Ab-initio Lattice Dynamics And Thermal Expansion of Be (0001) Surface

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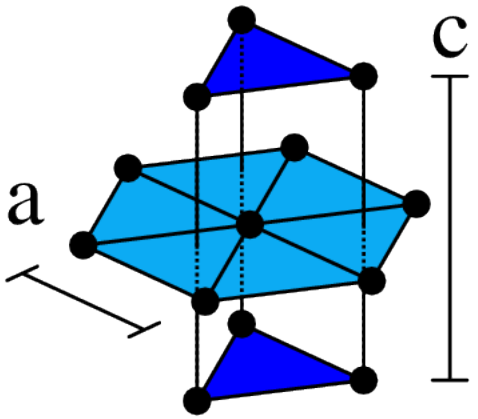
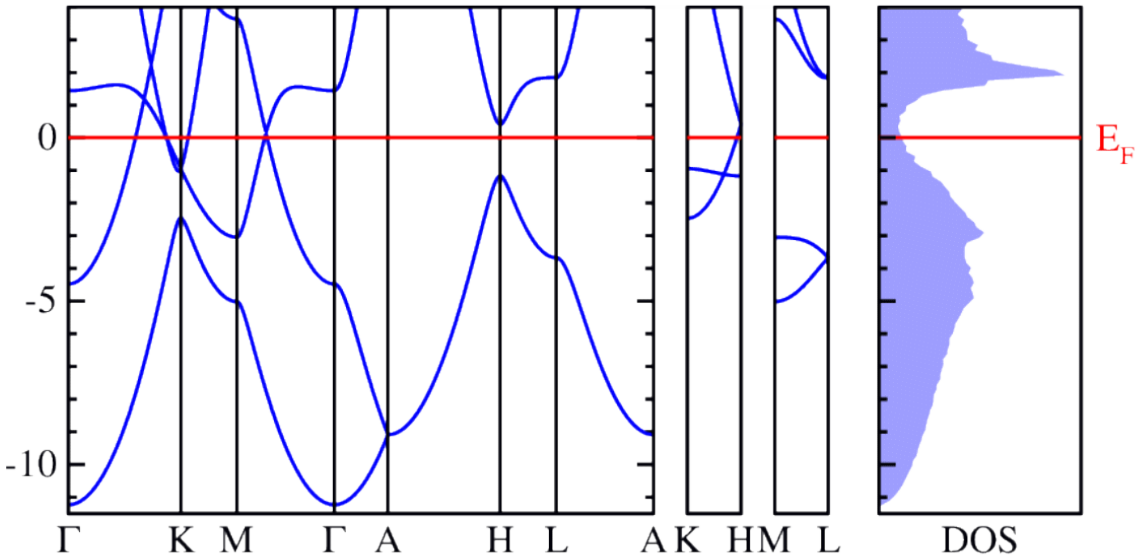
Beryllium: $1s^2\ 2s^2\ 2p^0$

s-p bonded by hybridization

Be_2 molecule: weakly bound (1nn)

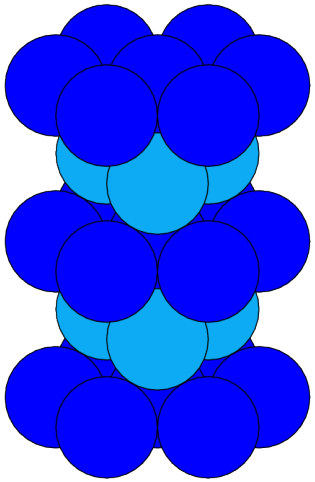
Bulk: Hexagonal Close Packed metal,
strongly bound (12nn),
contracted c/a ratio.
Partially covalent bond character





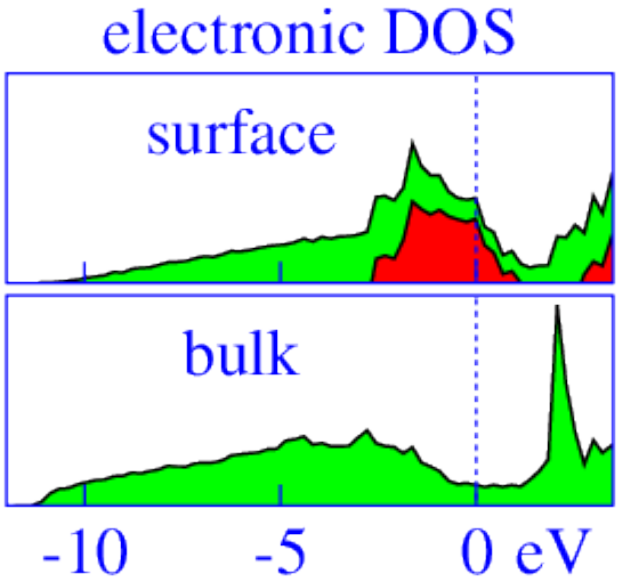
Surfaces ?

Be (0001) Surface



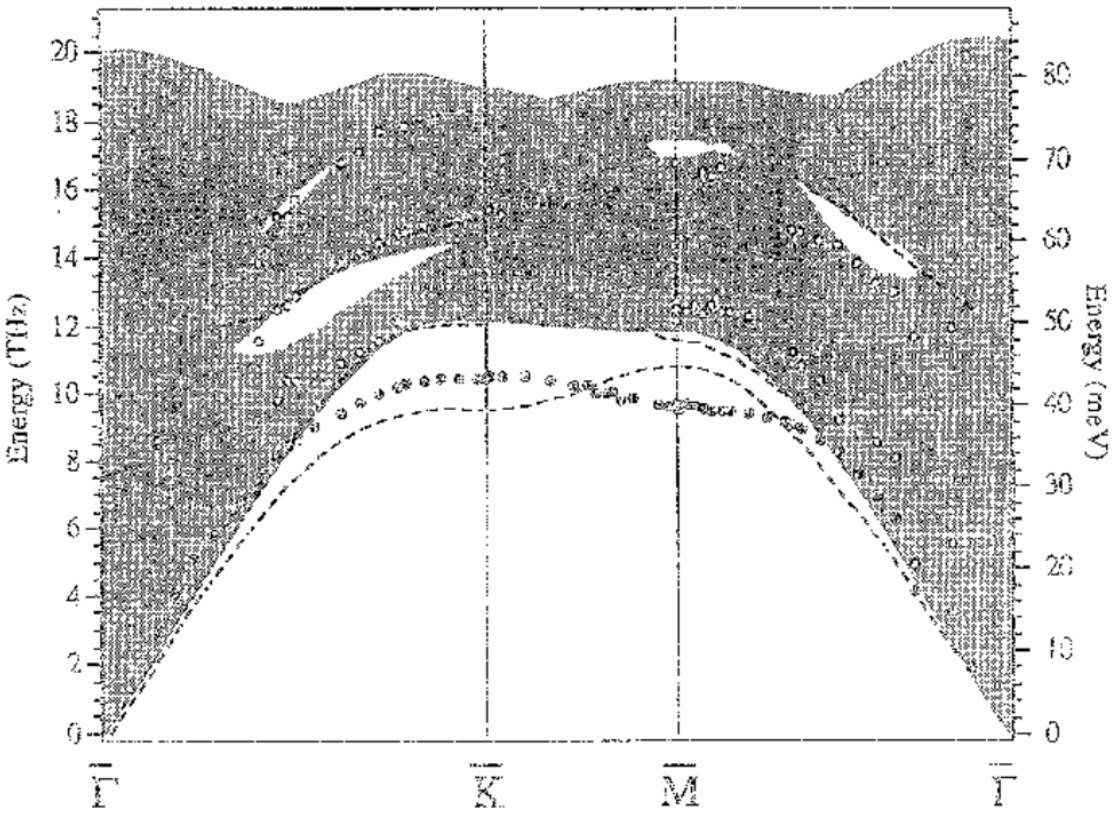
	300K	LDA	LDA
Δd_{12}	$+5.8\%$	$+2.7\%$	$+3.2\%$
Δd_{23}	-0.2%	$+1.2\%$	$+1.0\%$
Δd_{34}	$+0.2\%$	$+0.6\%$	$+0.4\%$

[300K] HL Davis et al. PRL 68, 2632 (1992)
[LDA] R Stumpf and PJ Feibelmann, PRB 51, 13748 (1995)
[LDA] M Lazzeri and SdG, Surf Sci 402–404, 715 (1998)



Surface Phonons form EELS

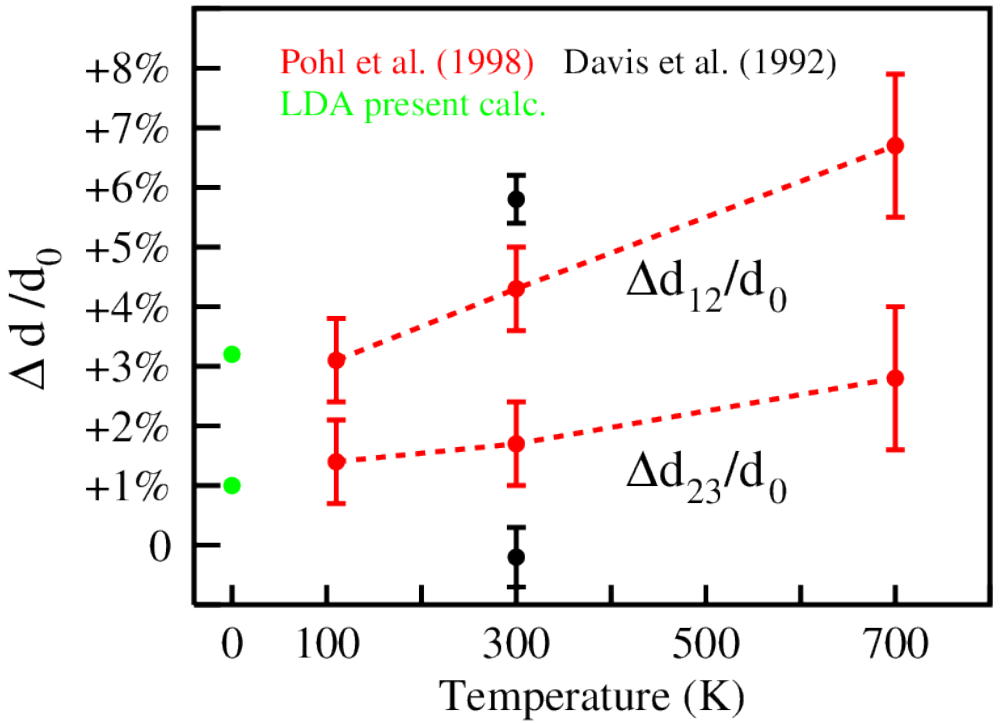
JB Hannon, EJ Mele and EW Plummer, PRB 53, 2090 (1996)



- Intense EELS features (Rayleigh wave)
- Weak EELS features
- Truncated bulk model

Anomalously Large Thermal Expansion !

K Pohl, J-H Cho, K Terakura, M Scheffler, and EW Plummer,
PRL 80, 2853 (1998)



At low temperature theory and experiment are in excellent agreement

α_{surf} is 6 times larger than α_{bulk} !

Computational details

- Local-density approximation (LDA) to DFT
- Plane wave (PW) pseudopotential (PP) approach
- PW's up to Ekin < 22 Ry
- PP with nlcc for Be
- Special points + smearing for BZ integration
- Supercell geometry to simulate isolated surfaces
  - 12 Be-layers
  - ~8 layers of vacuum
- Full structural optimization

- Vibrational properties from DFPT

- Thermal expansion from free energy in the Quasi-Harmonic Approximation (QHA)

- Validity of the QHA confirmed by MD simulations

Finite Temperature Properties of Solids

- Thermal expasivity

- Temperature dependence of elastic constants and other properties

- Temperature induces structural phase transitions

First-Principles Molecular Dynamics

$$\langle A \rangle = \frac{1}{Z} \int e^{-\beta E(q)} A(q) d^{3N} q = \lim_{T \to \infty} \frac{1}{T} \int A(q(t)) dt$$

- Above the Debye tempeature
- Long simulations needed at low temperature

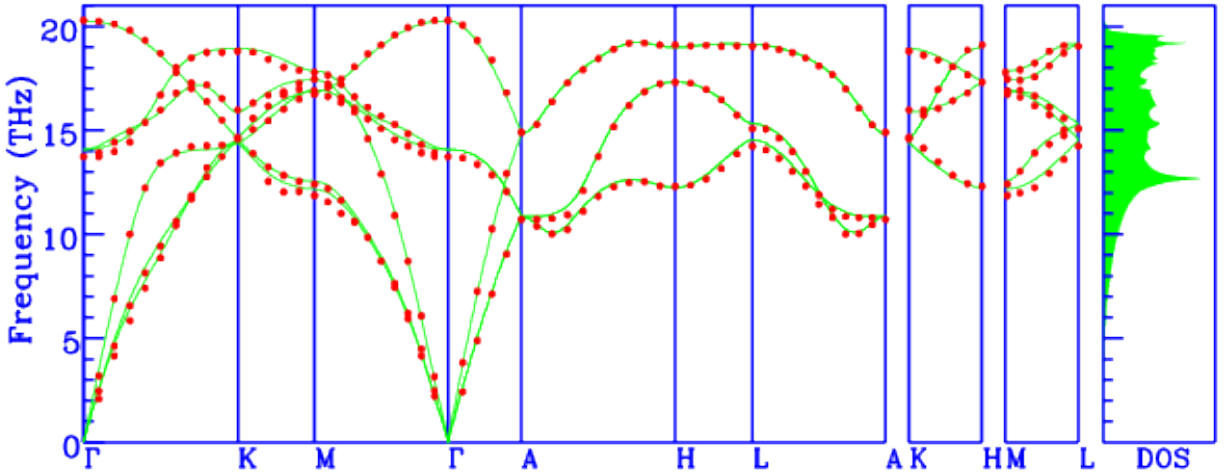
Quasi-Harmonic Approx + ab-initio Phonons

$$F(a) = E(a) + k_B T \sum_{\nu,q} \log \left[2 \sinh \left(\frac{\hbar \omega_\nu(q)}{2 k_B T} \right) \right]$$

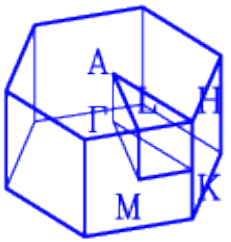
- well below the melting temperature
- both accurate and efficient using DFPT

Bulk Beryllium

Phonon Dispersion

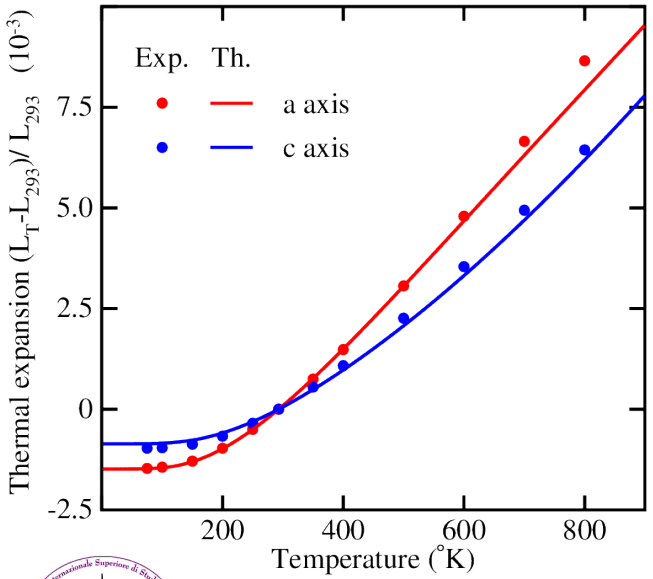


[Th] M Lazzeri & SdG, SS 402-404, 715 (1996)
[Exp] Stedman *et al*, J Phys F 6, 157 (176)



Structure

	Th	*Exp*
$a(a.u.)$	4.25	4.33
c/a	1.572	1.568
$B(GPa)$	125	110
ν_P	0.04	0.02/0.05

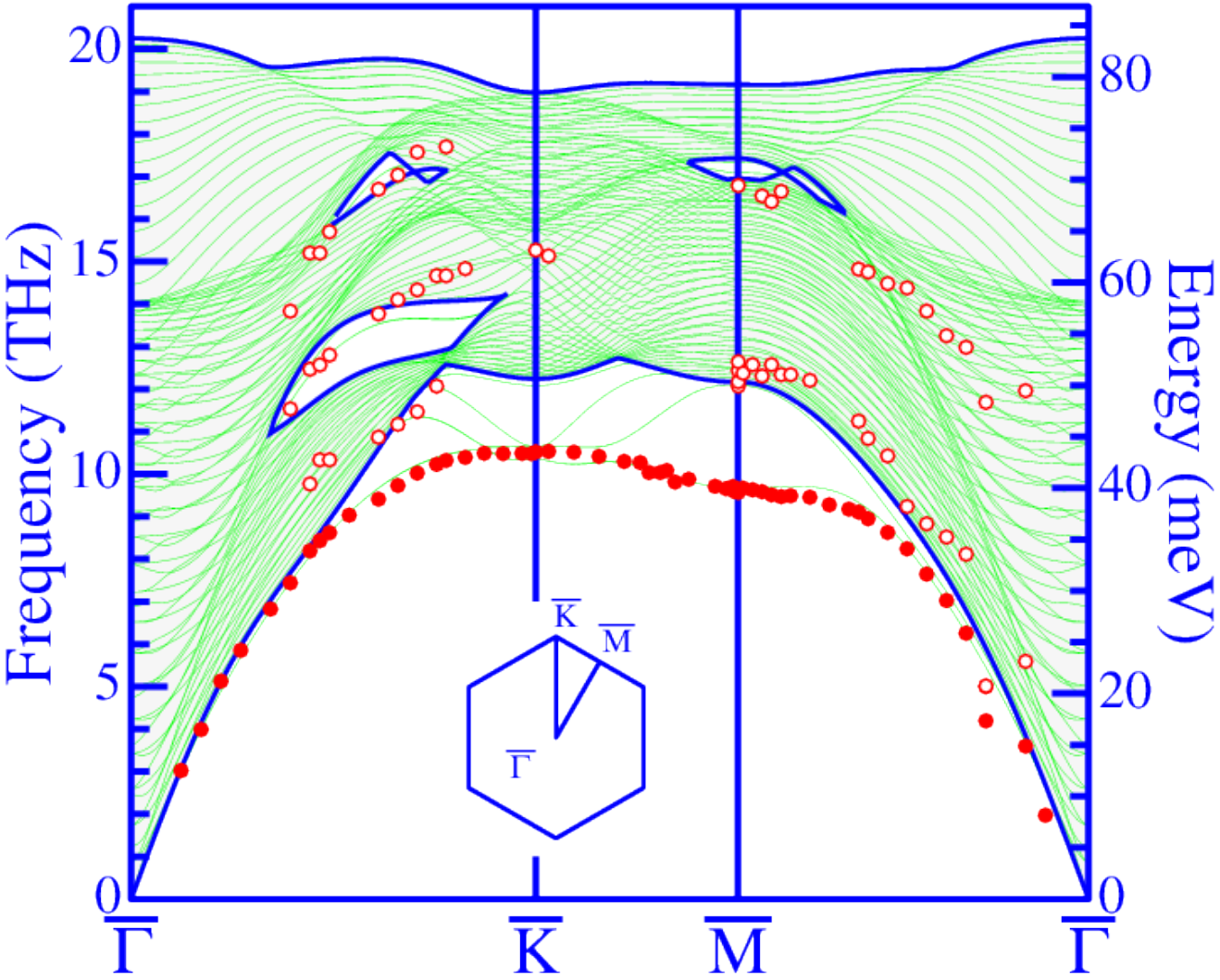


Thermal Expansion

Th: M Lazzeri & SdG, PRL 81, 2096 (1998)

Exp: *American Institute of Physics Handbook*, (McGraw-Hill, NY 1972)

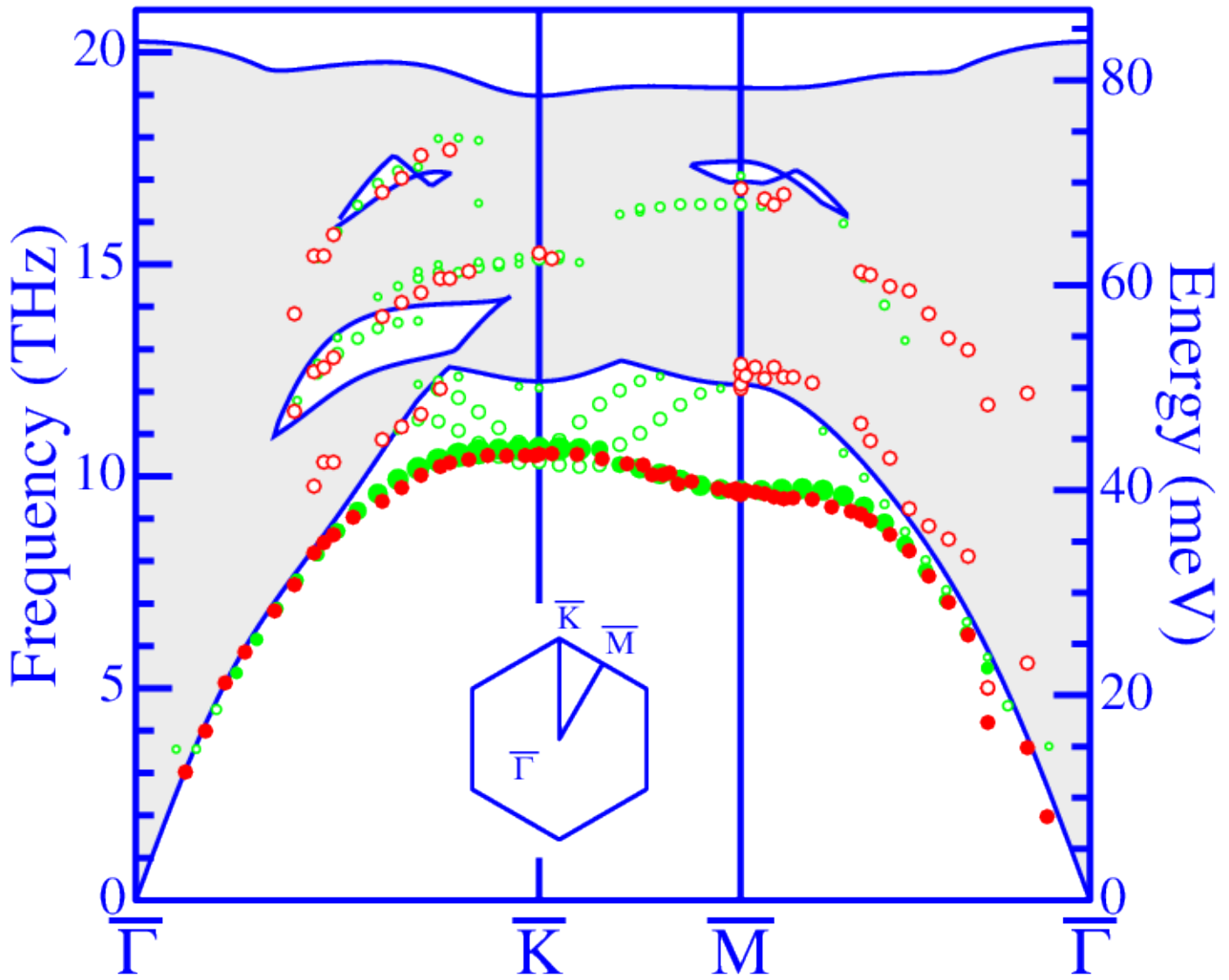
Phonon Dispersions of Be (0001)



EELS data: intense features (Rayleigh wave)

EELS data: weak features

EELS: JB Hannon, EJ Mele and EW Plummer, PRB 2090 (1996)



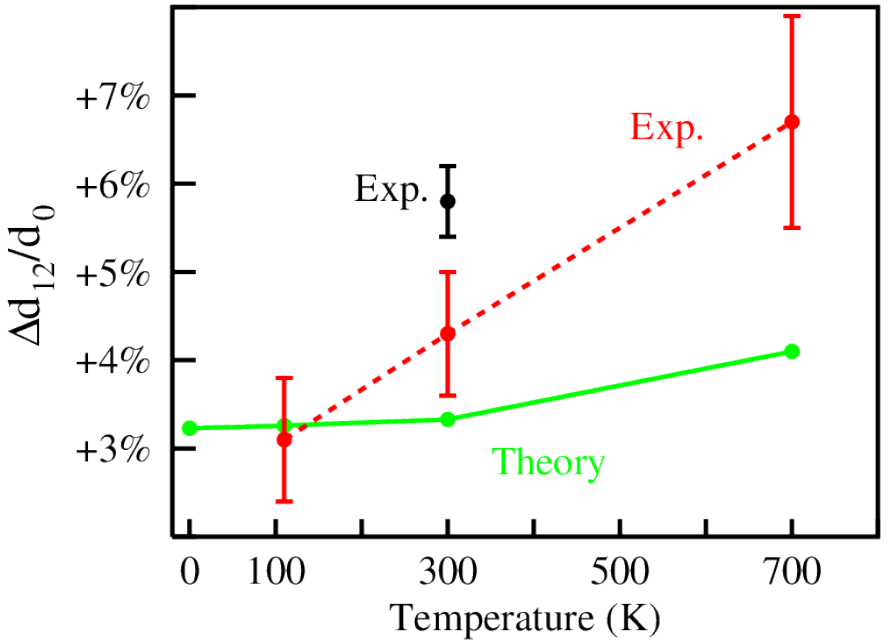
Theory: more than 30% (z-polarized) on the top layer

Theory: more than 50% on the 3 topmost layers

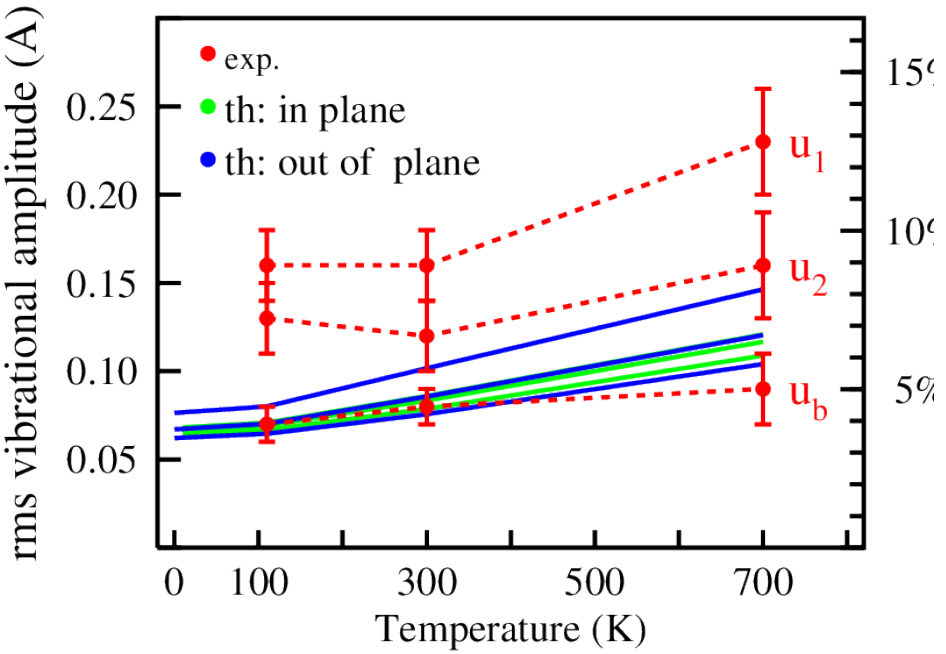
EELS data: intense features (Rayleigh wave)

EELS data: weak features

Surface Thermal Expansion

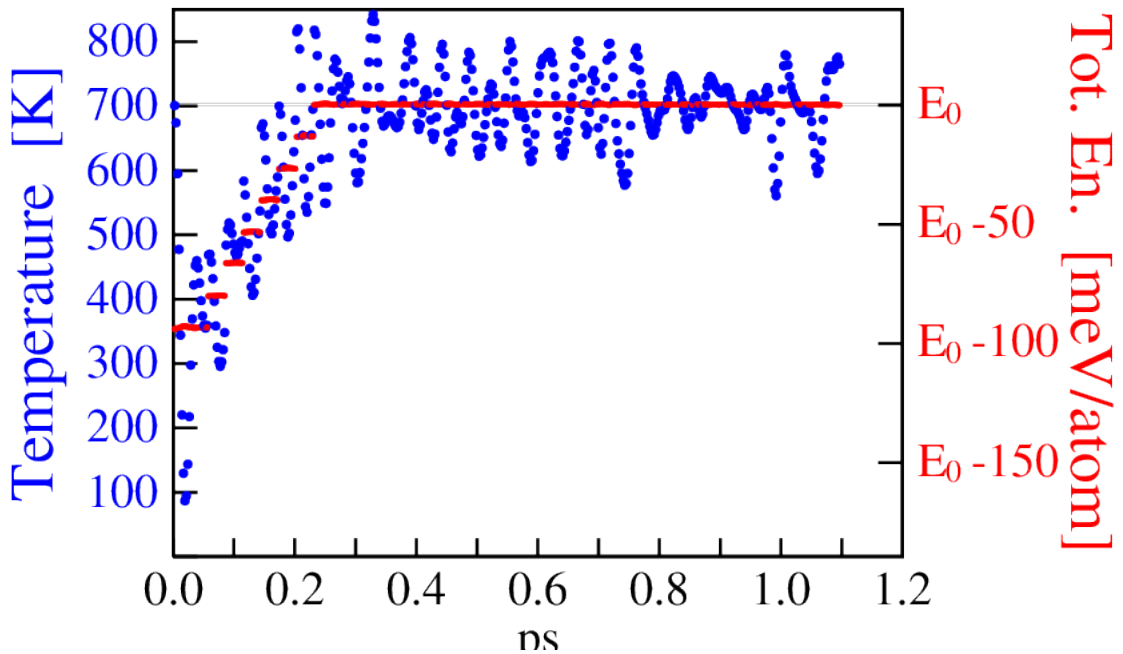


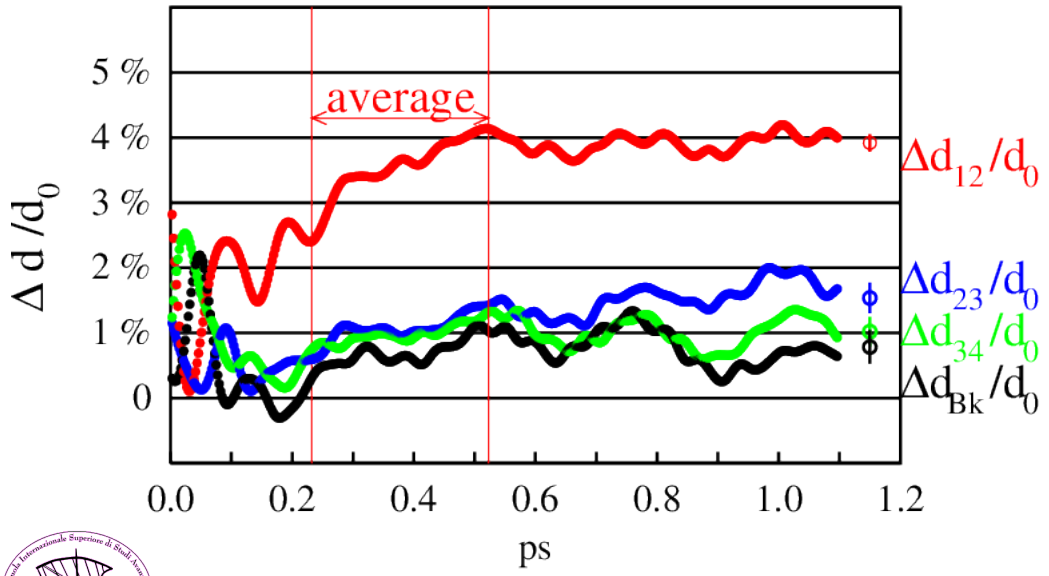
Vibrational Amplitude



Exp: LEED I-V HL Davis et al., PRL 68, 2632 (1992)
Exp: LEED I-V K Pohl et al., PRL 80, 2853 (1998)
Theory: M Lazzeri & SdG, PRL 81 2096 (1998)

First Principles Molecular Dynamics





700 K layer relaxation

	FPMD	*QHA*
Δd_{12}	$+3.9\%$	$+3.6\%$
Δd_{23}	$+1.6\%$	$-$
Δd_{34}	$+1.1\%$	$-$

700 K r.m.s. displ.

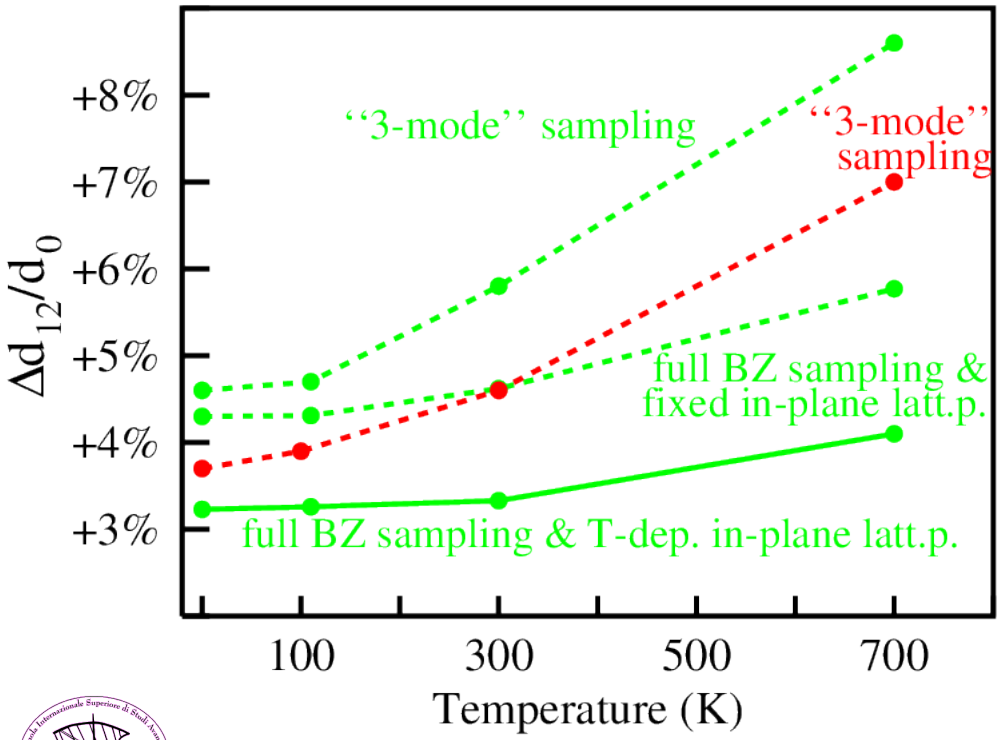
	FPMD	*QHA*
$u_1(\AA)$	0.16	0.14
$u_2(\AA)$	0.12	0.11
$u_3(\AA)$	0.11	0.10

Surface Thermal Expansion
Importance of the BZ sampling

Surface thermal expansion has been calculated by simplified QHA calculations where BZ sampling is replaced by 3 periodic surface modes.

Ag(111) S Narasimhan and M Scheffler, Z Chem Phys 202, 253 (1997)
Rh(001) J-H Cho and M Scheffler, PRL 78, 1299 (1997)
Be(0001) K Pohl *et al.*, PRL 80, 2853 (1998)

Accurate BZ sampling may be very important !

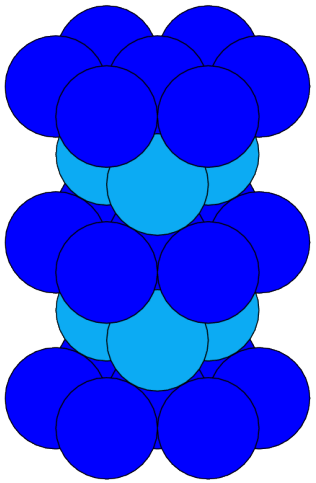


Theory:
M Lazzeri & SdG,
PRL 81, 2096 (1998)

Theory:
K Pohl, J-H Cho, K Terakura,
M Scheffer & EW Plummer,
PRL 80, 2853 (1998)

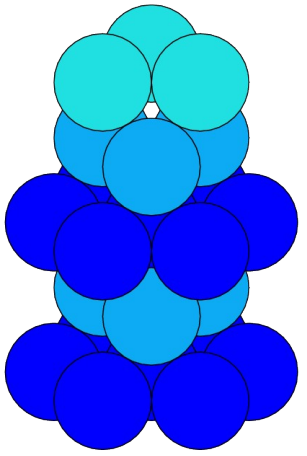
FCC-terminated Be (0001) Surface

FCC

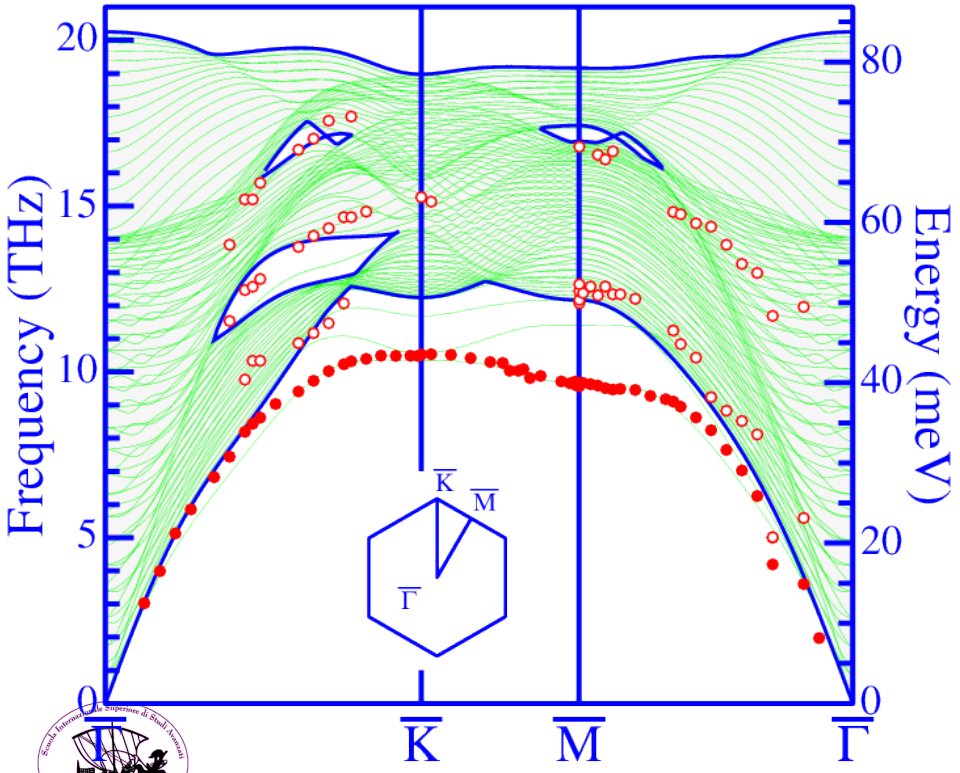


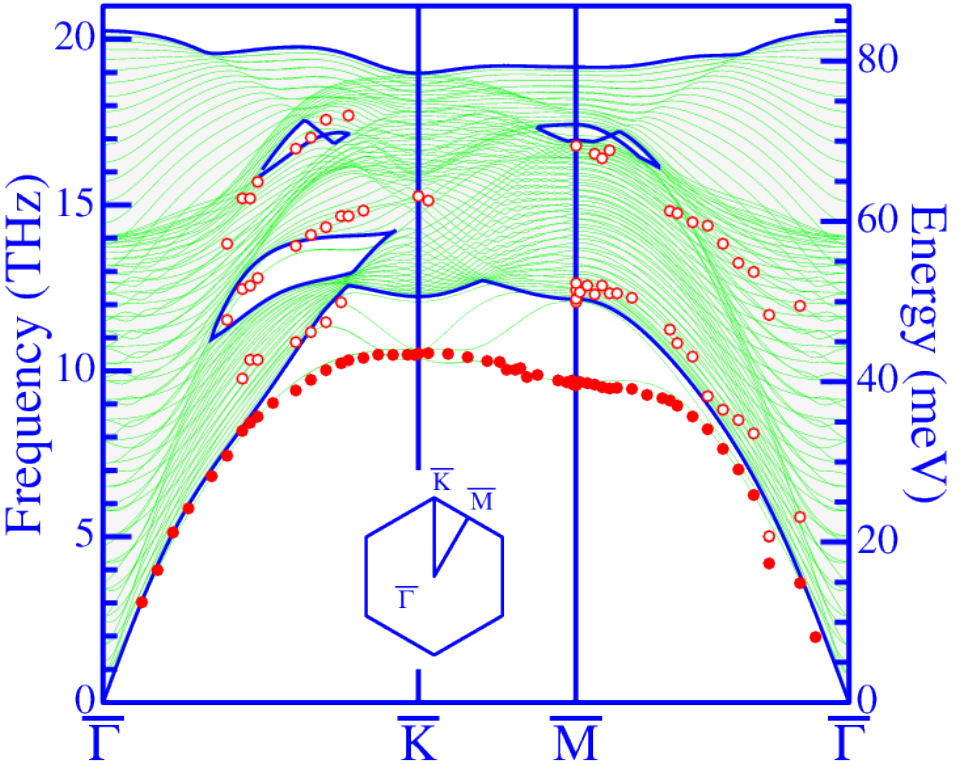
$$\Delta d_{12} \quad +5.4\%$$
$$\Delta d_{23} \quad +2.3\%$$
$$\Delta d_{34} \quad +0.1\%$$
$$\ldots$$

HCP



$$\Delta d_{12} \quad +3.2\%$$
$$\Delta d_{23} \quad +1.0\%$$
$$\Delta d_{34} \quad +0.4\%$$
$$\ldots$$





Conclusions

- Excellent agreement between teoretical and experimental low temperature structure.

- Excellent agreement between teoretical and experimental low surface vibrations.

- Surface thermal expansion:

  Quasi-Harmonic Approximation is accurate up to High temperature

  Accurate BZ sampling is necessary

  The ideally flat and clean Be(0001) surface displays a much smaller expansion than observed by LEED I-V

THE END