EUROPHYSICS LETTERS

Multilayer thermal expansion of Be(0001) determined from surface core level shifts

* * *

A. Baraldi, S. Lizzit, K. Pohl, P. Hofmann and S. de Gironcoli

EUROPHYSICS LETTERS

Taking full advantage of the service on Internet,
please choose the fastest connection:

http://www.edpsciences.org
http://edpsciences.nao.ac.jp
http://edpsciences-usa.org
http://www.epletters.ch
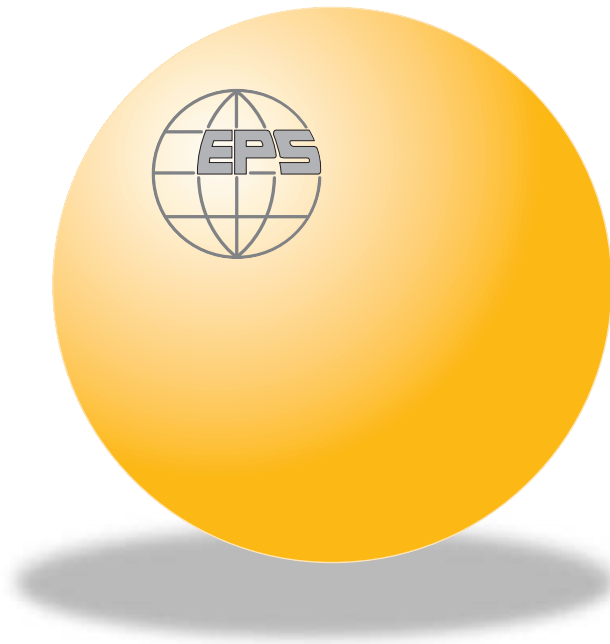
Europhysics Letter was launched more than fifteen years ago by the European Physical Society, the Société Française de Physique, the Società Italiana di Fisica and the Institute of Physics (UK) and owned now by 17 National Physical Societies/Institutes.

Europhysics Letters aims to publish short papers containing non-trivial new results, ideas, concepts, experimental methods, theoretical treatments, etc. which are of broad interest and importance to one or several sections of the physics community.

Europhysics letters provides a platform for scientists from all over the world to offer their results to an international readership.

Multilayer thermal expansion of Be(0001) determined from surface core level shifts

A. Baraldi[1,2,3], S. Lizzit[1], K. Pohl[4], P. Hofmann[5] and S. de Gironcoli[6]

[1] *Sincrotrone Trieste S.C.p.A. - S.S. 14 km 163.5, 34012 Trieste, Italy*
[2] *Dipartimento di Fisica, Università di Trieste - Via Valerio 2, 34127 Trieste, Italy*
[3] *Laboratorio TASC-INFM - S.S. 14 km 163.5, 34012 Trieste, Italy*
[4] *Department of Physics, University of New Hampshire - Durham, NH 03824, USA*
[5] *Institute for Storage Ring Facilities, University of Aarhus*
DK-8000 Aarhus C, Denmark
[6] *Scuola Internazionale Superiore di Studi Avanzati (SISSA) and INFM*
Via Beirut 2-4, I-34014, Trieste, Italy

Abstract. – We have determined the thermal expansion of the first three interlayer spacings of Be(0001) by comparing measured temperature-dependent surface core level shifts and surface state positions to values calculated with Density Functional Theory for different surface geometries. Our results reveal that, in the temperature range from 300 to 700 K, the 1st-to-2nd, 2nd-to-3rd and 3rd-to-4th interlayer coefficient of thermal expansion are 88 ± 15, -10 ± 15 and $-6 \pm 20 \times 10^{-6}\,\mathrm{K}^{-1}$, respectively. We have now set Be(0001) as a challenge for further theoretical improvements, since a complete theoretical understanding of surface thermal expansion does not exist.

Understanding the thermal properties of nanostructures is of outmost importance when it comes to making reliable predictions on their stability. By decreasing the size of nanoparticles and concomitantly increasing their surface-to-bulk ratio, the thermal behavior of the surface is going to dominate their properties. However, even if experimental evidence for enhanced surface thermal expansion and contraction exists for a variety of surfaces, a theoretical understanding of surface thermal expansion does not exist. Calculations for Ag(111) [1–4] and Al(110) [5] indicate that it is not well understood which surface phonon modes are important in the process.

An interesting case is the thermal expansion of Be(0001). Low Energy Electron Diffraction (LEED) investigation measured an anomalously large thermal surface expansion, 6 times larger than the bulk [6]. The top-layer outward relaxation increased from $+3.1\%$ to $+6.7\%$ (with respect to the corresponding bulk distance) upon raising the temperature from 110 K to 700 K, yielding a first-to-second interlayer coefficient of thermal expansion $\alpha_{12} = (d_{12})^{-1}(\partial d_{12}/\partial T) = 70 \times 10^{-6}\,\mathrm{K}^{-1}$, 6 times the bulk value of $12 \times 10^{-6}\,\mathrm{K}^{-1}$. This observation seems to be inconsistent with measurements reporting negligible anharmonicity in the surface phonon modes

normal to the surface [7]. A subsequent density functional perturbation theory study [8], in which the free energy of the system was calculated from full vibrational dispersions, found an increase of the first-to-second layer distance of only 1.1% in the same temperature range, much smaller than the LEED result. At the same time, the calculation correctly reproduced the bulk thermal expansion and the adequacy of the quasiharmonic approach for the surface was directly checked by comparing with a first-principles molecular-dynamics simulation [8].

Thus, we are left in a situation that the arguably most advanced calculation to date gives only a poor agreement with the experiment. If the LEED results are correct, this would mean that some essential physics of the surface thermal expansion is not yet included in the state-of-the-art calculations.

In this letter, we present a novel, independent, approach to determine the thermal expansion of Be(0001). Our strategy is to firstly measure the binding energy of the surface state at the $\bar{\Gamma}$ point of the surface Brillouin zone and the values of the surface core level shifts (SCLS) as a function of temperature. These data are then compared to calculated values for different geometries in order to determine the temperature-dependent interlayer distances. Our results confirm the anomalously large thermal expansion of the surface and establish Be(0001) as a firm experimental standard for advances in theoretical understanding.

The experiments have been carried out at the SuperESCA beamline of ELETTRA, Trieste, Italy [9]. The surface was cleaned by cycles of Ar^+ sputtering at 670 K and annealing to 720 K. The sample was heated by a filament mounted behind it. During the measurements, the heating current was chopped in order to avoid the influence of the magnetic field on the photoemission spectra. Surface order and cleanliness where checked by LEED and core level photoemission, respectively. The Be $1s$ core level measurements were taken for photon energies between 126 and 134 eV at normal photoelectron emission and with 40° photon incidence. The combined analyzer and monochromator energy resolution was 60 meV. The surface state data has been taken with 95 eV photons in the same geometry and with a total energy resolution of 100 meV.

Our calculations have been carried out with the PWSCF package [10], within the local-density approximation [11,12], using separable pseudopotentials [13] and plane-wave basis sets up to an energy cut-off of 22 Ry. Technical details and the Be pseudopotential were the same used as in our previous works on beryllium [8,14]. In the study of the electronic surface state we adopted a repeated-slab geometry with 16-layer Be slabs separated by a $\sim$ 25 a.u. thick vacuum region (equivalent to 8 atomic layers) to decouple the surfaces. Be $1s$ core excitation energies in different surface layers were calculated from first principles including final-state effects following the procedure of ref. [15]. We found that the error induced by the choice of a pseudopotential approach in the calculation of the core-level binding energy is of the order of 10 meV. We expect a much smaller error for the core-level *shifts*. From the comparison of the SCLS computed on super-cells with 12 or 16 Be layers and 1×1, 2×2 and 3×3 in-plane periodicity, we estimate that the periodicity error is less than 20 meV in the 12-layer 3×3 slab.

As a first attempt to discriminate between the two suggested thermal expansions [6,8], we have examined the temperature dependence of the surface state binding energy at the center of the Brillouin zone, $\bar{\Gamma}$. In fig. 1 the experimental results are compared to the theoretical results obtained assuming the large thermal expansion reported in ref. [6] and the small expansion reported in ref. [8]. Our experimental data are clearly in much better agreement with the LEED results of ref. [6]. However, the number of layers involved in the surface expansion is large and the determination of the energy position of a single electronic surface state is not sufficient to fully constrain the multilayer relaxation pattern and to provide a clear-cut answer to our question.
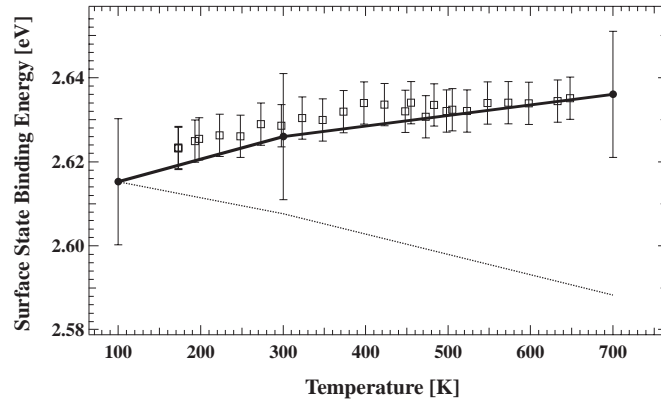
Fig. 1 – Temperature dependence of the surface state binding energy at $\overline{\Gamma}$ and a comparison with the calculated binding energies using the geometry determined by LEED in ref. [6] (solid line) and by first-principles calculations in ref. [8] (dotted line).

A more detailed analysis is based on a measurement of the temperature-dependent Be $1s$ core level spectrum. This contains five components, which stem from the inequivalent surface, sub-surface and bulk atoms [16]. Therefore, it gives us the opportunity to obtain information about the first layers separately. Figure 2 shows six Be $1s$ spectra selected from the set measured at $h\nu = 134\,\mathrm{eV}$ and at 18 temperatures ranging from $173\,\mathrm{K}$ to $648\,\mathrm{K}$. The five components of the spectra are emphasized in the $173\,\mathrm{K}$ spectrum. The high binding
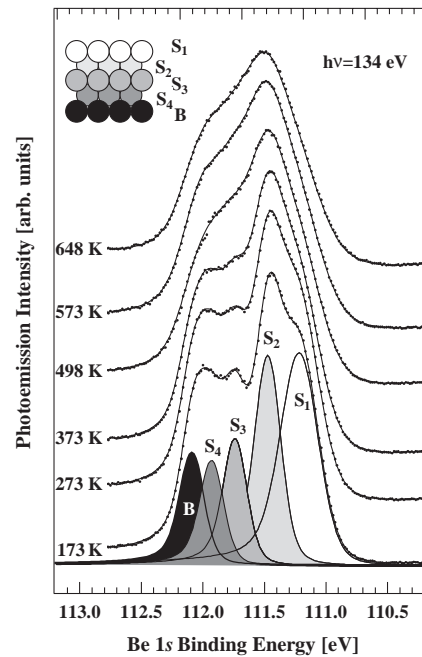
Fig. 2 – Be $1s$ core levels spectra from Be(0001) measured at temperatures ranging from $173\,\mathrm{K}$ to $648\,\mathrm{K}$.

Table I – *Selected measured surface core level shifts for several temperatures and theoretical shifts for the relaxed surface slab homogeneously scaled with the bulk thermal expansion, i.e. the first term on the r.h.s. of eq.* (2) *(energies in* meV*).*

		S_1	S_2	S_3	S_4	S_5
Experiment						
	173 K	−863	−607	−317	−152	−
	273 K	−854	−596	−325	−152	−
	373 K	−849	−593	−336	−152	−
	498 K	−829	−584	−341	−152	−
	573 K	−808	−587	−344	−152	−
	648 K	−794	−574	−345	−152	−
Theory						
	$a_{0\,K}$	−898	−610	−282	−111	−30
	$a_{300\,K}$	−891	−607	−280	−110	−30
	$a_{700\,K}$	−866	−597	−277	−109	−30

energy peak (B) originates from the bulk atoms, while the other four components (S_1, S_2, S_3, and S_4) arise from the four outermost atomic layers. The data have been fitted with five Doniach-Sunjic functions [17], convoluted with Gaussians to account for the instrumental, inhomogeneous and phonon broadening. In order to disentangle the various components in the spectra, we have measured the low-temperature Be $1s$ spectrum using the same procedure as in ref. [16], *i.e.* at 126, 130 and 134 eV photon energies, thus changing the relative weight of the different components. The whole data set has been fitted and SCLS of 152 ± 15, 317 ± 5, 606 ± 3 and 863 ± 4 meV towards lower binding energy have been obtained for S_4, S_3, S_2 and S_1 respectively, in close agreement with the previous results [16,18]. The spectra measured at different temperatures and photon energies have then been fitted treating the binding energy position of the various components as free parameters except for the S_4 shift that was fixed at 152 meV from the bulk peak. All other lineshape parameters were fixed to the values found in the low-temperature case, save the Gaussian widths that were left free to vary in order to mimic the vibrational broadening of the core-level lineshape [19].

In table I we report the experimental results for the temperature dependence of the different surface core level shifted peaks. While the SCLS corresponding to the first (S_1) and second (S_2) layer atoms decrease with temperature, the shift related to S_3 increases. The table also shows the calculated SCLS for a relaxed slab geometry at zero kelvin, confirming the assignment of the peaks to the correct layers. In the temperature range investigated here, the temperature dependence of the SCL shifts, measured at three different photon energies, is approximately linear with slopes of -0.138 ± 0.010, -0.086 ± 0.006 and $+0.065 \pm 0.018$ meV/K for S_1, S_2 and S_3, respectively.

In order to interpret these findings and extract information about the temperature-dependent surface geometry, we have theoretically studied the effect of the surface relaxation on the core-level shifts. We can split the thermal expansion of Be(0001) into two parts: i) a *homogeneous* expansion of the whole crystal according to the bulk thermal expansion coefficients that define for each temperature, given by the temperature dependence of *hcp* lattice parameters, $a(T)$ and $c(T)$, and ii) a *surface* expansion described by the percentual variation temperature dependence of the interlayer separation with temperature, scaled to the bulk interlayer separation at that temperature, $\lambda_{n,n+1} = d_{n,n+1}/d_{\text{bulk}}$, with $d_{\text{bulk}} = c(T)/2$. Since vibrational broadening does not significantly shift the peaks [19], the binding energy (BE) of a core hole

TABLE II – *Theoretical results for the change in S_n SCLS position induced by a $+1\%$ variation in the l-th interlayer separation ($\lambda_{l,l+1} = d_{l,l+1}/d_{\mathrm{bulk}}$). Values in* meV.

$\frac{\partial BE_{S_n}}{\partial \lambda_{l,l+1}} \times 100$	S_1	S_2	S_3	S_4	S_5
λ_{12}	**9.0**	**10.3**	-3.0	-1.6	-0.9
λ_{23}	-0.9	**9.8**	**10.5**	-2.6	-1.0
λ_{34}	-0.5	-1.8	**11.3**	**12.6**	-1.3
λ_{45}	-0.1	-0.1	-0.5	**14.3**	**14.8**
λ_{56}	0.0	0.4	0.7	0.5	**15.8**

in the n-th surface layer at a finite temperature can be obtained from a static calculation in the expanded geometry:

$$BE_{S_n}(T) = BE_{S_n}\big(a(T), c(T), \{\lambda_{m,m+1}(T)\}\big). \tag{1}$$

Now we need to calculate the dependence of each SCLS, on the variation of any interlayer separation (d_{12}, d_{23},...). We have checked that this dependence is remarkably linear for the expected interlayer variations and the full result can thus be obtained from the following expansion:

$$
\begin{aligned}
BE_{S_n}(T) \;=\; & BE_{S_n}\big(a(T), c(T), \{\lambda_{m,m+1}^0\}\big) + \\
& + \sum_l \frac{\partial BE_{S_n}\big(a(T), c(T), \{\lambda_{m,m+1}^0\}\big)}{\partial \lambda_{l,l+1}} \big(\lambda_{l,l+1}(T) - \lambda_{l,l+1}^0\big),
\end{aligned}
\tag{2}
$$

where the first term corresponds to the BE computed from the bulk thermal expansion only (the $\lambda_{n,n+1}^0$'s are the scaled interlayer separations obtained from the static equilibrium) and the needed first-order derivative of the core level BE in the n-surface layer is simply obtained from the change of the total force acting on the top l surface-layers of the slab when an atom in the n-th layer is excited. In table II we report the value of the derivatives (in meV per percentual variation of $\lambda_{n,n+1}$) calculated for the static equilibrium. Very similar values are obtained for homogeneously expanded slabs up to $700\,\mathrm{K}$. From table II it can be seen that the dilation of any interlayer separations $d_{n,n+1}$ (or $\lambda_{n,n+1}$) affects mainly the SCLS in the n-th and $(n+1)$-th surface layers, while its contribution is only minor for excitations in other layers. Therefore, *the temperature dependence of individual SCLS provides rather local information on the surface thermal expansion.*

We are now in a position to use the experimental temperature dependence of the SCLS in combination with eq. (2) to determine the surface expansion. From the measured average slopes of the SCLS temperature dependence, subtracting the contribution due to the homogeneous expansion of the slab and solving the linear system in eq. (2), we obtain the variations of $\lambda_{n,n+1}$, in the temperature range from 300 to $700\,\mathrm{K}$, where both experimental and theoretical SCLS variations are safely linear. In this temperature range we got $\Delta\lambda_{12} = 3.2 \pm 0.6\%$, $\Delta\lambda_{23} = -0.9 \pm 0.6\%$ and $\Delta\lambda_{34} = -0.7 \pm 0.8\%$. As no experimental information is available on the fourth and deeper layer SCLS temperature dependence, we have compared the results in two cases: i) homogeneous expansion for these inner layers or ii) no temperature variation of their SCLS. Although the computed thermal expansions for the deeper layers are different in the two cases, the results for the three outer layers are not affected. The quoted error bars reflect the experimental error bars and assume a 10% relative uncertainty in the theoretical values of the derivatives in eq. (2), accounting for about one third of the final error bars.

From these results surface-layer–dependent coefficients of thermal expansion can be obtained as $\alpha_{n,n+1} = (d_{n,n+1})^{-1}(\partial d_{n,n+1}/\partial T) = (\lambda_{n,n+1})^{-1}(\Delta\lambda_{n,n+1}/\Delta T) + \alpha_{\text{bulk}}$. The final results are 88 ± 15, -10 ± 15 and $-6 \pm 20 \times 10^{-6}\,\text{K}^{-1}$, for α_{12}, α_{23} and α_{34}, respectively.

These results are in very good agreement with the LEED experimental determination [6] for the first-to-second layer expansion, where a $70\pm30\times10^{-6}\,\text{K}^{-1}$ expansion has been reported. According to our present study, the second interlayer distance experiences a small or vanishing contraction. We wish to stress that, although the two structural determinations agree within their respective error bars, the present study provides much tighter bounds to the temperature dependence of interlayer separations. As a final check of our results, we have recalculated the temperature-dependent surface state binding energy after including the results of the expansion from the core-level study in the surface state theoretical calculations. The total resulting shift of $8.3\,\text{meV}$ is again in close agreement with the experimental surface state photoemission determination ($7.2\,\text{meV}$), even closer than the result obtained considering the structural data of the LEED experiment ($10.0\,\text{meV}$).

A satisfactory theoretical understanding of the large thermal expansion in Be(0001) remains to be reached. The present study shows that at least two (and maybe more) surface layers show an anomalous behavior, whose interplay could be non-trivial. While in our theoretical study of Be(0001) surface thermal expansion [8] only the relaxation of the topmost layer was considered, more recently the thermal multilayer relaxation of Mg(10$\bar{1}$0) has been successfully reproduced [22]. Further, the very large surface electron-phonon coupling in Be(0001), which has not been considered in previous studies, is peculiar of this system and may play a role in determining the surface relaxation at high temperature.

In conclusion, we have determined the thermal expansion of the first three interlayer spacings of Be(0001) by a novel approach which is based on the combination of high-resolution core level and valence band photoemission and first-principles calculations. Our results are in good agreement with an earlier LEED study and the anomalous thermal expansion of the first-to-second interlayer spacing on Be(0001) is therefore a well-established fact. On the other hand, the inability of theoretical calculations to explain the large surface thermal expansion of simple metal like Be clearly indicates that some of the essential physics is not yet captured. The new technique presented in this paper is quite different from LEED in that it probes the local structure of the emitting atoms and does not rely on long-range order. Therefore, it can be applied not only to other surfaces with core level shifts from sub-surface layers but in principle also to simple nano-structured systems.

$$* \, * \, *$$

REFERENCES

[1] Quong A. A. and Liu A. Y., *Phys. Rev. B*, **56** (1997) 7767.
[2] Narasimhan S. and Scheffler M., *Z. Phys. Chem.*, **202** (1997) 253.
[3] Xie J. J., de Gironcoli S., Baroni S. and Scheffler M., *Phys. Rev. B*, **59** (1999) 970.
[4] Al-Rawi A. N., Kara A., Staikov P., Ghosh C. and Rahman T. S., *Phys. Rev. Lett.*, **86** (2001) 2074.

[5] MARZARI N., VANDERBILT D., DE VITA A. and PAYNE M. C., *Phys. Rev. Lett.*, **82** (1999) 3296.

[6] POHL K., CHO J.-H., TERAKURA K., SCHEFFLER M. and PLUMMER E. W., *Phys. Rev. Lett.*, **80** (1998) 2853.

[7] HANNON J. B., PhD Thesis, University of Pennsylvania (1994).

[8] LAZZERI M. and DE GIRONCOLI S., *Phys. Rev. Lett.*, **81** (1998) 2096.

[9] BARALDI A., BARNABA M., BRENA B., COCCO D., COMELLI G., LIZZIT S., PAOLUCCI G. and ROSEI R., *J. Electron Spectrosc. Relat. Phenom.*, **76** (1995) 145.

[10] BARONI S., DAL CORSO A., DE GIRONCOLI S. and GIANNOZZI P., `http://www.pwscf.org`.

[11] KOHN W. and SHAM L. J., *Phys. Rev. A*, **140** (1965) 1133.

[12] CEPERLEY D. M. and ALDER B. J., *Phys. Rev. Lett.*, **45** (1980) 566 as parametrized by PERDEW J. P. and ZUNGER A., *Phys. Rev. B*, **23** (1981) 5048.

[13] KLEINMAN L. and BYLANDER D. M., *Phys. Rev. Lett.*, **48** (1982) 1425.

[14] LAZZERI M. and DE GIRONCOLI S., *Surf. Sci.*, **402-404** (1998) 715; **454-456** (2000) 442.

[15] PEHLKE E. and SCHEFFLER M., *Phys. Rev. Lett.*, **71** (1993) 2338.

[16] JOHANSSON L. I., GLANS P.-A. and BALASUBRAMANIAN T., *Phys. Rev. B*, **58** (1998) 3621.

[17] DONIACH S. and SUNJIC M., *J. Phys.*, **3** (1970) 285.

[18] ANDERSEN J. N., BALASUBRAMANIAN T., ALMBLADH C.-O., JOHANSSON L. I. and NYHOLM R., *Phys. Rev. Lett.*, **86** (2001) 4398.

[19] Andersen *et al.* [18] have shown that the Be $1s$ spectrum contains internal fine structure due to the intrinsic excitation of a narrow band of optical phonons. We [20] have calculated the vibrational broadening of each surface core level according to ref. [21]. The resulting curves display the experimentally observed fine structure and, once convoluted with a Gaussian and fitted to DS lineshape, indicate that the error in the peak position induced by the choice of a Gaussian vibrational lineshape is less than 5 meV over the temperature range (173–648 K) of our measurements.

[20] DE GIRONCOLI S., unpublished.

[21] MAEDER K. A. and BARONI S., *Phys. Rev. B*, **55** (1997) 9649.

[22] ISMAIL, PLUMMER E. W., LAZZERI M. and DE GIRONCOLI S., *Phys. Rev. B*, **63** (2001) 233401; LAZZERI M. and DE GIRONCOLI S., *Phys. Rev. B*, **65** (2002) 245402.