 350 K)



Ideal superstructure

- Na1 – Na2 hops perpendicular to stripes
- Translation of tri-vacancy clusters along stripes
- No bulk self-diffusion

T. J. Willis *et al.* Sci. Rep 8 3210 (2018)

AIMD Simulations of diffusion

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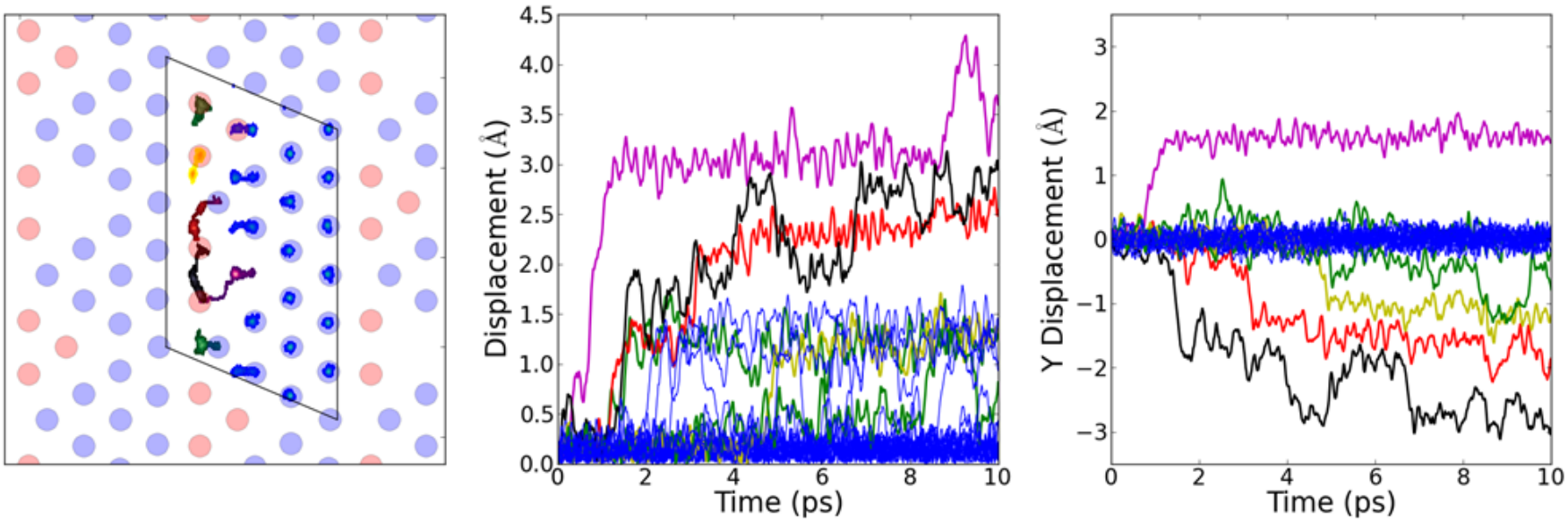
Disordered stripe phase (T = 350 K)



Vacancy on Na1 site in stripe

- Na1 – Na2 hops with components along stripes
- Chains of correlated hops of different ions
- Bulk self-diffusion along stripes

Acknowledgements

- Collaborators

  Jon Goff, David Voneshen, Dan Porter, Toby Willis: RHUL

  Bill David, Philippe Aeberhard, Oxford

  Matthias Gutmann, ISIS
- FUNDING – EPSRC, STFC
- Computer time EPSRC, STFC

CASTEP

ESRF
The European Synchrotron

Science & Technology Facilities Council

archer

EPSRC
Engineering and Physical Sciences Research Council

SCARF