KITP-CEM, Wednesday, August 21, 2002

Theory of phonon anharmonicity in MgB_2 and related compounds

Lilia Boeri, Emmanuele Cappelluti,
Luciano Pietronero, and GBB

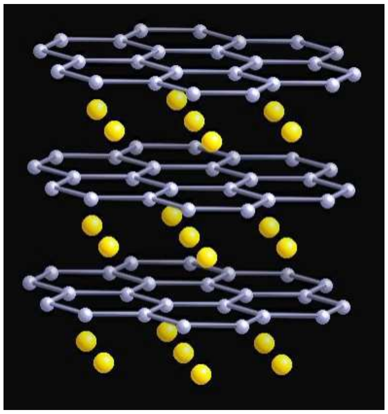
INFM Center for Statistical mechanics and Complexity and Dipartimento di Fisica, Università La Sapienza, 00185 Roma, Italy

MIUR Grant COFIN2001

Outline

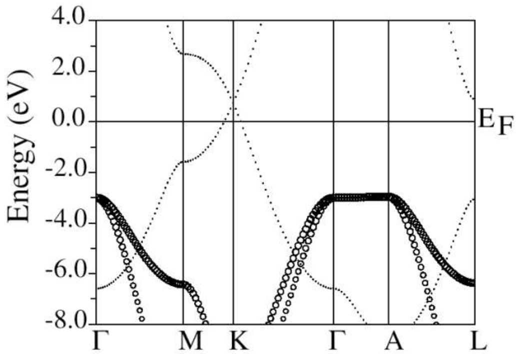
- MgB_2 geometry, electronic bands, Fermi surface
- Phonons, e-ph interaction and the E_{2g} mode
- Strong E_{2g} anharmonicity
- Simple model: strong e-ph + small E_F
- Conclusions

MgB_2 geometry



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

"primitive" graphite bands



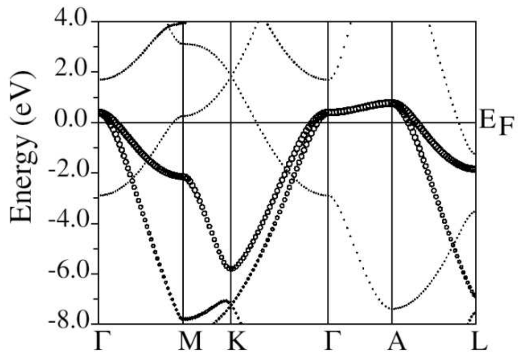
- σ bands
  - Covalent
  - Essentially 2D
  - Carbon sp_2 (s and $p_{x,y}$)
- π bands
  - 3D dispersion
  - Carbon p_z

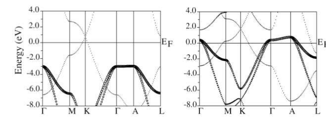
J.M. An, W.E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001);
K.D. Belashchenko, M. van Schilfgaarde, and V.P. Andropov,Phys. Rev. B **64**, 092503 (2001);

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

MgB_2 bands

Effect of the Mg ions, besides ionization & donation of electrons to the B network

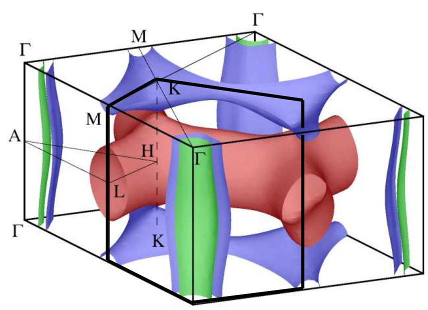




- σ bands
  - Covalent
  - Strongly 2D
  - Boron sp_2 (s and $p_{x,y}$)
- π bands
  - 3D dispersion
  - Boron p_z-Mg
  - Pulled down w.r.t. σ

J.M. 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);
J. Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, L.L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001);
Y. Kong, O.V. Dolgov, O. Jepsen, and O.K. Andersen, Phys. Rev. B **64**, 020501 (2001);
G. Satta, G. Profeta, F. Bernardini, A. Continenza, S. Massidda, Phys. Rev. B **64**, 104507 (2001).

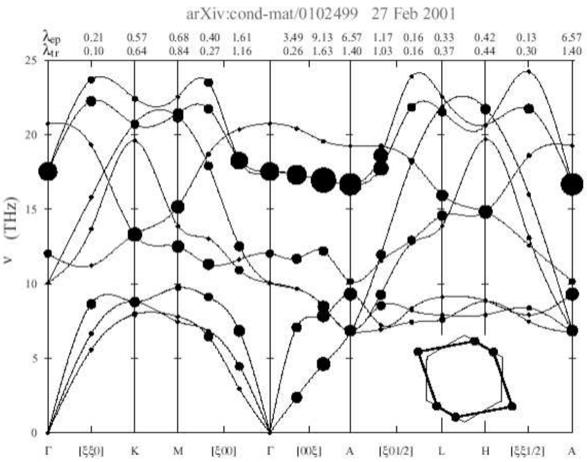
MgB_2 Fermi surface



- 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. Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, L.L. Boyer
Phys. Rev. Lett. **86**, 4656 (2001)

Phonons: the important one is E_{2g}



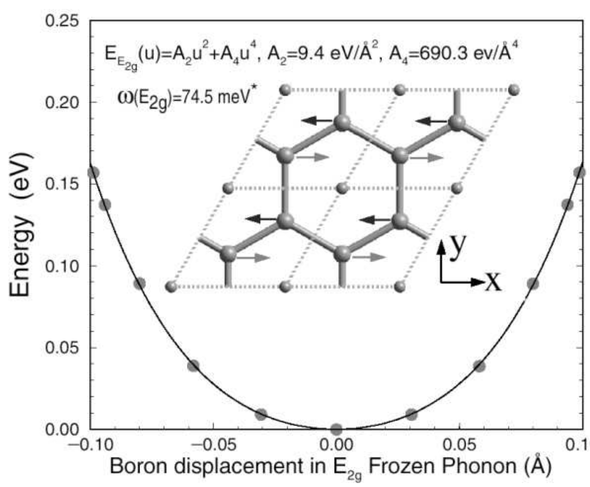
Kong, Dolgov,
Jepsen & Andersen
Phys. Rev. B **64**, 020501

DFT + FP-LMTO + LR

- Electronic structure
- Phonon spectrum
- e-ph interaction

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

T. Yildirim et al., Phys. Rev. Lett. **87**, 037001 (2001)
K. Kunc et al., J. Phys.: Cond. Mat. **13**, 9945 (2001)

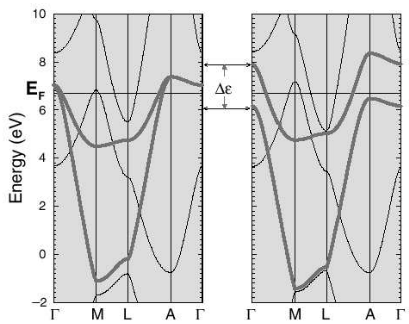


E_{2g} : strong e-ph *and* anharmonicity

VOLUME 87, NUMBER 3 PHYSICAL REVIEW LETTERS 16 JULY 2001

Giant Anharmonicity and Nonlinear Electron-Phonon Coupling in MgB_2: A Combined First-Principles Calculation and Neutron Scattering Study

T. Yildirim,[1] O. Gülseren,[1,2] J. W. Lynn,[1] C. M. Brown,[1,3] T. J. Udovic,[1] Q. Huang,[1,3] N. Rogado,[4] K. A. Regan,[4] M. A. Hayward,[4] J. S. Slusky,[4] T. He,[4] M. K. Haas,[4] P. Khalifah,[4] K. Inumaru,[4] and R. J. Cava[4]



- In-plane motion of the B atoms
- Change of the B-B orbital overlap
- Large e-ph for the planar, B-derived, σ 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~~

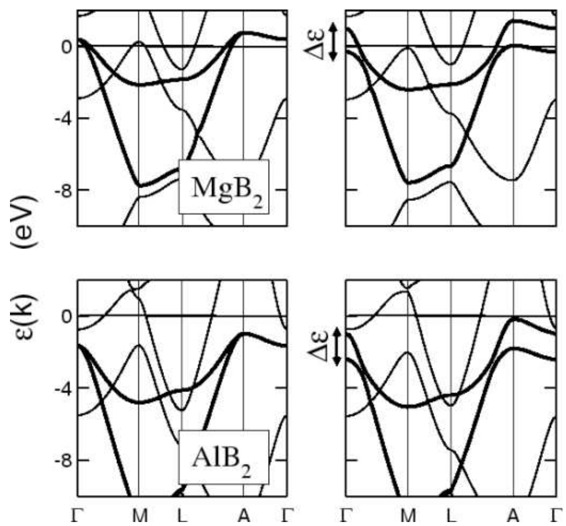
Understanding the E_{2g} anharmonicity: comparison of MgB_2, AlB_2, and graphite

- AlB_2
  - much higher frequency (~120meV), NO anharmonicity: expt & theo, K.-P. Bohnen et al. PRL **86**, 5771 (2001)
  - Yet the AlB_2 σ 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 σ bands, besides a large $\partial\varepsilon/\partial u$, the small hole Fermi energy ($\varepsilon_\sigma^{top} - E_F$) 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

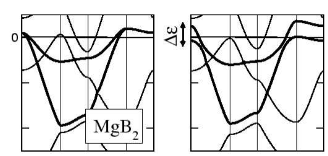
*** Based on the ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org)**

E_{2g} deformation potential in MgB_2, AlB_2, and graphite

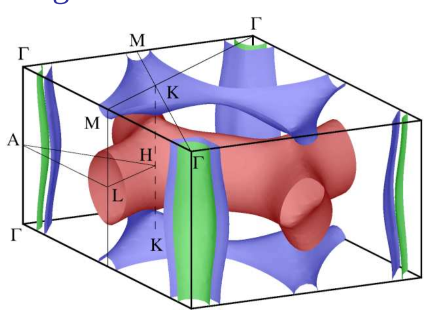


- Bands of the perfect crystal (left) and of the E_{2g}- distorted crystal for MgB_2 (upper panel) and AlB_2 (lower panel).
- The shift and splitting is almost the same, but in MgB_2 the hole Fermi energy is small and, upon distortion, one of the two σ bands completely sinks below the E_F (horiz. line).
- In AlB_2, instead, both σ bands are always below E_F.
- By artificially charging (+,++) graphite (not shown) we may sweep E_F through the σ bands.

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



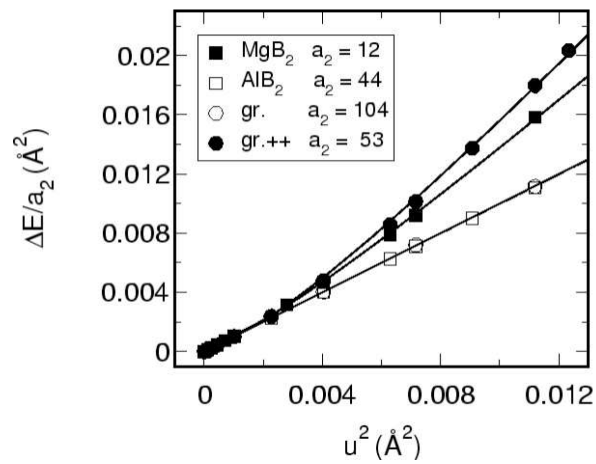
E_{2g} phonon: effects on the Fermi surface



- Blue σ cylinders expand
- Green σ cylinders shrinks and eventually disappears

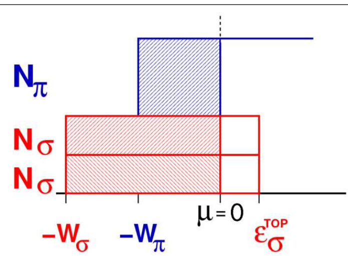
(numerical k-space integration must be careful)

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)



π band, with

DOS = Nπ if −Wπ < ε
 = 0 otherwise

2 degenerate σ bands, each with

DOS = Nσ if −Wσ < ε < μ = 0
 = 0 otherwise

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

$$\varepsilon_1(\mathbf{k},u) = \varepsilon_1(\mathbf{k}) - gu$$

$$\varepsilon_2(\mathbf{k},u) = \varepsilon_2(\mathbf{k}) + gu$$

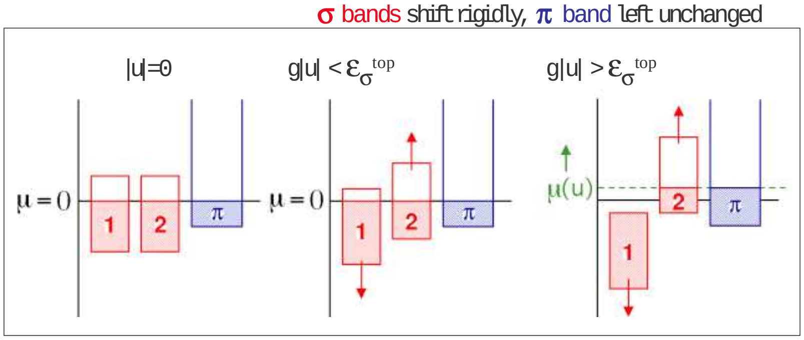
σ bands : rigid shift

$$\varepsilon_\pi(\mathbf{k},u) = \varepsilon_\pi(\mathbf{k})$$

π band : left unchanged

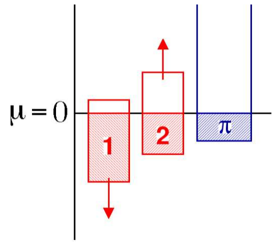
Model total energy upon lattice distortion

σ bands shift rigidly, π band left unchanged



$$E(u) = 2\sum_{\mathbf{k},i} \varepsilon_i(\mathbf{k}) n_i(\mathbf{k},u) + 2\sum_{\mathbf{k}} \varepsilon_\pi(\mathbf{k}) n_\pi(\mathbf{k},u) +$$
$$+ 2gu \sum_{\mathbf{k}} [n_2(\mathbf{k},u) - n_1(\mathbf{k},u)] + \tfrac{1}{2} M \omega_{2q}^2 u^2$$

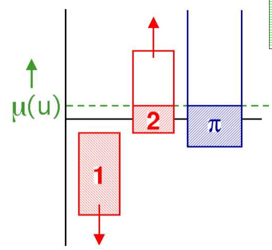
Two regimes



$g|u| < \varepsilon_\sigma^{top}$

$$\Delta E(u) = \frac{1}{2} M \omega_{2g}^2 u^2 - 2 N_\sigma g^2 u^2$$

For $g|u| > \varepsilon^{top}$ the σ band #1 is completely full; it no longer compensates the loss of electrons from the σ band #2. Since the number of electrons must be conserved throughout the distortion, μ shifts. This produces anharmonicity.

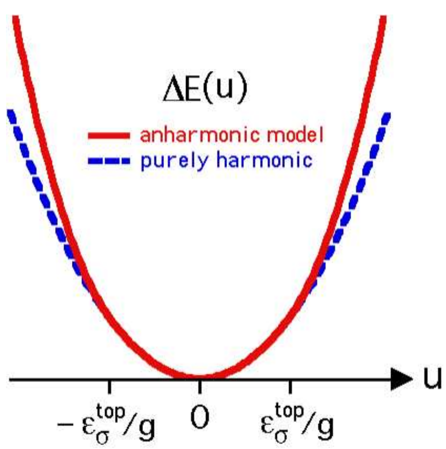


$g|u| > \varepsilon_\sigma^{top}$

$$\mu(u) = \frac{N_\sigma}{N_\sigma + N_\pi} \left(g|u| - \epsilon_\sigma^{top}\right)$$

$$\Delta E(u) = \frac{1}{2} M \omega_{2g}^2 u^2 - 2 N_\sigma g^2 u^2 + \frac{N_\sigma (2N_\sigma + N_\pi)}{N_\sigma + N_\pi} \left(g|u| - \epsilon_\sigma^{top}\right)^2$$

Model anharmonicity



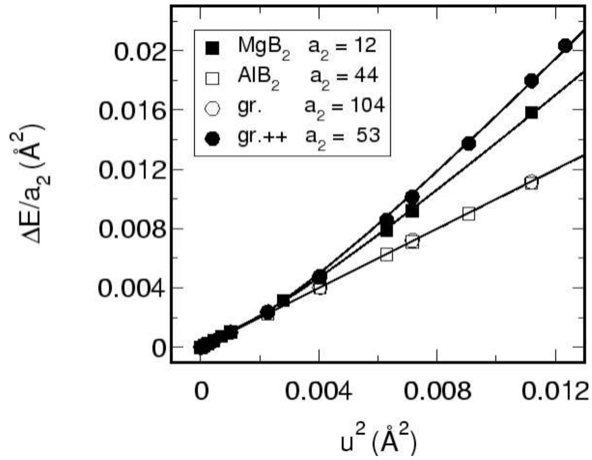
Parameters: from LDA

- Hole Fermi energy ε_σ^{top}
- Deformation potential g
- Harmonic spring constant
- $N\sigma$, $N\pi$

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

Frozen E_{2g} phonon energies: model vs. LDA

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



The symbols correspond to LDA calculations.
Perfectly harmonic phonons all collapse on the y=x straight line in this plot.
The other solid lines in this plot correspond to the simple model of anharmonicity.

Conclusions

- LDA: common features of hexa. systems
- Model: large deformation pots + small E_F
- Frequency renormalization *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++?

Parameters

For those who don't trust me...

LDA data fit

Parameters extracted from LDA data.

	g	ϵ_σ^{top}	a_2
MgB_2	12.02	0.45	12
AlB_2	11.74	-1.63	44
gr.	28.29	-2.89	104
gr.$^{++}$	30.86	1.17	53

AlB_2 and graphite :

$$\Delta E(u) = \frac{1}{2} M \omega_{2g}^2 u^2 = a_2 u^2$$

From a_2 we obtain ω_{2g}.

MgB_2 and graphite^{++} :

$$\Delta E(u) = \frac{1}{2} M \omega_{2g}^2 u^2 - 2 N_\sigma g^2 = a_2 u^2 \qquad |u| < u_c$$
$$\Delta E(u) = \frac{1}{2} M \omega_{2g}^2 u^2 - 2 N_\sigma g^2 u^2 + \frac{N_\sigma (2N_\sigma + N_\pi)}{N_\sigma + N_\pi} (g|u| - \epsilon_\sigma^{top})^2$$

N_σ, N_π adjusted to fit LDA E *vs.* u data

MgB_2 : 0.11, 0.39
graphite^{++} : 0.07, 0.30