Ross Angel

I determine the atomic-scale structures of minerals, and how they change with pressure, temperature and composition

Structure ➔ Function ➔ Geology and Geophysics

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Equations of State - Summary

- What are EoS and what are they used for?
- Measurement methods (very brief)
- EoS theory and formulations
- PV data analysis
Elastic versus plastic

- **Elastic deformation**
  - E.g. springs
  - Reversible
  - no permanent change
  - Hooke law: \( F = -kx \)

- **Plastic deformation**
  - Irreversible, permanent change
  - Material flow

Elastic, plastic deformation, brittle failure

Bond compression

Bond bending

On-line Eos class, Ross J Angel
Equation of State

- Defines the elastic relationship of volume to intensive variables:
  - \( V = f(T,P,H,X,\ldots) \)
  - Normally \( V = f(P,T) \)
  - Isothermal EoS: \( V = f(P) \)
  - Can also be defined as \( \rho = f(P) \)
  - Or as the change in elastic properties with pressure

Hooke law: \( F = -kx \)
Linear EoS

Equations of state in the Earth

- Rocks exert a pressure
- Useful approximation
  - 3 km in the crust = 1 kbar
  - 30 km in the crust = 1 GPa

\[ P = \rho gh \]
Equations of state for minerals

- An equation of state for a mineral defines:
  - the variation of density of a mineral with \( P, T \)
  - (partly) the seismic velocities
  - Volume changes at transitions and slopes of phase boundaries

![Image of equations and transitions](image1)

Diamond inclusions

- Inclusion at 0.4 GPa
- The hole in the diamond is at room pressure, but same \( V \) as olivine
- Use EoS to determine pressure at which they had same \( P \) and \( V \)

![Image of diamond inclusions and transitions](image2)

Nestola et al (2011) EPSL, 305:249
Equations of state – chemistry and physics

- The P-V behaviour implies the elastic properties
  - Bonding
  - Softening at transitions
  - Materials applications

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Elasticity basics: volume/bulk

- Elasticity is a material property:
  - relates applied stress and resulting strain
  - compliances describe “softness”
  - moduli describe “stiffness”

- For volume change with pressure:
  - Stress is \( dP \)
  - Strain
  - Compressibility: \( \beta_v = -\frac{1}{V} \left( \frac{dV}{dP} \right) \)
  - Volume compliance
  - Bulk modulus: \( K = -V \left( \frac{dP}{dV} \right) \)
**EoS: basic definitions**

- We normally describe an EoS in terms of the room pressure parameters....
  - **Room pressure volume** $V_0$
  - **Bulk modulus**
    \[ K_0 = -V_0 \left( \frac{\partial P}{\partial V} \right)_{P=0} \]
  - **Bulk modulus derivative**
    \[ K'_0 = \left( \frac{\partial K}{\partial P} \right)_{P=0} \]
  - **Etc....**
    \[ K''_0 = \left( \frac{\partial^2 K}{\partial P^2} \right)_{P=0} \]

These parameters can be determined from P-V or K-P measurements.

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**The diamond-anvil cell**

- Apply hydrostatic stress
Volume measurements

- Almost all by diffraction: \( d(\text{hkl}) = \frac{\lambda}{2\sin \theta_{\text{hkl}}} \)

Results of diffraction experiments...PV data

- Quartz, SiO₂
- Albite, NaAlSi₃O₈
- CuCO₃
Choice of EoS

- There is no absolute thermodynamic basis for specifying a correct form for an EoS
  - All EoS are based upon assumptions
  - The validity of the assumptions can only be judged in terms of the accuracy with which the EoS reproduces P-V or elastic data

- EoS are stress-strain relationships
  - Each implies a different K-P relationship as well as V-P

- Practical EoS are derived from
  - An assumed inter-atomic potential
  - An assumed relationship between EoS parameters and P
  - An assumed relationship between free energy and strain (and a choice of strain definition)

- Your choice depends on
  - Accuracy
  - Reliability in extrapolation (?)
  - Convenience

Why not use a polynomial?

\[ \frac{V}{V_0} = 1 + aP + bP^2 \ldots \]
Derivation from inter-atomic potentials

- **General idea:**
  - Inter-atomic potential gives energy as function of distance
  - Includes attractive (e.g. Madelung)
    \[ \phi_{12} = -\frac{Z_i Z_j e^2}{r_{12}} \]
    \[ \phi_i = \sum \phi_{ij} = -\frac{AZ_i Z_j e^2}{r_{ij}} \]
  - and repulsive terms ...many choices...e.g. Born-Mie Eos:
    \[ \phi_{12} \propto \frac{1}{r_{12}^n} \]

- Inter-atomic potential gives energy as function of distance
- So we have energy as function of volume
  \[ E \left( \frac{V}{V_0} \right) = E \left( \frac{r}{r_0} \right) \]
- And pressure is defined as:
  \[ P = -\frac{\partial E}{\partial V} \]

Vinet EoS…

- Derived from general interatomic potential
  \[ f_r = \left( \frac{V}{V_0} \right)^{\frac{3}{2}} \]
  \[ P = 3K_0\left( \frac{1 - f_r}{f_r^{\prime\prime}} \right) \exp \left[ \frac{3}{2} (K' - 1)(1 - f_r) \right] \]

- Simple, 3 parameter equation of state, but has an implied value of \(K''\):
  \[ K'' = \frac{-1}{K_0} \left[ \frac{K'}{2} + \left( \frac{K'}{2} - \frac{19}{36} \right) \right] \]

- Advantages
  - Excellent for simple solids
  - Accurate to high compression

- Disadvantages
  - Not intended for complex materials with significant degrees of internal structural freedom.
  - No extension to refinable \(K''\)

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EoS of quartz

\[ K = -V \frac{\partial P}{\partial V} \]
Equations of state: Murnaghan

- Actually derived from concept of finite strain
- But also can be derived by assuming K is linear with P
  \[ -V \frac{\partial P}{\partial V} = K_0 + KP \]
  \[ \int_0^V \frac{\partial P}{K_0 + KP} = \int_{V_0}^{V} \frac{-\partial V}{V} \]
  \[ V = V_0 \left( 1 + \frac{KP}{K_0} \right)^{\frac{1}{\gamma}} \]
  \[ P = K_0 \left[ \left( \frac{V}{V_0} \right)^{\frac{1}{\gamma}} - 1 \right] \]

- Advantages
  - Can be inverted, easily integrated
  - ...great for thermo databases

- Disadvantages
  - K’ is constant, K” = 0
  - Does not fit P-V data for V/V_0 < 0.9
  - ...crust only

Finite strain EoS

- Assumes strain energy is a polynomial in strain f
  \[ \Psi = af^2 + bf^3 + cf^4 + .... \]

- Pressure is then:
  \[ P = -\frac{\partial E}{\partial V} \]
  \[ P = -\frac{d\Psi}{dV} = -\frac{d\Psi}{df} \frac{df}{dV} \]
  \[ P = -\frac{df}{dV} \left[ 2af + 3bf^2 + 4cf^3 + .... \right] \]

- So we need a definition of strain f
**Infinitesimal and Finite strain**

- Conventional elasticity theory works with infinitesimal strains:
  \[ \epsilon = \frac{l - l_0}{l_0} \]
  \[ \epsilon_p = \frac{V - V_0}{V_0} = \frac{V}{V_0} - 1 \]

- Under compression the volume changes are not small......finite strain
  \[ f_L = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right] \]

**Finite strain definitions**

- Infinitesimal strains defined with respect to the initial state are called **Lagrangian**:
  \[ \epsilon_p = \frac{V - V_0}{V_0} = \frac{V}{V_0} - 1 \]
- Lagrangian finite strains are also defined with respect to the initial state:
  \[ f_L = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right] \]
- Eulerian strains are defined with respect to the final state:
  \[ f_E = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right] \]
- Note sign convention

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On-line Eos class, Ross J Angel
**Birch-Murnaghan EoS**

- **Finite strain EoS**
  - Assumes strain energy is a polynomial in $f$
  
  \[
  V = af^2 + bf^3 + cf^4
  \]
  
  \[
  P = \frac{-dV}{dV} = \frac{-dV}{df} \frac{df}{dV}
  \]
  
  \[
  P = \frac{-df}{dV} \left[ 2af + 3bf^2 + 4cf^3 \right]
  \]
  
  - Do derivatives up to $K''$, substitute back and…

\[
P = 3K_e f_e \left( 1 + 2f_e \right)^{5/4} \left[ 1 + \frac{3}{2} \left( K''_e - 4 \right) f_e + \frac{3}{2} \left( K_e K''_e + \left( K''_e - 4 \right) \left( K''_e - 3 \right) + \frac{35}{9} \right) f_e^2 \right]
\]

\[
K = K_e \left( 1 + 2f_e \right)^{5/4} \left[ 1 + \left( 3K''_e - 5 \right) f_e + \frac{9}{2} \left( K_e K''_e + K''_e \left( K''_e - 4 \right) + \frac{35}{9} \right) f_e^2 \right]
\]

**Advantages**
- Fits P-V data for $V/V_0$ to 0.8
- Provides correct $K_0$
- Good for crust and mantle

**Disadvantages**
- Cannot be inverted
- VdP integrals must be numerical
- Problem for thermo databases
**Birch-Murnaghan EoS – truncations**

Truncation:
- **2nd order (in energy)**
  - Coefficient of $f_2 E$ must be zero
  - $V_0$ and $K_0$ are material parameters
  - $K_0' = 4$

\[
P = 3K_0 \left(1 + 2f \right)^{5/2} f
\]
\[
K = K_0 \left(1 + 2f \right)^{5/2} \left(1 + 7f \right)
\]
\[
K' = \frac{(4 + 49f^2/3)}{1 + 7f} = \frac{(K_0^2 + 49f^2/3)}{1 + 7f}
\]

**Birch-Murnaghan EoS – truncations**

Truncation:
- **3rd order (in energy)**
  - Coefficient of $f_3 E$ must be zero
  - $V_0, K_0, K_0'$ are material parameters

\[
P = 3K_0 \left(1 + 2f \right)^{5/2} \left(1 + \frac{3}{2} \left(3K_0' - 4\right) f_2 \right)
\]
\[
K = K_0 \left(1 + 2f \right)^{5/2} \left(1 + \frac{9}{2} \left(3K_0' - 4\right) f_2 \right)
\]

\[
K^* = \frac{-1}{K_0} \left(3 - K' \right) \left(4 - K'' \right) + \frac{35}{9}
\]

- **4th order (in energy)**
  - Coefficient of $f_4 E$ non-zero
  - $V_0, K_0, K_0', K_0''$ are material parameters
Finite-strain EoS of quartz

\[ K = -V \frac{\partial P}{\partial V} \]

Birch-Murnaghan EoS for quartz

\[ K' = \frac{\partial K}{\partial P} \]

\[ K'' = \frac{\partial^2 K}{\partial P^2} \]

\[ P = 3K_0 f_\rho \left( 1 + 2f_\rho \right)^{3/2} \left( \frac{3}{2} f_\rho (K' - 4) f_\rho + \frac{3}{2} K_0 f_\rho (K'' - 4) (K' - 3) + \frac{35}{9} f_\rho^2 \right) \]
**Natural strain EoS**

- Derived from
  - An assumed relationship between free energy and strain
  - and a choice of strain definition

- Natural Strain (Poirier)

\[
\begin{align*}
  f_N &= \frac{1}{3} \ln \left( \frac{V}{V_0} \right) \\
  P &= 3K_n \left( \frac{V_0}{V} \right) f_N \left[ 1 + \frac{3}{2} (K' - 2) f_N + \frac{3}{2} \left( 1 + K_n K'' + (K' - 2) \right) f_N^2 \right]
\end{align*}
\]

**Choice of EoS: Precision and Accuracy**

- The bulk modulus and its derivatives are thermodynamic variables of precise definition:

\[
K = -V \left( \frac{\partial P}{\partial V} \right) \quad K' = \left( \frac{\partial K}{\partial P} \right) \quad K'' = \left( \frac{\partial K'}{\partial P} \right) = \left( \frac{\partial^2 K}{\partial P^2} \right)
\]

- An EoS says how these change with \( P \)

- But there is no absolute thermodynamic basis for specifying a correct form for an EoS
  - All EoS are based upon assumptions
**Equations of state – choice of form**

- Assume how parameters vary with pressure
  - Murnaghan

- Assume how energy varies with strain
  - Birch-Murnaghan
  - Vinet
  - Natural strain

- Assume a truncation

- *The validity of the assumptions can only be judged in terms of the accuracy with which the EoS reproduces P-V or elastic data*

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**Equations of State – Further reading**

  - In RM Hazen and RT Downs (eds.), *High-temperature and high-pressure crystal chemistry*, MSA. pp. 35-60, Reviews in Mineralogy and Geochemistry, vol. 41
  - Available from [www.minsocam.org](http://www.minsocam.org)
  - Short version in EoSFit manual at [www.rossangel.com](http://www.rossangel.com)


- Technical papers:
Choice of EoS: Precision and Accuracy

- The validity of an EoS can only be judged in terms of the accuracy with which it reproduces P-V or elastic data.

<table>
<thead>
<tr>
<th>$V_0$, $\Delta V$</th>
<th>$K_0$, GPa</th>
<th>$K'$</th>
<th>$K''$, GPa$^{-1}$</th>
<th>$\sigma_V$, GPa</th>
<th>$\sigma_P$, GPa</th>
<th>$P_{obs}$ - $P_{calc}$</th>
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</thead>
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<tr>
<td>BM2 112.97(2)</td>
<td>41.5(3)</td>
<td>(4.0)</td>
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<td>128</td>
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<td>BM3 112.98(2)</td>
<td>37.12(9)</td>
<td>5.99(5)</td>
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<td>0.025</td>
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</tr>
<tr>
<td>BM4 112.98(2)</td>
<td>36.89(22)</td>
<td>6.26(24)</td>
<td>[-.41(12)</td>
<td>0.93</td>
<td>0.026</td>
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<td>NS2 112.95(5)</td>
<td>46.5(6)</td>
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<td>6.91(7)</td>
<td>[-.825]</td>
<td>1.15</td>
<td>0.026</td>
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</tr>
<tr>
<td>NS4 112.98(2)</td>
<td>36.90(24)</td>
<td>6.23(29)</td>
<td>[-.39(31)</td>
<td>0.93</td>
<td>0.026</td>
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<td>Vinet 112.98(2)</td>
<td>37.02(9)</td>
<td>6.10(4)</td>
<td>[-.319]</td>
<td>0.90</td>
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<td>Murn. 112.98(2)</td>
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<td>5.43(4)</td>
<td>[0]</td>
<td>1.57</td>
<td>0.033</td>
<td></td>
</tr>
</tbody>
</table>

From Angel, 2000, MSA RiM v 41

Elasticity measurement: $K_0 = 37.12(6)$ GPa (McSkimin et al 1965)

Step 1: start the analysis

- P-V plots
  - Data consistency/scatter
  - Esd evaluation
  - …no help with K, K'

Not precise: large $\sigma(V), \sigma(P)$

Precise: small $\sigma(V), \sigma(P)$

**Birch-Murnaghan EoS**

\[
P = 3K_0F_E \left( 1 + 2F_E \right)^{\frac{3}{2}} \left[ 1 + \frac{3}{2}(K' - 4)F_E + \frac{3}{2} \left( K_0K'' + (K' - 4)(K' - 3) + \frac{35}{9} \right) F_E^2 \right]
\]

**Truncation:**
- **2nd order (in energy)**
  - Coefficient of \( F_E \) must be zero
  - \( V_0 \) and \( K_0 \) refined
  - \( K' = 4 \)

- **3rd order (in energy)**
  - Coefficient of \( F_E^2 \) must be zero
  - \( V_0 \) \( K_0 \) \( K' \) refined

- **4th order (in energy)**
  - Coefficient of \( F_E^2 \) non-zero
  - \( V_0 \) \( K_0 \) \( K' \) \( K'' \) refined

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**Step 2: f-F plots**

- **Rearrange BM4 Eos:**
  \[
  F_E = K_0 + \left( \frac{3K_0}{2} \right)(K' - 4)F_E + \left( \frac{3K_0}{2} \right)K_0K'' + (K' - 4)(K' - 3) + \left( \frac{35}{9} \right) F_E^2 + \ldots
  \]

- **Becomes a simple polynomial**

  \[
  F_E = \frac{P}{3(1 + 2F_E)^{\frac{3}{2}}}
  \]

  \[
  f_E = \left( \frac{V_0}{V} \right)^e - 1
  \]

- **Straight line: 2nd or 3rd order EoS**
  - \( K' > 4 \)
  - \( K' = 4 \)
  - \( K' < 4 \)

**Eulerian strain:** \( f \)
Using f-F plots

BM4 Eos:

$$F_E = K_0 + \left(\frac{3K_0}{2}\right) (K'_0 - 4) f_E + \left(\frac{3K_0}{2}\right) K_0 K''_0 + \left(\frac{4}{9}\right) f_E^2 + ...$$

$$f_E = \frac{P}{3f(1+2f_E)^{\frac{3}{2}}}$$

$$f_E = \frac{\left(\frac{V_0}{V}\right)^{\frac{3}{2}} - 1}{2}$$

Curved line: 4th order EoS

$$K'_0 < 4$$

$$\frac{\partial K'_0}{\partial P} = K''_0 > 0$$

$$K'_0 = 4$$

Eulerian strain: $$f$$

Step 2: f-F plots example

Nestola et al. (2008)
Step 3: Fit Equations of State

- Birch-Murnaghan EoS

\[ f_e = \left( \frac{V}{V_0} \right)^{1/2} - 1 \]

\[ P = 3K_0 f_e \left( 1 + 2f_e \right)^{5/2} \left( 1 + \frac{3}{2} (K'' - 4)f_e + \frac{3}{2} K_0 K'' + (K'' - 4)(K'' - 3) + \frac{35}{9} f_e^2 \right) \]

- \( K_0 \) and \( V_0 \) are scaling parameters: always refine
  - Fit by least squares
  - Use esd(P) and esd(V) to weight the data

- Refine increasing derivatives (\( K', \ K'' \)) until:
  - no improvement in fit,
  - or results meaningless

- Lets do it!

Using EoSFit

- DOS executable from www.rossangel.com
  - No graphics
  - Plot data in Excel, Origin etc

- Copy exe to data folder
  - Or create shortcut in data folder

- Create data file
  - Export from graphics software
  - Edit with Notepad

- Run the program
Quality of fit: did we get it right??

- There is no substitute for visual examination and critical thinking!
  - Is the fit correct?
  - Does the model represent the data?
  - Does $V_0$ from the fit match the observed value?
  - ....misfit vs esd(P)

Quality of fit: fF plot

- There is no substitute for visual examination and critical thinking!
  - Is the fit correct?
  - Does the model represent the data?

BM4 fits the data: $K_0 = 54.4(4) \text{ GPa}$
Overall quality of fit

- **Unweighted R value**
  - Smaller is perhaps better
  \[ R = \frac{\sum |y_{obs} - y_{calc}|}{\sum y_{obs}} \]

- **Weighted R-value**
  - Smaller is perhaps better
  \[ R_W = \left( \frac{\sum w(y_{obs} - y_{calc})^2}{\sum w y_{obs}^2} \right)^{\frac{1}{2}} \]

- **Goodness of fit**
  - Weighted-chi-squared
  - Allows for degrees of freedom
  - Smaller really is better
  - \( S = \chi^2_w = \left( \frac{\sum w(y_{obs} - y_{calc})^2}{n - p} \right)^{\frac{1}{2}} \)
  - \( S = 1 \) when model agrees with data within the uncertainties of the data
  - \( S > 1 \)
  - Line misses 2/3 of 1\( \sigma \) error bars
  - Esd's too small, or....
  - Model inadequate
  - Look at pattern of residuals
  - \( S < 1 \)
  - Line passes >2/3 of 1\( \sigma \) error bars
  - Esd's too big, or....
  - Model over-fitted

Goodness of fit

- **\( S = 1 \)**
  - Model agrees with data within the uncertainties of the data
  - Line passes through 2/3 of 1\( \sigma \) error bars
  - Line passes through 95% of 2\( \sigma \) error bars

- **\( S > 1 \)**
  - Line misses 2/3 of 1\( \sigma \) error bars
  - Esd's too small, or....
  - Model inadequate
  - Look at pattern of residuals

- **\( S < 1 \)**
  - Line passes >2/3 of 1\( \sigma \) error bars
  - Esd's too big, or....
  - Model over-fitted
**Fitting Results: anorthoclase 1**

|     | $V_0 : Å^{3}$ | $K_0 : GPa$ | $K' : GPa^{-1}$ | $K'' : GPa^{-1}$ | $\chi^2 / \nu$ | $|P_{obs} - P_{calc}|_{max}$ |
|-----|----------------|-------------|-----------------|------------------|-----------------|------------------------------|
| BM2 | 683.02(18)     | 56.1(3)     | [4.0]           | [-.069]          | 21.2            | -.14                          |
| BM3 | 682.76(14)     | 58.0(6)     | 3.41(15)        | [.063]           | 10.6            | -.073                         |
| BM4 | 682.92         | 54.4(4)     | 6.4(3)          | -1.16(13)        | 0.75            | -.017                         |

Conclude: BM4 fits data best. Is this correct……? Are the parameters physically reasonable?

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**Is the result reasonable?**

- There is no substitute for critical thinking!
  - Are the parameters $K$, $K'$ what you expect for the type of structure?
  - Do they agree with independent measurements?
  - Do they form systematic trends with composition or other parameters?
Anorthoclase: bulk modulus variation

$K'$ is not constant!

A warning about f-F plots

Both $F_E$ and $f_E$ contain $V_0$
- $V_0$ is not known exactly, only experimentally with esd!
- An incorrect $V_0$ curves the $f$-$F$ data
- And the fitted EoS will not pass through the data points!
**Analysing PV data - summary**

- Use $f-F$ plots to examine the data
  - They indicate order of EoS
  - And whether the behaviour is "normal"

- Determine parameters by LS fit
  - Use proper weighting
  - Refine the correct parameters
  - Critically examine the results

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**EoS: Summary**

- The bulk modulus and its derivatives are thermodynamic variables of precise definition:
  \[
  K = -V \left( \frac{\partial P}{\partial V} \right) \\
  K' = \frac{\partial K}{\partial P} \\
  K'' = \frac{\partial K'}{\partial P} = \left( \frac{\partial^2 K}{\partial P^2} \right)
  \]

- An EoS says how these change with $P$

- But there is no absolute thermodynamic basis for specifying a correct form for an EoS
  - All EoS are based upon assumptions

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Maier et al (2011) PRB 83:134106

Maier et al (2011) PRB 83:134106

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