SISSA ISAS

Temperature Effects on Surface Core Level Spectra

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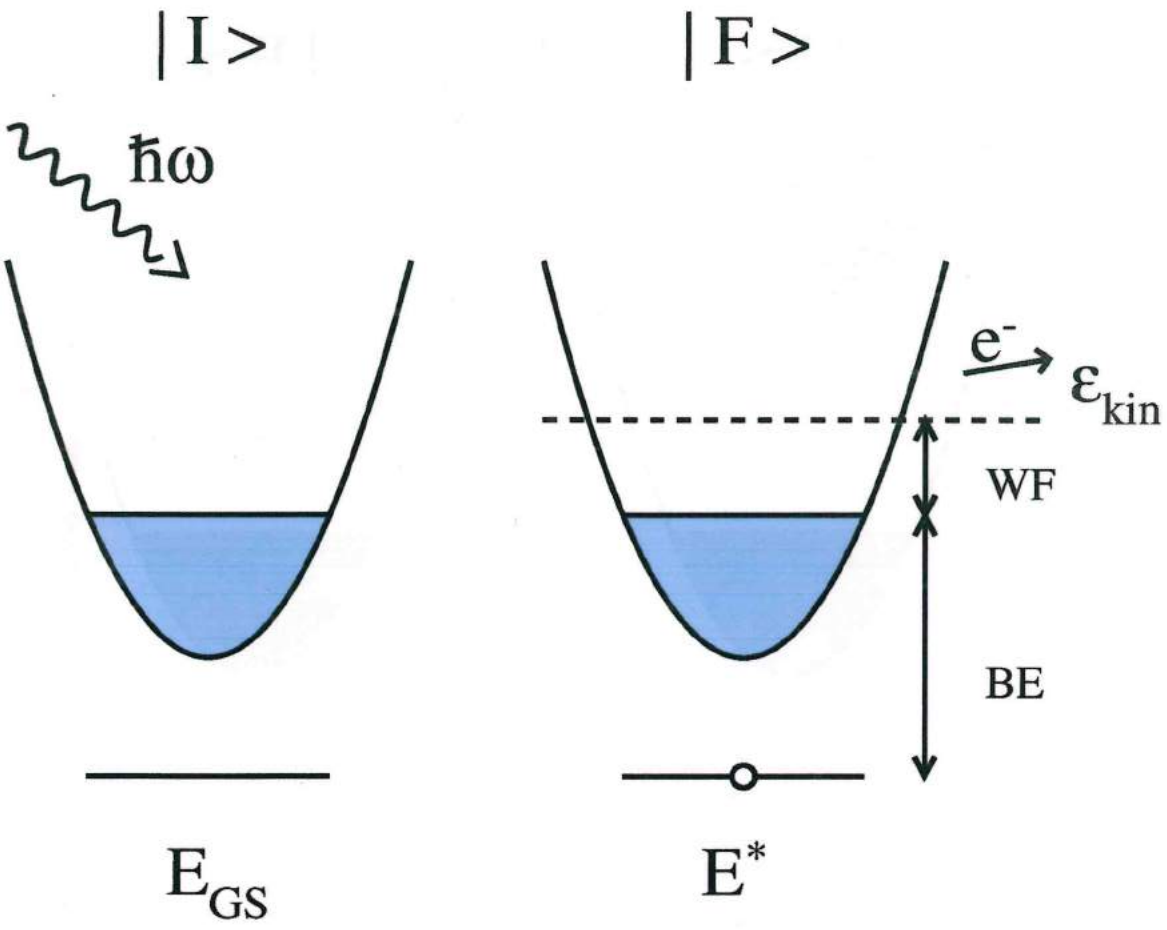
SISSA and INFM-Democritos

Outline

- Calculation of vibrational broadening of SCLS
- Be (0001)
  - Core Level Linewidth vibrational fine Structure
    C.-O. Almbladh, N. Vast
  - Surface Thermal Expansion from SCLS
    A. Baraldi, S. Lizzit, K. Pohl, Ph. Hofmann
- Rh (001)
  - Surface Enhancement of Vibrational Broadening
    D. Loffreda

Final State theory of SCLS



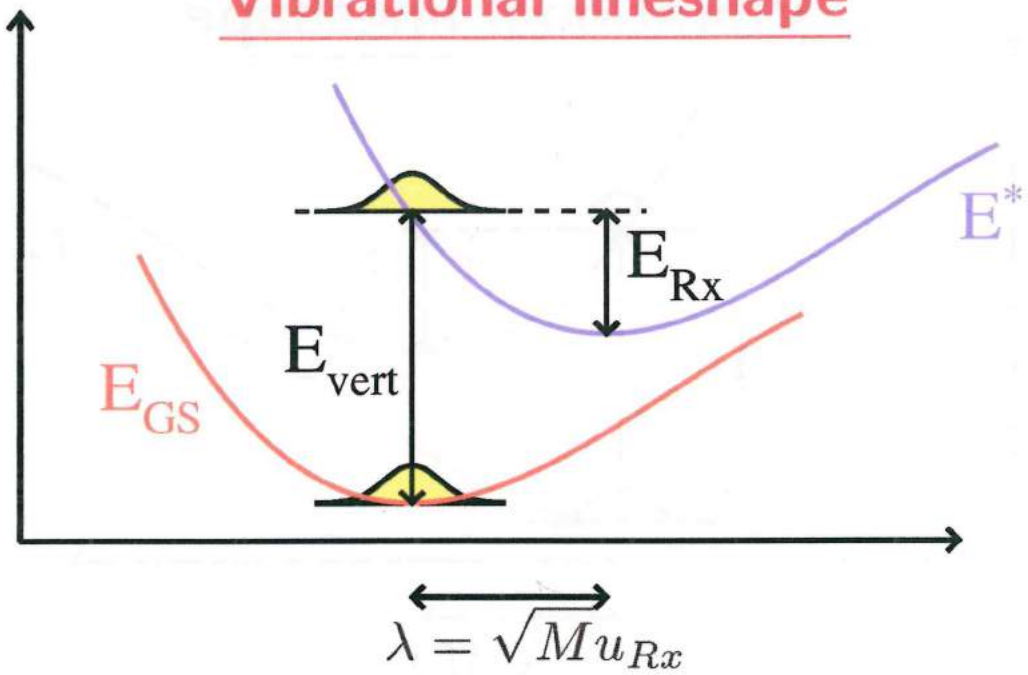
$$BE = E^* - E_{GS} = \hbar\omega - \varepsilon_{kin} - WF$$

$$BE = E^{AE}[(N-1)A + A^*] - E^{AE}[NA]$$

$$= E^{PS}[(N-1)A + A^*] - E^{PS}[NA]$$
$$+ \quad E^{AE}[A^*] - E^{AE}[A] - E^{PS}[A^*] + E^{PS}[A]$$

E Pehlke and M Scheffler Phys Rev Lett **71** 2338 (1993)

Vibrational lineshape



$$P_{i\to f}(\omega) = |\langle i|\mathbf{e}.\mathbf{p}|f\rangle|^2 \, c(\omega)$$

$$c(\omega) = \left\langle \sum_{n'} |\langle n|n'\rangle|^2 \, \delta(\hbar\omega - (E_{f,n'} - E_{i,n})) \right\rangle_i$$

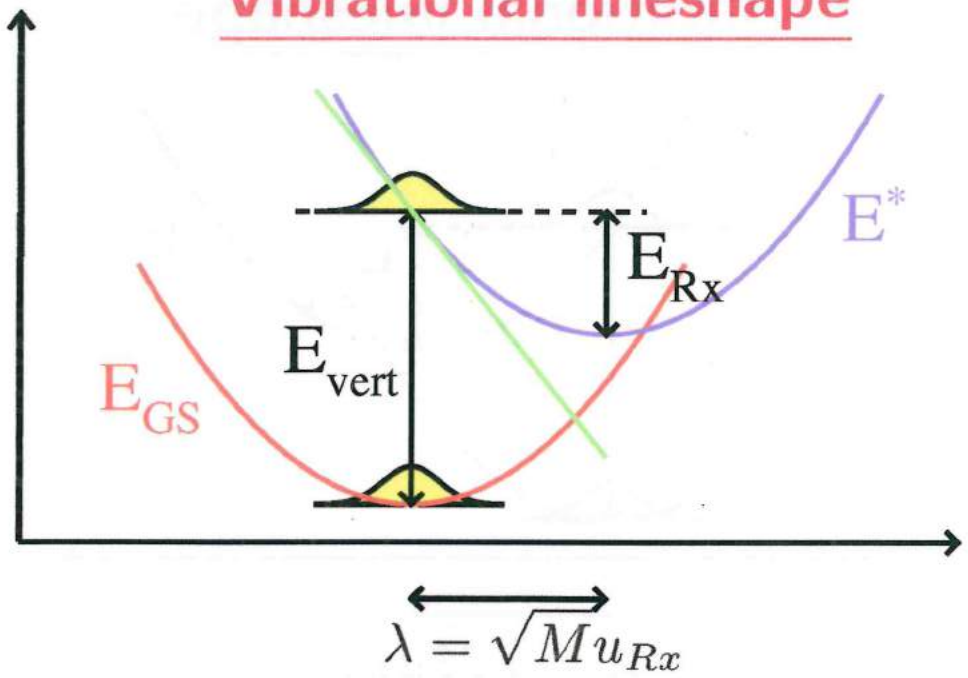
computed Fourier transforming

$$c(t) = \frac{\mathrm{Tr}\left\{\exp\left[-(\beta - it)H_i\right]\exp\left[-itH_f\right]\right\}}{\mathrm{Tr}\quad \exp\left[-\beta H_i\right]}$$

In the harmonic approximation
$H_i = E_{GS} + \frac{1}{2}u\ \Phi_I\ u + \frac{p^2}{2M}$,
$H_f = E^* + \frac{1}{2}(u - u_{Rx})\Phi_F(u - u_{Rx}) + \frac{p^2}{2M}$
propagators can be conveniently obtained with operations on $2M \times 2M$ matrices.

K. Maeder and S. Baroni, Phys. Rev. B **55**, 9649 (1997).

Vibrational lineshape



Linear coupling Strength

$$c(\omega) \propto g(\omega) + \frac{1}{2!}[g \circ g](\omega) + \frac{1}{3!}[g \circ g \circ g](\omega) + \dots$$

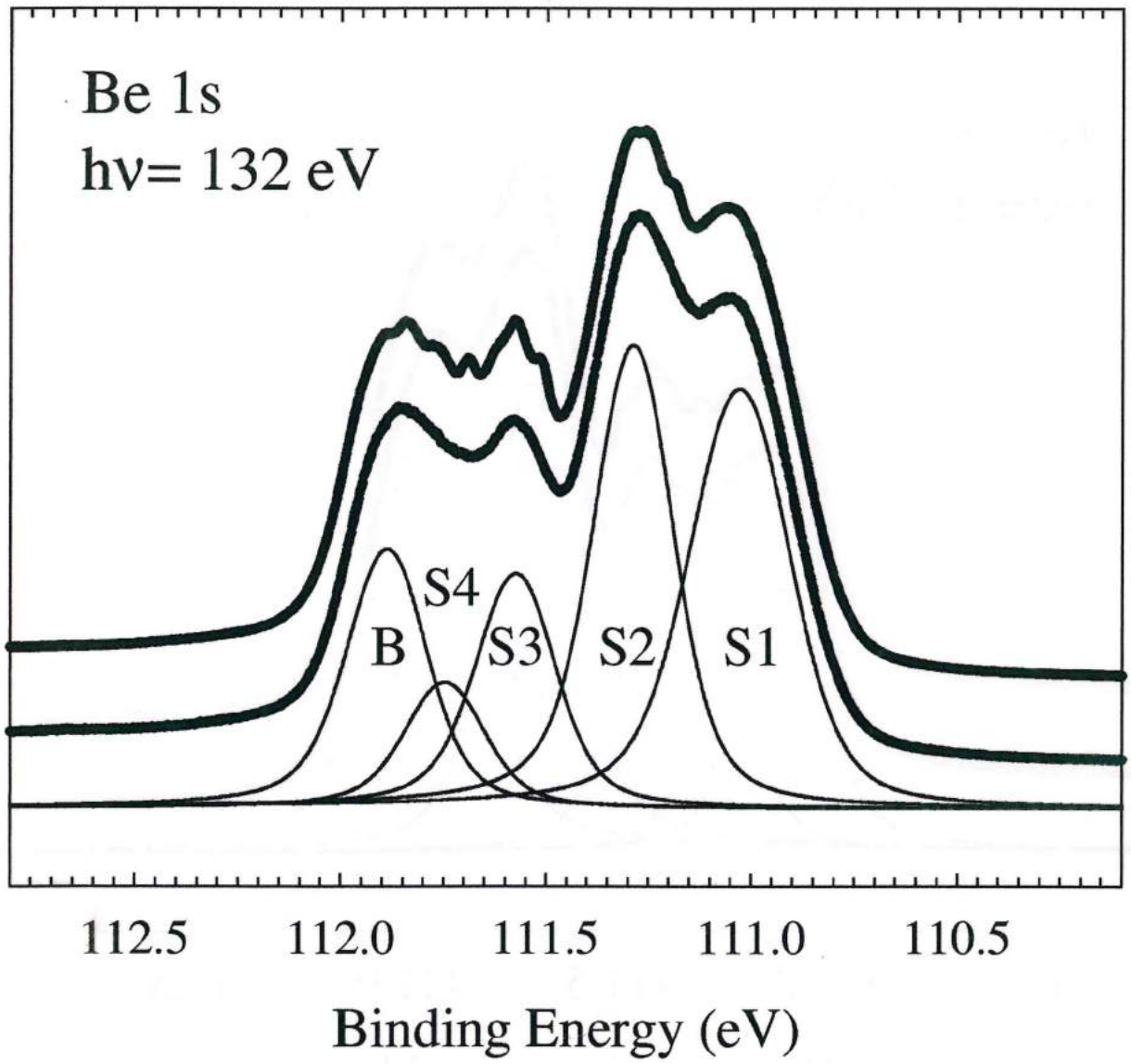
$$g(\omega) = \sum_{\nu} \frac{\lambda_{\nu}^2 \omega_{\nu}}{2} \delta\left(\omega - \omega_{\nu}\right)$$

In the classical limit

$$c(\omega) = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{\beta}{2E_{Rx}}} \exp\left[-\frac{\beta}{4E_{Rx}}\left(\hbar\omega - E_{vert}\right)^2\right]$$

$$\sigma^2 = \frac{2E_{Rx}}{\beta} = 2E_{Rx}K_BT$$

High Resolution Surface Core Level Spectra in Be (0001)



- J.N. Andersen, T. Balasubramanian, C.-O. Almbladh, L.I. Johansson and R. Nyholm, Phys. Rev. Lett. **86**, 4398 (2001).

Computational details

- Local-density approximation (LDA) to DFT
- Plane waves (PW) Pseudopotential (PP) approach
- PW's up to $|\mathbf{k}+\mathbf{G}|^2 \leq 22$ Ry
- PP with NLCC for Be
- Special points + smearing for BZ integration

Electronic Ground State

- Repeated-slab geometry to simulate surfaces
  - 12 Be-layers
  - $\approx$ 8 layers of vacuum
- Full structural optimization

Core Excited System

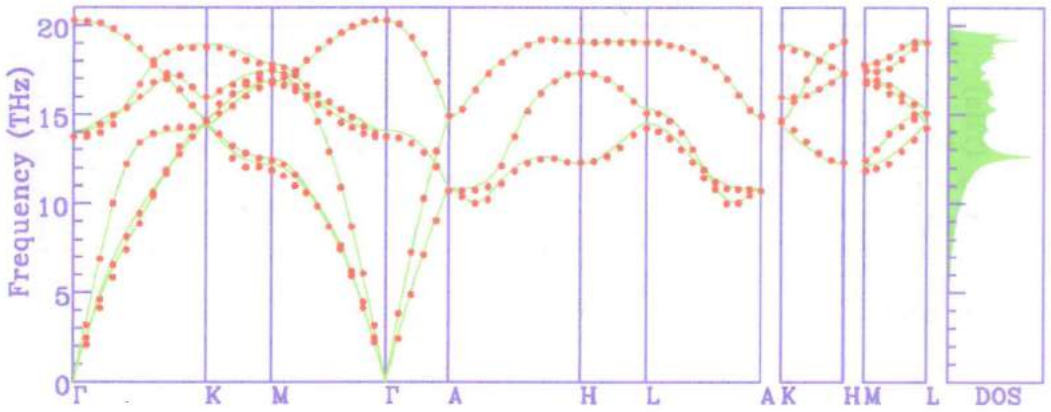
- Repeated-slab geometry to simulate surfaces
  - 12 Be-layers
  - 3×3 inplane periodicity
  - $\approx$ 8 layers of vacuum
- PP with NLCC for Be and for core-excited Be atom
  E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).
- Vibrational Broadening from first-principles (DFPT)
  K. Maeder and S. Baroni, Phys. Rev. B **55**, 9649 (1997).
  S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi,
  Rev. Mod. Phys. **73**, 515 (2001).

http://www.pwscf.org

Structure of bulk Be

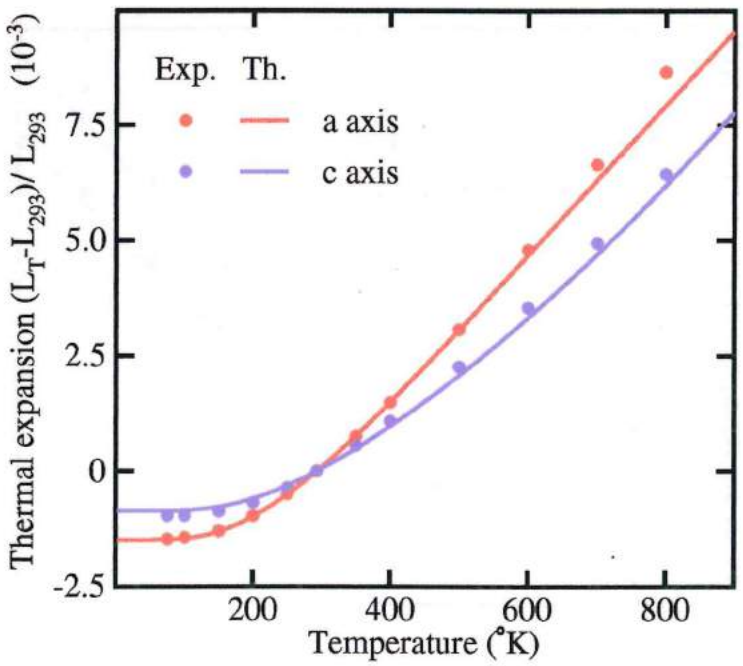
	a_0 (a.u.)	$(c/a)_0$	B_0 (Mbar)	ν_P
Theory	4.25	1.572	1.25	0.04
Expt.	4.33	1.568	1.1	0.02–0.05

Bulk Phonon Dispersion

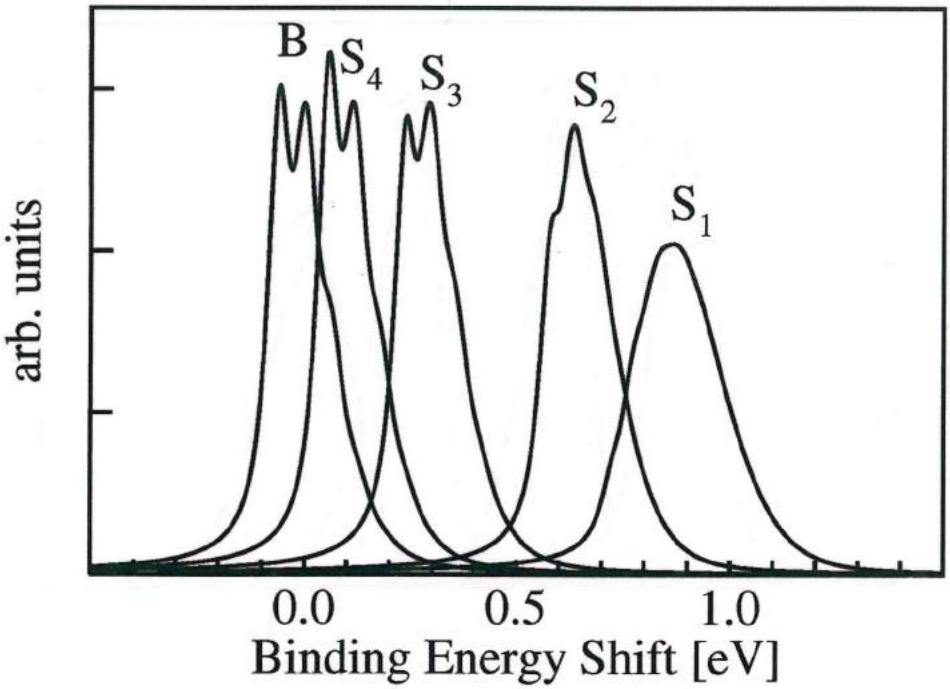


- Exp: Stedman *et al.*, J. Phys. F **6**, 157 (1976)
- M.Lazzeri, S.deGironcoli, Surf.Sci. **402-404**, 715 (1998).

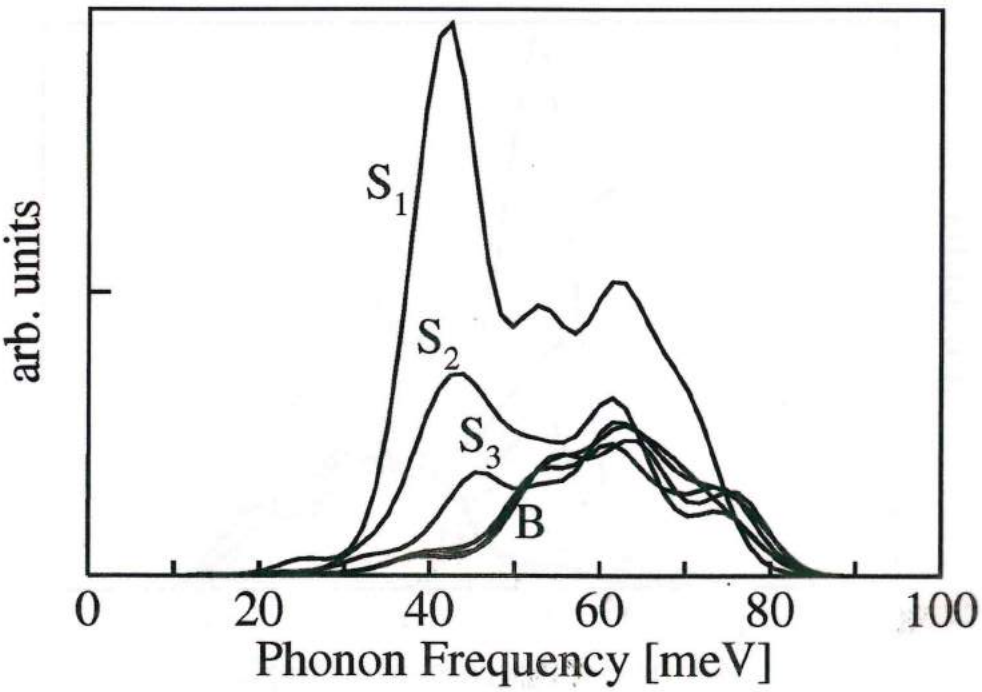
Bulk Thermal Expansion



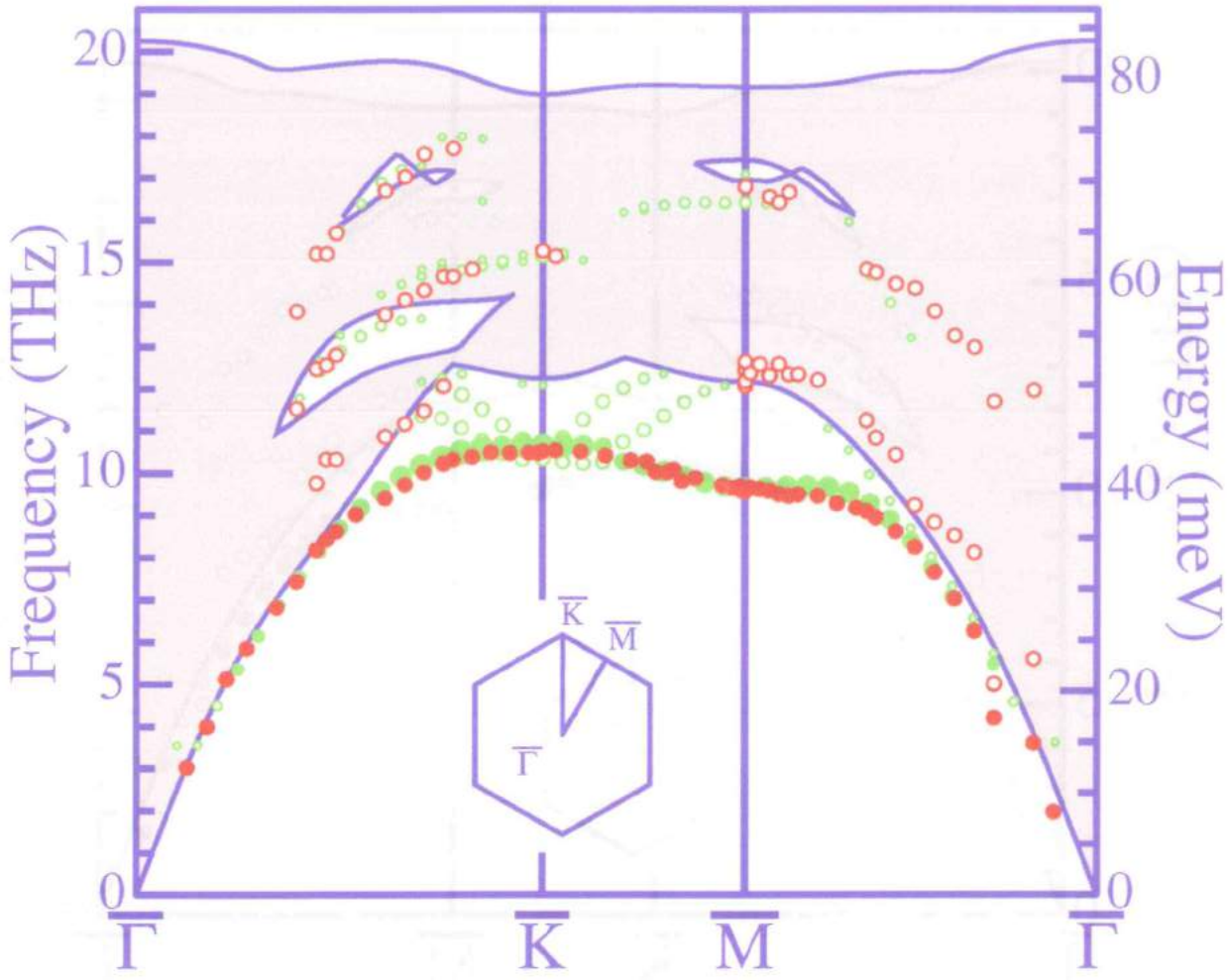
High Resolution Surface Core Level Spectra in Be (0001): Theory



Linear coupling strength



Phonon Dispersions of Be (0001)



- EELS data: intense features (Rayleigh wave)
- EELS data: weak features
- Present calculation: > 30 % (z-polarized) on top layer
- Present calculation: > 50 % on 3 topmost layers

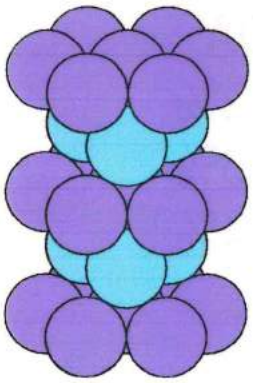
Exp: J.B.Hannon, E.J.Mele and E.W.Plummer, PRB 53, 2090 (1996)
Theory: M. Lazzeri, S. de Gironcoli, Surf. Sci. **402-404**, 715 (1998)

Be SCLS fine structure: conclusions

Calculation reproduces well the multi-phonon replicas recently observed in low-temperature high-resolution photoemission spectra emerging from bulk and inner surface layers in Be (0001). Phonon replicas are related to a peak in $g(\omega)$ around $\approx$ 60 meV.

The absence of marked multi-phonon replicas in the photoemission spectrum from the topmost surface layer is due to a stronger lattice relaxation around surface core-hole defect and to its coupling to surface phonons.

Be (0001) Surface Relaxation

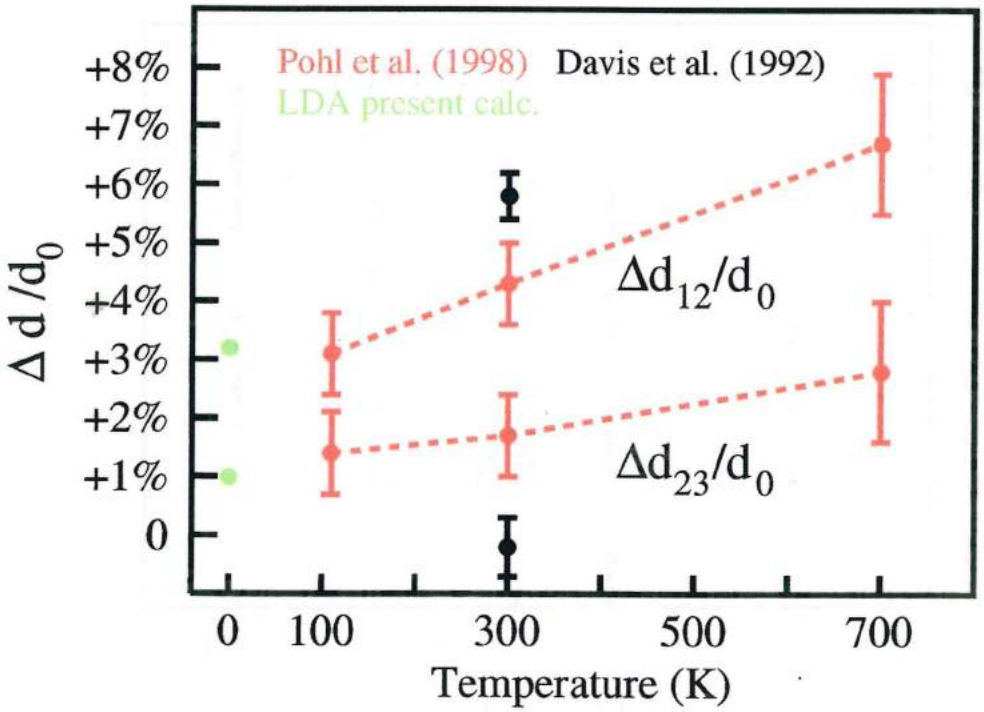


	300K	LDA	LDA
Δd_{12}	+5.8%	+2.7%	+3.2%
Δd_{23}	−0.2%	+1.2%	+1.0%
Δd_{34}	+0.2%	+0.6%	+0.4%
...			

[300K] H.L.Davis *et al.* PRL 68, 2632 (1992)
[LDA] R.Stumpf and P.J.Feibelmann, PRB 51, 13748 (1995)
[LDA] M.Lazzeri, and S.deGironcoli, PRL 81, 2096 (1998).

Anomalously Large Thermal Expansion !

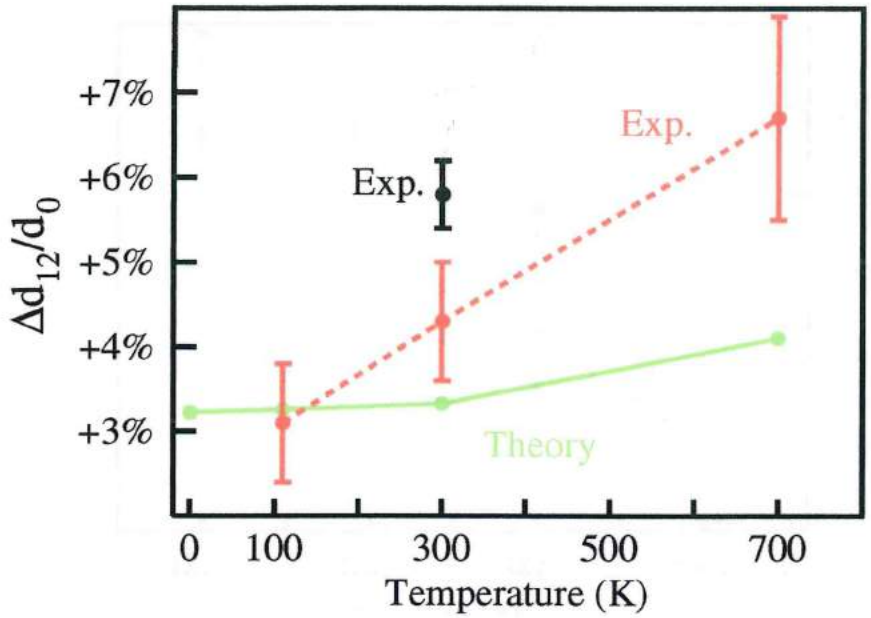
K.Pohl, J.-H.Cho, K.Terakura, M.Scheffler, and E.W.Plummer,
PRL 80, 2853 (1998)



At low temperature theory and experiment are in excellent agreement

α_{Surf} is 6 times larger than α_{Bulk} !

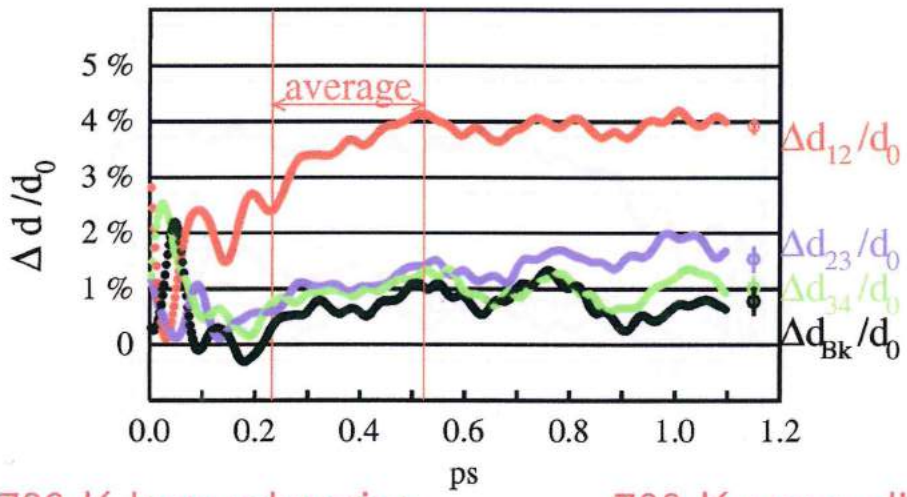
Surface Thermal Expansion



- Exp: LEED I-V H.L.Davis *et al.*, PRL 68, 2632 (1992)
- Exp: LEED I-V K.Pohl *et al.*, PRL 80, 2853 (1998)

First-Principles Molecular Dynamics

Simulation Cell: 8 layers with 3×3 periodicity + $\approx$ 4 layers of vacuum



700 K layer relaxation

	FPMD	QHA
Δd_{12}	+3.9%	+3.6%
Δd_{23}	+1.6%	–

700 K r.m.s. displacements

	FPMD	QHA
u_1 (Å)	0.16	0.14
u_2 (Å)	0.12	0.11

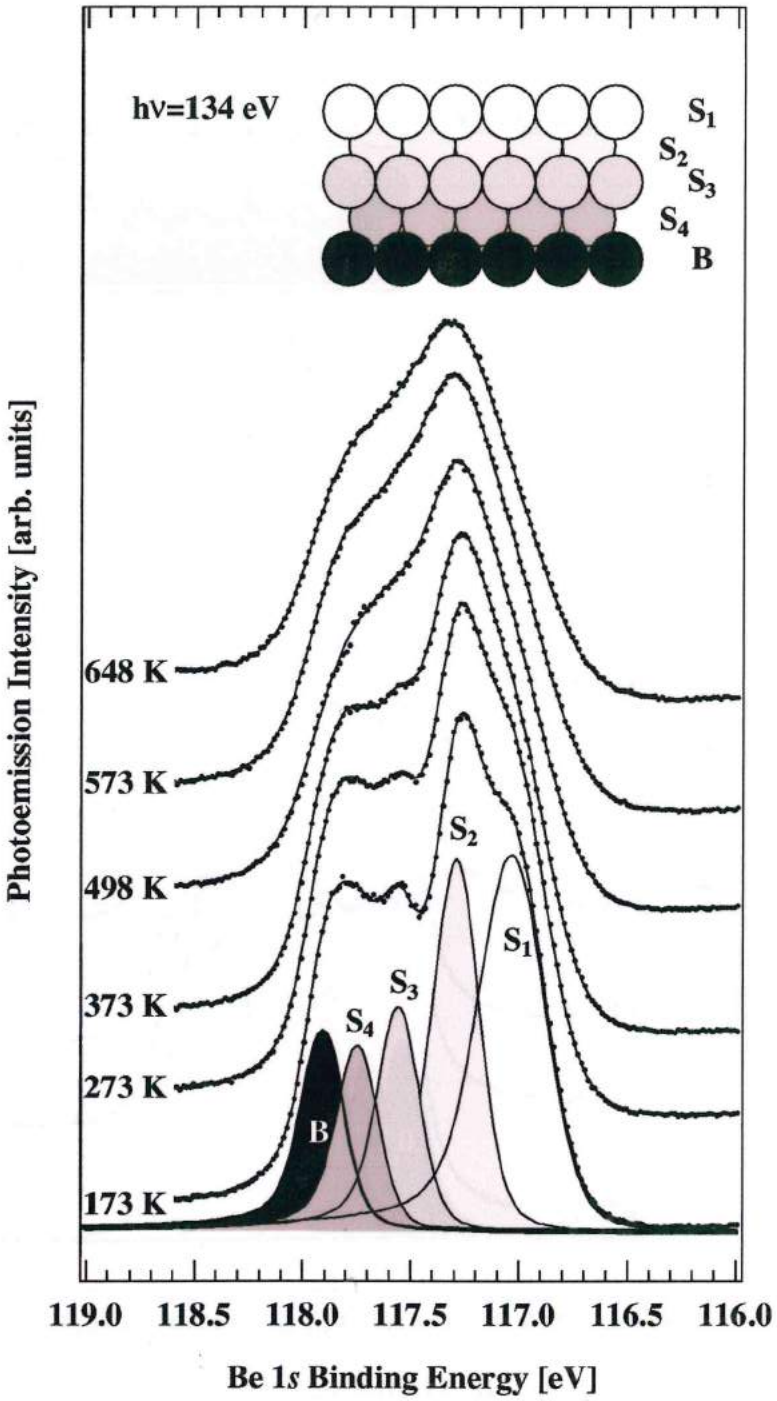
Be (0001) surface thermal expansion

a different approah

Availability of high-brillance synctrotron radiation sources allows to accurately determine the temperature variation of surface core-level shifts (SCLS) of Be (0001), that, in turn, reflects the changes with temperature of the structural parameters.

Combining experimental determination and first-principles planewave pseudopotential calculations of SCLS of Be(0001), we will readdress the issue of thermal expansion of this surface.

Temperature dependence of Be (0001) Surface Core Level Shifts



- A. baraldi, S. Lizzit, K. Pohl, Ph. Hofmann, and S de Gironcoli, unpub.

Surface Core level shifts of Be(0001)

	S1	S2	S3	S4	S5
Expt.	-870	-605	-335	-160	—
Theory:					
"static"	-924	-620	-284	-111	-30
"zero T"	-898	-610	-282	-111	-30

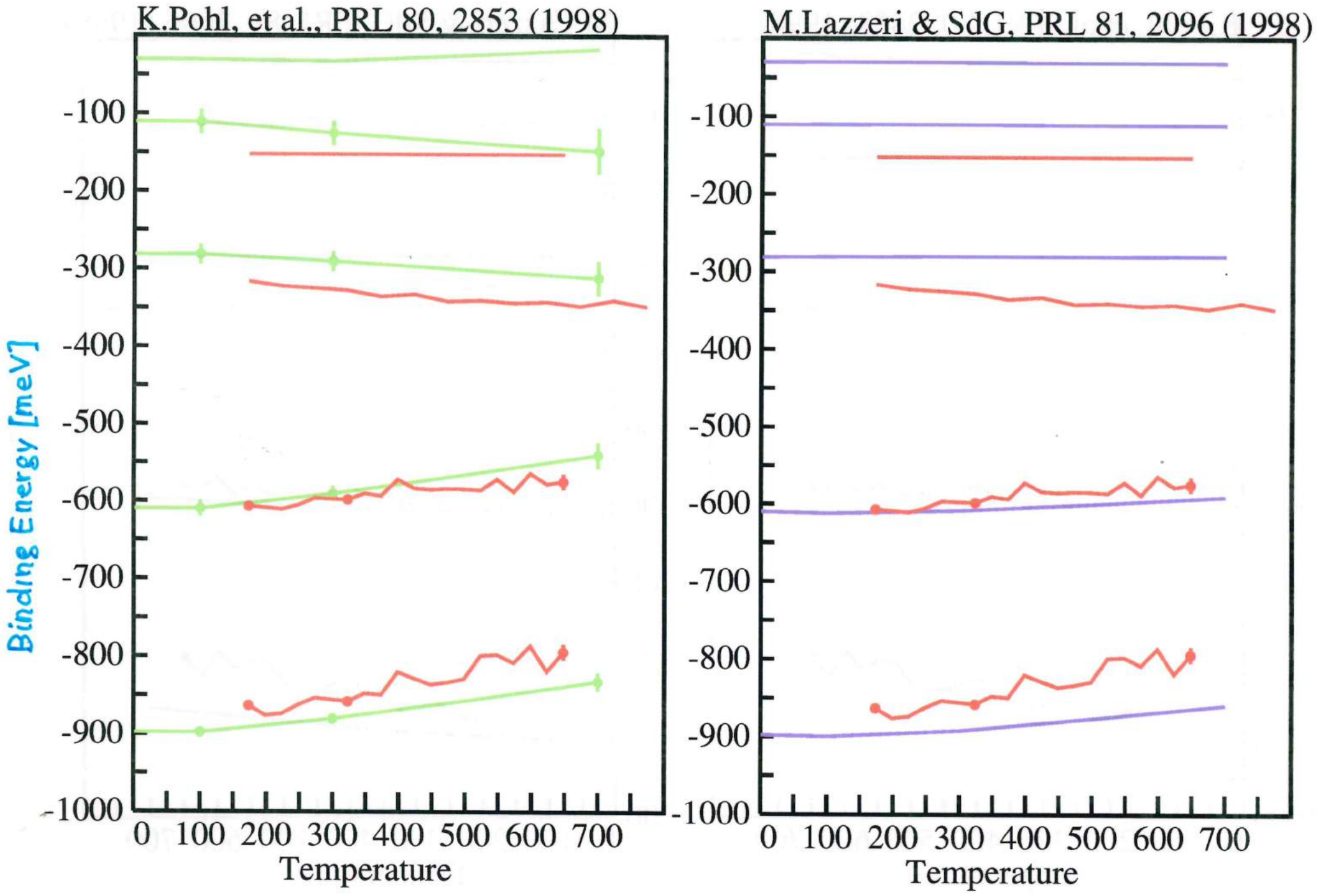
Shift of SCLS w.r.t percetual variation of d_{ij}

	S1	S2	S3	S4	S5
Δd_{12}	9.0	10.3	-3.0	-1.6	-0.9
Δd_{23}	-0.9	9.8	10.5	-2.6	-1.0
Δd_{34}	-0.5	-1.8	11.3	12.6	-1.3
Δd_{45}	-0.1	-0.1	-0.5	14.3	14.8
Δd_{56}	0.0	0.4	0.7	0.5	15.8

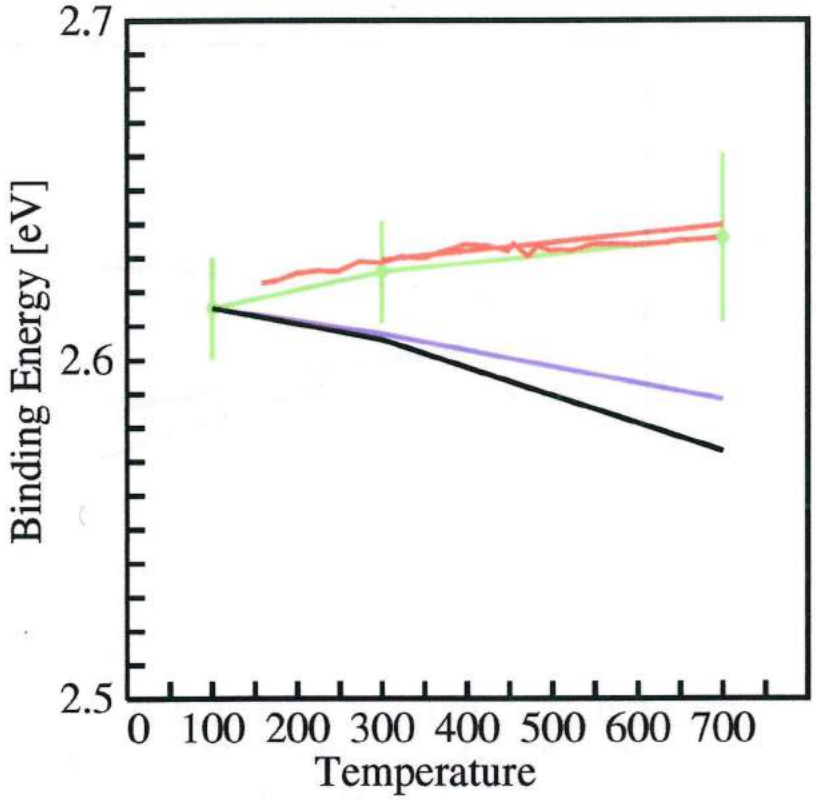
Shift of SCLS with inplane lattice parameter

	S1	S2	S3	S4	S5
a_{0K}	-898	-610	-282	-111	-30
a_{100K}	-898	-610	-282	-111	-30
a_{300K}	-891	-607	-280	-110	-30
a_{500K}	-879	-603	-279	-110	-30
a_{700K}	-866	-597	-277	-109	-30

(3x3)-supercell calculations



Temperature dependence of Be (0001) Surface State



Inverting the Exptl SCLS Temp dependence

$$\frac{dS_1}{dT} = -0.138 \pm 0.010 \text{ meV/K}$$
$$\frac{dS_2}{dT} = -0.086 \pm 0.006 \text{ meV/K}$$
$$\frac{dS_3}{dT} = +0.065 \pm 0.018 \text{ meV/K}$$

$$\Longrightarrow \quad \alpha_{12} = 88 \pm 15\ 10^{-6}\ \text{K}^{-1}$$
$$\alpha_{23} = -10 \pm 15\ 10^{-6}\ \text{K}^{-1}$$
$$\alpha_{34} = -6 \pm 20\ 10^{-6}\ \text{K}^{-1}$$

$$\alpha_{bulk} = 12\ 10^{-6}\ \text{K}^{-1}$$

Be surface thermal expansion: conclusions

Comparing measured temperature-dependent SCLS and surface state positions to values calculated with DFT for different surface geometries it has been possible to determine the multilayer thermal expansion of the first three interlayer spacings of the Be (0001) surface.

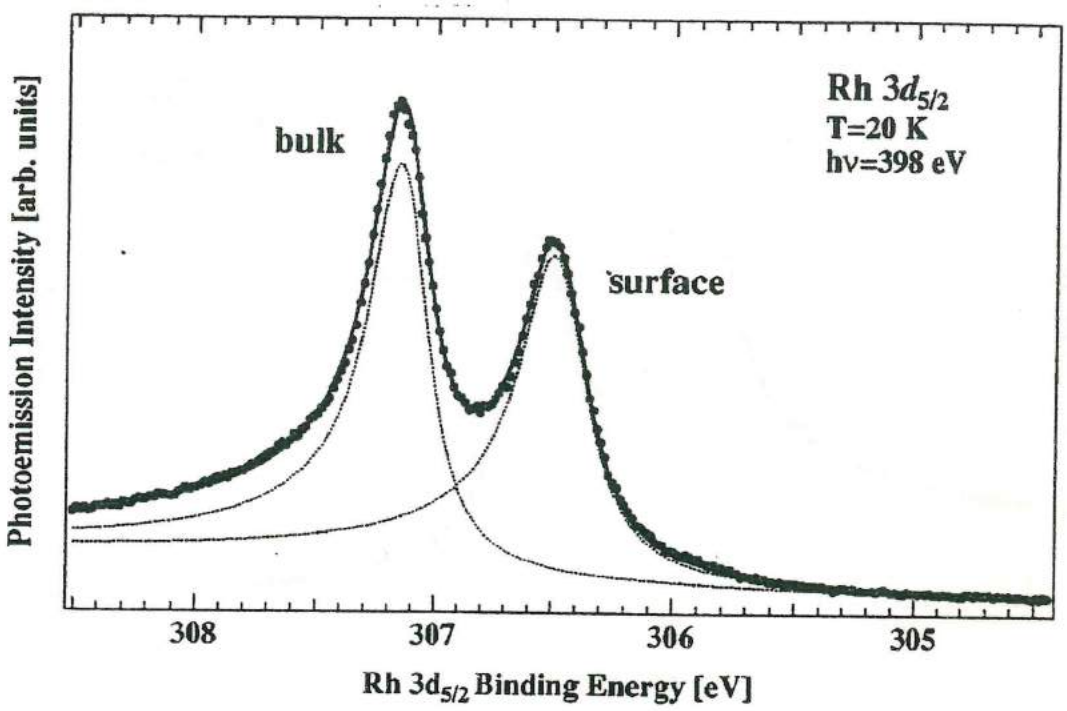
Comparison of experimental and theoretical SCLS indicates a tendency to a large thermal expansion but does not provide a clear-cut conclusion.

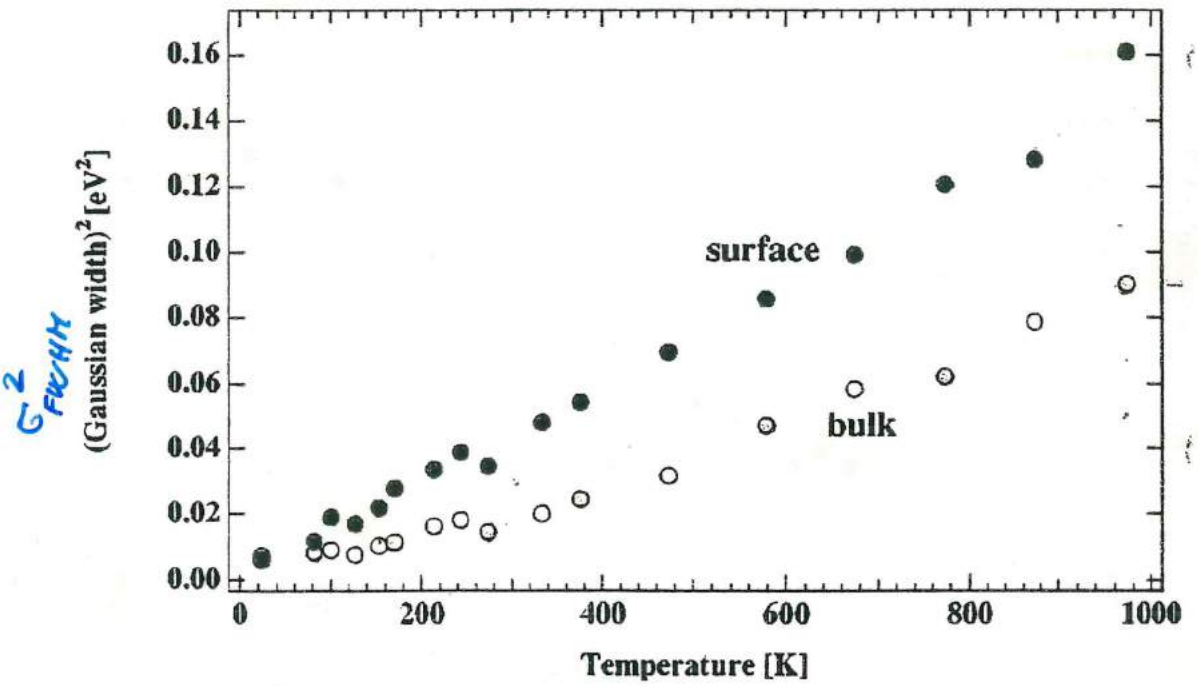
Analysis of the temperature behavior of the electronic surface state position at $\overline{\Gamma}$ more clearly indicates a tendency to a large thermal expansion.

This work confirms a previous Low Energy Electron Diffraction study which reported a strong thermal surface expansion in Be(0001) but it is in disagreement with the most advanced theoretical calculation available at present.

VIBRATIONAL BROADENING OF Rh (001) SCLS

Baraldi, Comelli, Lizzit, Rosei and Rodwcci, PRB 61, 12773 (2000)



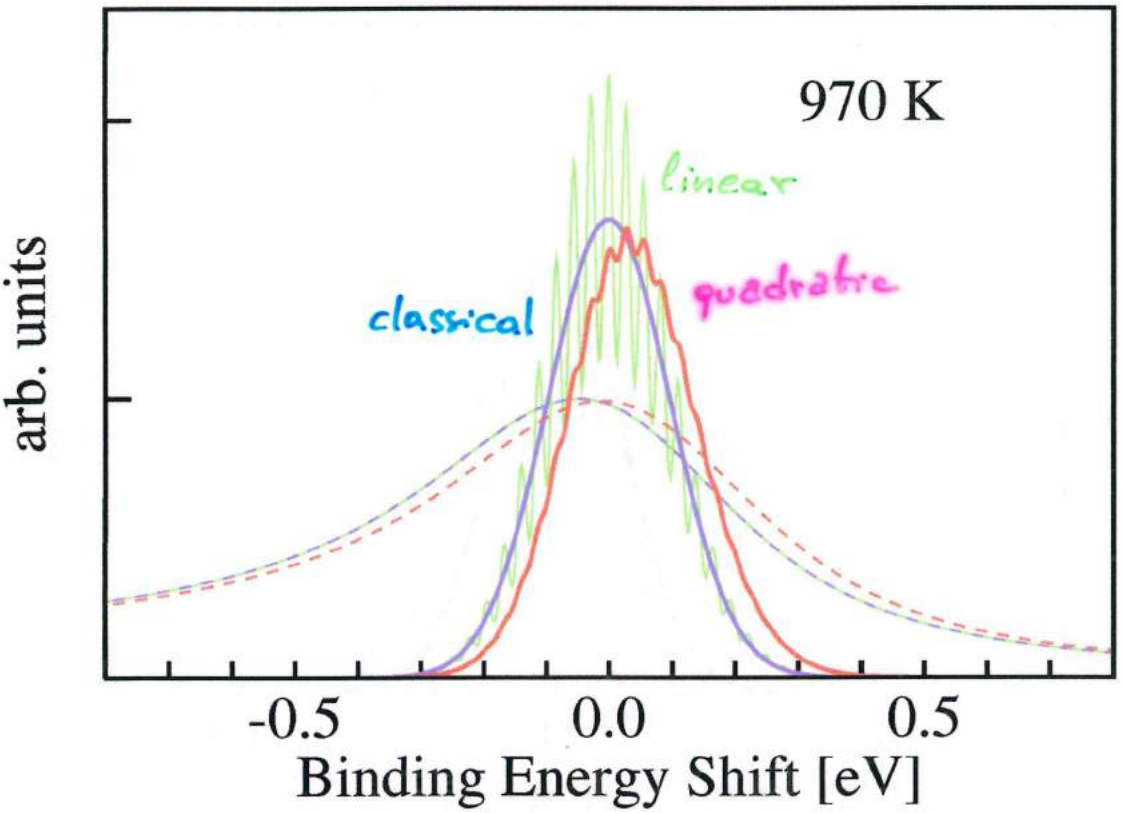


$\sigma_{FWHM} = 2.35\,\sigma$

Vibrational broadening in Rh Bulk

- Local-density approximation (LDA) to DFT
- PW's up to $|\mathbf{k}+\mathbf{G}|^2 \leq 30$ Ry
- US PP for Rh and Rh*
- Special points + smearing for BZ integration
- Supercell geometry: $4 \times 4 \times 4$ supercell
- Full structural optimization
- Linear and quadratic coupling calculations

Results



- Linear and Quadratic couplings give very similar width
- Classical and Quantum results give very similar width
- Bulk line-width is only 50 % of the observed result

Vibrational broadening in Rh (001) Surface

- Supercell geometry: 7 Rh layer + $\approx$ 6 layer vacuum
- Full structural optimization
- Gaussian Linewidth estimated from relaxation energy

σ^2_{FWHM} [eV^2] (970 K)	p(1×1)	p(2×2)	p(3×3)	p(4×4)	Exp
S_1	0.065	0.086	0.101	0.114	0.16
S_2			0.040	0.043	-
$Bulk$	0.048 ($4 \times 4 \times 4$)		0.050	0.046	0.09

- Sub-surface Core-level components may play a role

SCLS [eV]	p(3×3)	Exp
S_1	0.620	0.621±0.009
S_2	-0.102	-0.082±0.008

Conclusions

It is possible to address several issues on SCLS temperature effects fully from first-principles.

This allow to :

- Analyze in detail high-resolution line-shape
- Extract from SCLS structural changes with temperature
- Identify additional SCLS component in some material