Theory of phonon anharmonicity in MgB$_2$ and related compounds

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Outline

- MgB$_2$ geometry, electronic bands, Fermi surface
- Phonons, e-ph interaction and the E$_{2g}$ mode
- Strong E$_{2g}$ anharmonicity
- Simple model: strong e-ph + small E$_F$
- Conclusions
The Theory of Phonon Anharmonicity in MgB$_2$ and Related Compounds

**MgB$_2$ geometry**

- Boron layers (light blue)
  - Graphite-like (stacking)
  - $a = 3.1\,\text{Å}$, $c = 3.5\,\text{Å}$
- Magnesium planes (yellow)
  - Each Mg atom fills a nearly spherical pore
  - Doubly ionized, donates 2 electrons to the B network

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**“primitive” graphite bands**

- $\sigma$ bands
  - Covalent
  - Essentially 2D
  - Carbon $sp_2$ ($s$ and $p_{x,y}$)
- $\pi$ bands
  - 3D dispersion
  - Carbon $p_z$

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J.M. An, W.E. Pickett, Phys. Rev. Lett. 86, 4366 (2001);  
K.D. Belashchenko, M. van Schilfgaarde, and V.P. Andropov, Phys. Rev. B 64, 092503 (2001);

MgB$_2$ vs. graphite: isoelectronic, but some of the positive charge is now available in the form of positive Mg$^{++}$ ions between the $sp_2$ planes.
Theory of Phonon Anharmonicity in MgB$_2$ and Related Compounds (Aug 21, 2002)

MgB$_2$ bands

- **σ** bands
  - Covalent
  - Strongly 2D
  - Boron sp$_2$ (s and p$_{x,y}$)

- **π** bands
  - 3D dispersion
  - Boron p$_z$-Mg
  - Pulled down w.r.t. σ

\[ J.M. \text{ An, W.E. Pickett, Phys. Rev. Lett. 86, 4366 (2001);} \]
\[ K.D. \text{ Belashchenko, M. van Schilfgaarde, and V.P. Andropov, Phys. Rev. B 64, 092503 (2001);} \]
\[ Y. \text{ Kong, O.V. Dolgov, O. Jepsen, and O.K. Andersen, Phys. Rev. B 64, 020501 (2001);} \]
\[ G. \text{ Satta, G. Profeta, F. Bernardini, A. Continenza, S. Massidda, Phys. Rev. B 64, 104507 (2001).} \]

MgB$_2$ Fermi surface

- Green and blue cylinders, hole like, bonding p$_{x,y}$
- Blue tubular network, hole like, bonding p$_z$
- Red tubular network, electron like, antibonding p$_z$

\[ J. \text{ Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, L.L. Boyer} \]
\[ \text{Phys. Rev. Lett. 86, 4656 (2001)} \]
Phonons: the important one is $E_{2g}$

Kong, Dolgov, Jepsen & Andersen
Phys. Rev. B 64, 020501
DFT + FP-LMTO + LR
- Electronic structure
- Phonon spectrum
- e-ph interaction

$E_{2g}$ mode at $k=0$

**E\(_{2g}\)**: strong e-ph *and* anharmonicity

**Giant Anharmonicity and Nonlinear Electron-Phonon Coupling in MgB\(_2\): A Combined First-Principles Calculation and Neutron Scattering Study**


- In-plane motion of the B atoms
- Change of the B-B orbital overlap
- Large e-ph for the planar, B-derived, \(\sigma\) conduction bands at \(E_F\)
- Band structure with and without a lattice distortion of a zone-center \(E_{2g}\) phonon
- Anharmonicity effectively increases the phonon frequency (~70meV ~80meV)
- Anharmonicity exclusive of \(E_{2g}\)
- Anharmonicity helps superconductivity

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Understanding the \(E_{2g}\) anharmonicity: comparison of MgB\(_2\), AlB\(_2\), and graphite

- AlB\(_2\)
  - much higher frequency (~120meV), NO anharmonicity: expt & theo, K.-P. Bohnen et al. PRL 86, 5771 (2001)
  - Yet the AlB\(_2\) \(\sigma\) bands are very similar (An &. Pickett, PRL 86) to MgB\(_2\); their deformation potential must also be large
- What about graphite? (bands & bonds also very similar)

- Guess: for the \(\sigma\) bands, besides a large \(\partial\varepsilon/\partial u\), the small hole Fermi energy (\(E_{\sigma}^{\text{top}} - E_F\)) is crucial
- Plan:
  - LDA\(^*\) bands, \(E_{2g}\) frozen-phonon total energies for MgB\(_2\), AlB\(_2\), graphite, and virtual graphite++
  - Check deformation potential
  - Check anharmonicity
  - Make a simple model

\(^*\) Based on the ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org)
The shift and splitting is almost the same, but in MgB$_2$, the hole Fermi energy is small and, upon distortion, one of the two $\sigma$ bands completely sinks below the $E_F$ (horiz. line).

In AlB$_2$ instead, both $\sigma$ bands are always below $E_F$.

By artificially charging (+,++) graphite (not shown) we may sweep $E_F$ through the $\sigma$ bands.

L. Boeri et al., PRB 65, 214501 (2002)

E$_{2g}$ phonon: effects on the Fermi surface

- Blue $\sigma$ cylinders expand
- Green $\sigma$ cylinders shrinks and eventually disappears

(numerical k-space integration must be careful)
Frozen $E_{2g}$ phonon energies in MgB$_2$, AlB$_2$, and graphite

Perfectly harmonic phonons all collapse on the $y=x$ straight line in this plot. The symbols correspond to LDA calculations [L. Boeri et al., PRB 65, 214501 (2002)]

Simple model for anharmonicity
Perfect lattice ($u=0$)

Particle No.

\[ N(u=0) = 2 \int_{-W_\sigma}^{\mu=0} N_\sigma d\varepsilon + \int_{-W_\pi}^{\mu=0} N_\pi d\varepsilon = 2N_\sigma W_\sigma + N_\pi W_\pi \]

Energy

\[ E(u=0) = 2 \int_{-W_\sigma}^{\mu=0} N_\sigma \varepsilon d\varepsilon + \int_{-W_\pi}^{\mu=0} N_\pi \varepsilon d\varepsilon = N_\sigma W_\sigma^2 + \frac{1}{2} N_\pi W_\pi^2 \]
Model bands upon lattice distortion

\[ \varepsilon_1(k, u) = \varepsilon_1(k) - gu \]
\[ \varepsilon_2(k, u) = \varepsilon_2(k) + gu \]
\[ \varepsilon_\pi(k, u) = \varepsilon_\pi(k) \]

\( \sigma \) bands: rigid shift
\( \pi \) band: left unchanged

Model total energy upon lattice distortion

\[ E(u) = 2 \sum_{k,i} \varepsilon_i(k) n_i(k, u) + 2 \sum_k \varepsilon_\pi(k) n_\pi(k, u) + 2gu \sum_k [n_2(k, u) - n_1(k, u)] + \frac{1}{2}M \omega_{2u}^2 u^2 \]
**Theory of Phonon Anharmonicity in MgB\(_2\) and Related Compounds**

**Two regimes**

\[ \Delta E(u) = \frac{1}{2} M \omega^2 |g| u^2 - 2 N_\sigma g^2 u^2 \]

For \( g|u| > \varepsilon_{\text{top}} \) the \( \sigma \) band #1 is completely full; it no longer compensates the loss of electrons from the \( \sigma \) band #2. Since the number of electrons must be conserved throughout the distortion, \( \mu \) shifts. This produces anharmonicity.

\[ \mu(u) = \frac{N_\sigma}{N_\sigma + N_\pi} (g|u| - \varepsilon_{\text{top}}) \]

\[ \Delta E(u) = \frac{1}{2} M \omega^2 |g| u^2 - 2 N_\sigma g^2 u^2 + \frac{N_\sigma(2N_\sigma + N_\pi)}{N_\sigma + N_\pi} (g|u| - \varepsilon_{\text{top}})^2 \]

**Model anharmonicity**

Parameters: from LDA

- Hole Fermi energy \( \varepsilon_{\text{top}} \)
- Deformation potential \( g \)
- Harmonic spring constant
- \( N_\sigma, N_\pi \)

L. Boeri et al., PRB 65, 214501 (2002)
Conclusions

- LDA: common features of hexa. systems
- Model: large deformation pots + small $E_F$
- Frequency renormalization \textit{and} anharm.
- Strong renormalization only close to $k=0$
- Way to predict phonon hardening (OKA)
- Anharmonicity; nonadiabaticity ($\omega \sim E_F$)?
- Real materials like graphite++?
**Theory of Phonon Anharmonicity in MgB$_2$ and Related Compounds (Aug 21, 2002)**

**LDA data fit**

Parameters extracted from LDA data.

<table>
<thead>
<tr>
<th></th>
<th>$g$</th>
<th>$\epsilon_0^{\text{top}}$</th>
<th>$a_2$</th>
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<tr>
<td>MgB$_2$</td>
<td>12.02</td>
<td>0.45</td>
<td>12</td>
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<td>AlB$_2$</td>
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<td>-1.63</td>
<td>44</td>
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<tr>
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</tr>
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</table>

**Parameters**

For those who don’t trust me...

**AlB$_2$ and graphite**:

$\Delta F(u) = \frac{1}{2} M \omega_g^2 u^2 = a_2 u^2$

From $a_2$ we obtain $\omega_{2g}$.

**MgB$_2$ and graphite++**:

$\Delta F(u) = \frac{1}{2} M \omega_g^2 u^2 - 2 N_{\text{eff}} u^2 = a_2 u^2 \quad |u| < u_c$

$\Delta F(u) = \frac{1}{2} M \omega_g^2 u^2 - 2 N_{\text{eff}}^2 u^2 + \frac{N_{\text{eff}}^3 + N_{\text{eф}}}{N_{\text{eф}} + N_{\text{ф}}} (|u| - \epsilon_0^{\text{top}})^2$

$N_{\text{eф}}, N_{\text{ф}}$ adjusted to fit LDA $E$ vs. $u$ data

- MgB$_2$: 0.11, 0.39
- graphite++: 0.07, 0.30