

X-ray absorption spectroscopy and valence band photoemission spectroscopy investigations of the Ge(111) surface above the 1050 K high-temperature phase transition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 1959

(<http://iopscience.iop.org/0953-8984/9/9/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:14

Please note that [terms and conditions apply](#).

## X-ray absorption spectroscopy and valence band photoemission spectroscopy investigations of the Ge(111) surface above the 1050 K high-temperature phase transition

G Paolicelli<sup>†</sup>, V R Dhanak<sup>‡</sup>, A Goldoni<sup>§</sup>||, S Modesti<sup>§</sup>||, M Sancrotti<sup>§</sup><sup>+</sup> and A Santoni<sup>¶</sup>

<sup>†</sup> INFN, Unità Roma III, Via della Vasca Navale 84, I-00146 Roma, Italy

<sup>‡</sup> IRC for Surface Science, Liverpool University, PO Box 147, Liverpool L69 3BX, UK

<sup>§</sup> Laboratorio TASC-INFN, Padriciano 99, I-34012 Trieste, Italy

|| Dipartimento di Fisica, Università di Trieste, via Valerio 2, I-34100 Trieste, Italy

¶ ENEA-INN, Divisione Nuovi Materiali, CP 2400, I-00100 Roma, Italy

Received 5 September 1996, in final form 25 November 1996

**Abstract.** The Ge(111) surface has been investigated as the temperature was varied in the 300 K–1150 K range by valence band (VB) photoemission spectroscopy and x-ray absorption spectroscopy above the Ge 3d edge. VB photoemission shows that the high-temperature surface has a metallic character and that at temperatures above the 1050 K high-temperature phase transition a clear change of the surface electronic structure occurs. Metallicity at high temperature was also detected by absorption spectroscopy which shows the presence of a well-defined Fermi edge at an energy value consistent with earlier core photoemission results. From absorption data and numerical simulations the width of the Ge(111) surface conduction band was found to be 1.1 eV.

Understanding the nature of phase transitions taking place on Ge(111) as a function of temperature is of great theoretical and experimental interest because this surface can be chosen as a model case for a clean semiconductor.

At room temperature the clean Ge(111) shows a stable  $c(2 \times 8)$  surface reconstruction [1] which turns into a  $(1 \times 1)$  surface at about 600 K due to the lack of long-range order of the adatom lattice [2]. The  $(1 \times 1)$  structure can be observed up to about 1050 K. Beyond this temperature ( $T_c$ ), which is only 160 K below the Ge bulk melting point ( $T_m$ ), pioneer work carried out by McRae and Malic showed that the surface undergoes a further structural phase transition [3]. Subsequent experimental work carried out by several groups and aimed at the elucidation of the Ge(111) surface structure at temperatures between  $T_c$  and  $T_m$  has delivered contradictory results. Static disorder [4], defects [5], a solid metallic phase [6] and liquid-like dynamical disorder [7–9] have been proposed for describing the high-temperature Ge(111) surface phase.

The occurrence of a possible liquid-like dynamical disorder confined to the first bilayer (incomplete surface melting) on the Ge(111) surface above  $T_c$  has been further supported by molecular dynamics (MD) calculations [10]. Recent high-resolution electron energy-loss

<sup>+</sup> Also at: Dipartimento di Fisica, Politecnico di Milano, Piazza L Da Vinci 34, 20133 Milano, Italy.

(HREELS) data [11] and photoemission results [12] showed a strong metallicity of the Ge(111) surface above  $T_c$  in agreement with first-principles dynamical calculations [10].

In this paper we present x-ray absorption spectroscopy (XAS) and valence band (VB) photoemission measurements of the Ge(111) high-temperature phase transition.

The photoemission and absorption spectroscopy data were monitored as functions of temperature in the range from RT up to about 1150 K. Ge(111) VB data were taken at 21.2 eV photon energy both for normal and for 20° off-normal emission and XAS spectra were measured above the Ge(111) 3d edge by partial-electron-yield spectroscopy.

High-temperature photoemission results show a VB lineshape which seems to evolve towards that of the liquid and indicate that the high-temperature Ge(111) surface phase transition has a metallic character. This picture is also confirmed by the XAS results which consistently show intense absorption at the Fermi level above  $T_c$ .

Absorption experiments were performed with a resolution of about 0.2 eV at BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH) at beamlines TGM1 and TGM7 using a UHV system with base pressure  $1 \times 10^{-10}$  mbar equipped with a CLAM analyser and LEED optics. Photoemission experiments were carried out in a different UHV system with base pressure  $\sim 5 \times 10^{-11}$  mbar equipped with LEED optics and an angle-integrated analyser operated at 0.35 eV resolution. Radiation from an unpolarized discharge lamp operated either at the He I energy (21.2 eV) or at the Ar I energy ( $\sim 11.8$  eV) was used.

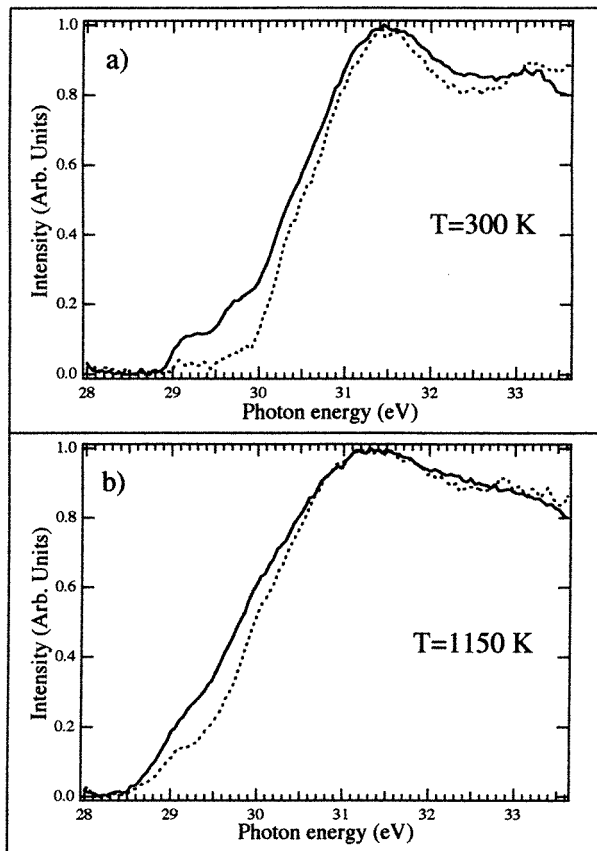
The sample was an Sb-doped 0.3 mm thick Ge(111) wafer ( $r = 0.1 \Omega \text{ cm}$ ). The  $c(2 \times 8)$  surface was prepared by  $\text{Ar}^+$  sputtering and annealing cycles up to 1100 K. Cleanliness and surface order were checked by photoemission and LEED which showed at RT a well defined  $c(2 \times 8)$  surface reconstruction. During data acquisition the sample was resistively heated by current pulses. Temperature was monitored by an infrared pyrometer calibrated against a thermocouple and the Ge bulk melting point. The maximum error affecting the temperature reading was estimated to be less than  $\pm 20$  K.

Absorption spectra above the Ge(111) 3d edge for temperatures ranging from RT up to 1150 K were measured by partial-electron-yield spectroscopy. For bulk sensitivity the secondary-electron collecting window was set at 1 eV while satisfactory surface sensitivity was achieved with a kinetic energy of about 11 eV.

Figures 1(a) and 1(b) show the superimposed surface-sensitive and bulk-sensitive Ge(111) 3d absorption edges taken at room temperature (RT) and at high temperature respectively. The overall structure of the RT spectra (figure 1(a)) is in good agreement with previously published data. Within an estimated photon energy accuracy of  $\pm 0.1$  eV, we find the positions of the  $3d_{5/2}$  and  $3d_{3/2}$  surface excitons at about 29.2 eV and 29.7 eV respectively. These values are in excellent agreement with those measured on a Ge(111) surface cleaved *in situ* and reported in the literature [13]. Moreover, the prominent bulk structures at 31.4 eV and 33.1 eV in our RT results also compare well with the data reported in reference [13].

On the Ge(111)  $c(2 \times 8)$  surface the Fermi level is pinned at 0.1 eV from the valence band maximum. As the bulk  $3d_{5/2}$  binding energy extracted from photoemission data [12] is  $29.3 \pm 0.02$  eV and the threshold-to-bulk absorption is at about 30.1 eV, by taking into account a band-gap value at RT of 0.7 eV it seems that the bulk absorption edge is not appreciably affected by excitonic effects.

The surface exciton peaks are observed up to 600 K, i.e. the  $c(2 \times 8)$ -to- $(1 \times 1)$  transition temperature. Above this temperature they become broader and starting from 1040 K they disappear into a broad tail extending below the bulk 3d edge (figure 2). A closer examination of the absorption spectra has revealed that data from 1085 K up to 1150 K are not modified

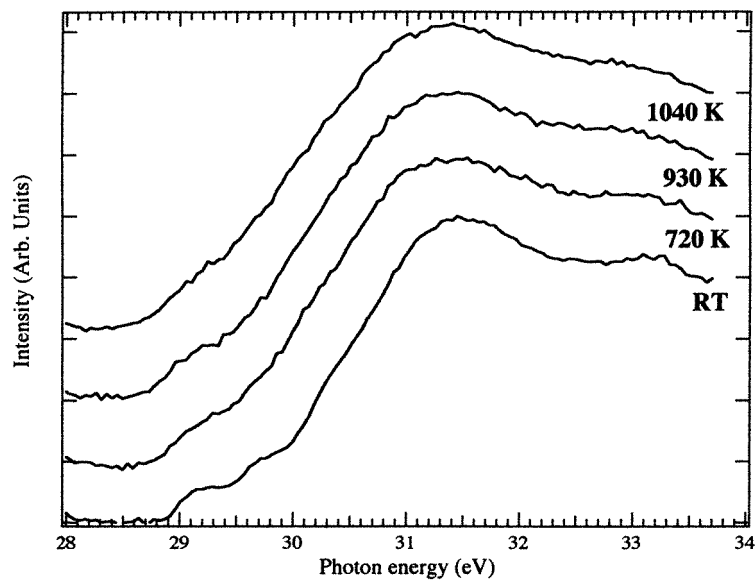


**Figure 1.** (a) Surface-sensitive (full line) and bulk-sensitive (dotted line) partial-yield absorption spectra taken at room temperature above the Ge(111) 3d absorption edge. (b) Ge(111) 3d surface-sensitive (full line) and bulk-sensitive (dotted line) partial-yield absorption spectra measured at 1150 K. The spectra are normalized to the same height.

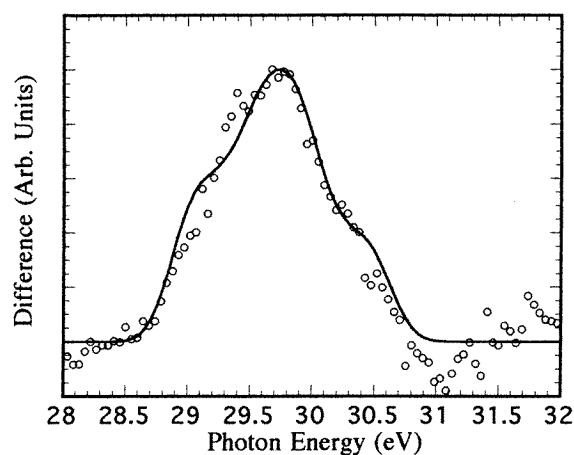
in shape any more: this finding can be used to locate the high-temperature phase transition threshold between 1040 K and 1085 K, in agreement with literature data.

The situation at high temperature is depicted in figure 1(b) where a bulk-sensitive and a surface-sensitive absorption spectrum measured at  $T = 1150$  K are shown superimposed on each other.

From Ge(111) 3d core photoemission data the  $3d_{5/2}$  binding energy of atoms in the metallic overlayer, assumed liquid-like, was found to be  $29.01 \pm 0.03$  eV [12]. On the basis of this finding, the visible step about 0.4 eV wide and located at 28.9 eV is then assigned to a Fermi edge onset indicating that the surface has acquired a metallic character. The observed width of about 0.4 eV compares very well with the intrinsic width obtained from photoemission data at the same temperature [12] and with the width extracted from numerical simulations (see below). It is worth noting that the Fermi edge is still visible, with less intensity though (but with the same width), in the bulk-sensitive absorption spectrum. By observing that in the RT bulk-sensitive absorption data surface contributions are hardly distinguishable from the background, we see that this behaviour could be indicative of an



**Figure 2.** Surface-sensitive partial-yield absorption spectra taken at different temperatures below the high-temperature phase transition.

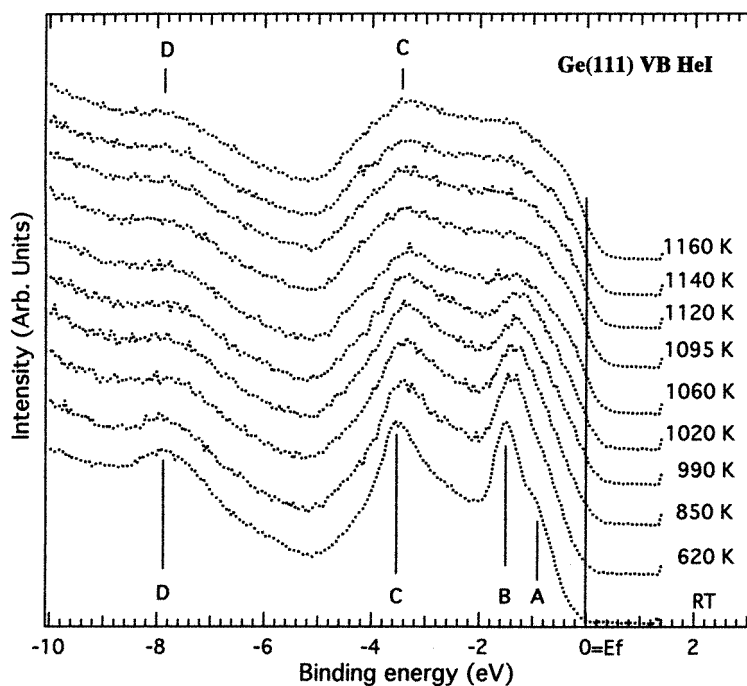


**Figure 3.** Empty circles: the difference spectrum obtained by subtracting the high-temperature bulk-sensitive absorption spectrum from the surface-sensitive absorption spectrum of figure 1(b). Before subtraction a linear background has been stripped from the data which were subsequently normalized to the same height. Full line: theoretical simulation (for an explanation, see the text).

increased thickness of the metallic-like surface layers.

Figure 3 shows the difference spectrum (empty circles) obtained by subtracting the bulk-sensitive 3d absorption edge from the surface-sensitive 3d absorption edge at 1150 K. Before subtraction, both spectra were background stripped and normalized. The full line shows a numerical simulation of the difference absorption spectrum obtained by convoluting

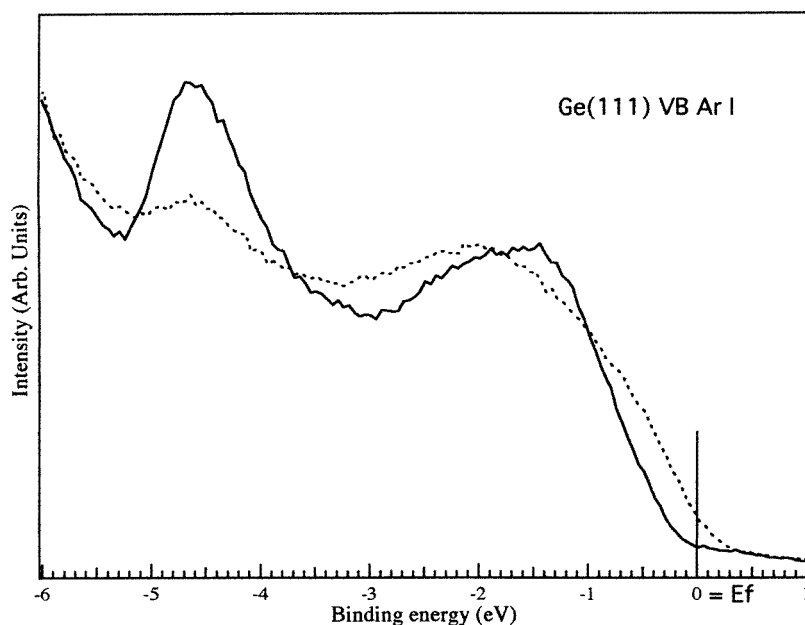
a constant density of states (DOS) 1.1 eV wide with two Gaussians split by 0.60 eV and with a height ratio 6:4 simulating the surface 3d core levels. As can be seen from figure 2, the simulation allows a fair reproduction of the experimental behaviour. The Gaussian width obtained by simulation is 0.36 eV (FWHM) and this value is in good agreement with the experimental intrinsic width observed with 3d core photoemission [12]. By noting that, according to theory [10], about 82% of the available states are contained in an energy interval of the empty part of the surface DOS of a melted bilayer on Ge(111) about 1.2 eV wide (from  $E_F$ ), it is seen that the assumed constant DOS width of 1.1 eV of the simulation compares fairly well with the MD calculations. However, it is worth saying that uncertainties in the absolute normalization of the partial-yield spectra could introduce errors in the evaluation of the surface contribution width.



**Figure 4.** The evolution of the Ge(111) VB angle-integrated photoemission spectra as a function of increasing temperature. The binding energy is referred to the Fermi level  $E_F$ . The data were taken with unpolarized He I radiation at a  $20^\circ$  off-normal emission angle and have been normalized to the area.

By studying the evolution of the shape of the valence band as a function of temperature, it was possible to gain additional information about the nature of the Ge(111) surface at high temperature. Figure 4 shows the Ge(111) valence band angle-integrated photoemission data taken with He I photons at  $20^\circ$  off-normal emission for temperatures ranging from RT up to 1160 K. The RT VB spectra are in good agreement with similar data reported in the literature [14]. The binding energy is referred to the Fermi level  $E_F$ . The two features visible at about 0.8 eV (peak A) and 1.4 eV (peak B) in the RT Ge(111)  $c(2 \times 8)$  angle-integrated spectra have been assigned to surface states. The peak C at 3.5 eV was assigned to a surface-related structure (see Aarts *et al* in reference [14]), which at the photon energy

used (21.2 eV) is partly masked by a bulk band transition. The broad feature D at 7.5 eV has been also assigned to a bulk band transition, though with possible overlapping surface effects (see Bringans *et al* in reference [14] and figure 4 in reference [10]). On increasing the temperature, the features broaden and peaks B and C are observed to lose intensity and to shift slightly to lower binding energies up to 1020 K, the last temperature at which measurements were made below the high-temperature transition. Above the transition, the region of the spectrum which contained features A, B and C is observed to flatten substantially and only a weak structure at the position of feature C is visible in the spectra. The shoulder A has already become indistinguishable in the 620 K VB spectrum. The position of feature D is found to remain constant in the measured range and after an initial loss (e.g. compare the spectra at RT and at 620 K) its intensity does not change appreciably. The overall evolution of the valence band features as a function of temperature points clearly towards a modification of the surface electronic structure. In fact, only features C and D, associated with possible bulk transitions, can still be observed at high temperatures, where the valence band spectrum is dominated by a broad bump extending about 5 eV from Fermi level. The measured shape of the valence band at temperatures above  $T_c$  seems to be similar to that found for liquid Ge. In fact, UPS measurements performed on liquid Ge by Indlekofer *et al* [15] together with total DOS calculations for liquid Ge by Jank and Hafner [16] have shown that the valence band structure above the melting temperature presents an analogous quite structureless broad feature about 5 eV wide.



**Figure 5.** Angle-integrated Ge(111) VB photoemission spectra taken at two different temperatures at normal emission with unpolarized Ar I radiation. Full line: RT; dotted line: 1160 K. The data have been normalized to the area.

As mentioned above, the Fermi edge is pinned 0.1 eV above the VBM on this surface and therefore no emission intensity is detected at RT. From about 800 K emission at the Fermi edge is observed which was found to steadily increase up to 1020 K, i.e. slightly

below the transition temperature. From this point, increasing the temperature up to 1160 K did not cause appreciable changes of the VB lineshape close to the Fermi level region. The data do not show a sharp Fermi edge: in fact, the overlapping contribution from bulk Ge and the width of the edge, estimated to be about 0.4 eV ( $\sim 4k_B T$ ) at 1200 K, prevent the build-up of a sharp step. The intensity at  $E_F$  can be due either to a finite density of states or to the high-temperature-induced broadening of photoemission features close to but below  $E_F$ . In order to try to discriminate between these two possibilities, a very simplified model has been used to simulate the photoemission data. Following the procedure described in detail in reference [12], a constant function of value  $N_s$  was added to the room temperature VB spectrum to simulate emission at the Fermi level. The sum was then multiplied by the Fermi cut-off distribution function and the result convoluted with a Gaussian function simulating the experimental broadening. According to previous results [12], simulations of data above 1100 K have shown that the spectral shape near  $E_F$  could not be reproduced for  $N_s = 0$ , while a good fit of the high-temperature data could be obtained by using  $N_s$ -values of about 60% of the VB intensity at 1 eV binding energy (B.E.). This result indicates that the observed emission at  $E_F$  is due to an increased metallic character of the high-temperature surface. Valence band photoemission measurements performed with Ar I photons (figure 5) have delivered similar results. In this case, the best simulation of data above 1100 K was obtained with an  $N_s$ -value of about 30% of the intensity measured at 1 eV B.E. The smaller  $N_s$ -value can be explained as due to the increased escape depth of electrons at this photon energy, thereby indicating that metallicity is confined to a region close to the surface. It is worth noting that because of the rough approximations of the method, the  $N_s$ -values extracted from the simulation are only qualitatively meaningful.

The occurrence of work-function variations related to the status of the Ge(111) surface was also studied by monitoring the low-energy secondary cut-off position as a function of temperature from RT up to beyond the high-temperature phase transition ( $\sim 1160$  K) (not shown). Secondary cut-off data did not show any appreciable change within 0.015 eV for all of the temperatures of the measured range. This result seems to indicate that the work function remains substantially unaffected by the processes occurring on the high-temperature surface.

In conclusion, we have performed valence band photoemission and x-ray absorption spectroscopy measurements on the Ge(111) surface below and above the high-temperature phase transition. The evolution of the VB lineshape as a function of temperature shows a clear surface structure modification taking place above  $T_c$ . Numerical simulations have shown that the intensity observed at the Fermi edge via photoemission is due to the metallic character of the high-temperature surface. The Fermi edge energy position detected by absorption spectroscopy was found to be in agreement with core photoemission data results.

The quite appreciable Fermi edge intensity observed at high temperature in the bulk-sensitive absorption data could indicate an increased thickness of the metallic layer. The width of the surface conduction band above  $T_c$  could also be evaluated from the experimental data and was found to be in agreement with the predictions obtained by molecular dynamics calculations.

## Acknowledgments

This work was partly supported by BESSY in the framework of the European Community Human Capital and Mobility Programme, contract No CHGE-CT93-0027. Two of the authors (GP and AS) would like to thank the Surface Science group at the ESRF for making available the UPS system.



## References

- [1] Palmberg P W and Peria W T 1967 *Surf. Sci.* **6** 57  
Chadi D J and Chiang C 1981 *Phys. Rev. B* **23** 1843
- [2] Feenstra R M, Slavín A J, Held G A and Lutz M A 1991 *Phys. Rev. Lett.* **66** 3257  
Hwang I and Golovchenko J 1992 *Science* **258** 1119
- [3] McRae E G and Malic R A 1987 *Phys. Rev. Lett.* **58** 1437
- [4] Modesti S and Santoni A 1989 *Solid State Commun.* **73** 315  
Abraham M, Le Lay G and Hila J 1990 *Phys. Rev. B* **41** 9828
- [5] Mak A, Evans-Lutterodt K W, Blum K, Noh D Y, Brok J D, Held G A and Birgeneau R J 1991 *Phys. Rev. Lett.* **66** 2002
- [6] Meli C A, Greene E F, Lange G and Toennies J P 1995 *Phys. Rev. Lett.* **74** 2054
- [7] Silfhout R G 1992 *Thesis* University of Leiden
- [8] Denier van der Gon A W, Gay J M, Frenken J W M and van der Veen J F 1991 *Surf. Sci.* **241** 335
- [9] Tran T T, Thevuthasan S, Kim Y J, Friedman D J, Kaduwela A P, Herman G S and Fadley C S 1993 *Surf. Sci.* **281** 270
- [10] Takeuchi N, Selloni A and Tosatti E 1994 *Phys. Rev. Lett.* **72** 2227
- [11] Modesti S, Dhanak V R, Sancrotti M, Santoni A, Persson B N J and Tosatti E 1994 *Phys. Rev. Lett.* **73** 1951
- [12] Santoni A, Dhanak V R, Goldoni A, Sancrotti M and Modesti S 1996 *Europhys. Lett.* **34** 275
- [13] Eastman D E and Freeouf J L 1974 *Phys. Rev. Lett.* **33** 1601
- [14] Himpsel F J, Eastman D E, Heimann P, Reihl B, White C W and Zehner D M 1981 *Phys. Rev. B* **24** 1120  
Bringans R D and Höchst H 1982 *Phys. Rev. B* **25** 1081  
Bringans R D, Uhrberg R I G and Bachrach R Z 1986 *Phys. Rev. B* **34** 2373  
Aarts J, Hoeven A J and Larsen P K 1988 *Phys. Rev. B* **37** 8190
- [15] Indlekofer G, Oelhafen P, Lapka R and Güntherodt H J 1988 *Z. Phys. Chem.* **157** 465  
Indlekofer G 1988 *PhD Thesis* University of Basel
- [16] Jank W and Hafner H 1990 *Phys. Rev. B* **41** 1497