



ELSEVIER

Surface Science 331-333 (1995) 1435-1440

surface science

## Determination of anisotropic vibrations by tensor LEED

U. Löffler<sup>a,\*</sup>, U. Muschiol<sup>a</sup>, P. Bayer<sup>a</sup>, K. Heinz<sup>a</sup>, V. Fritzsche<sup>b</sup>, J.B. Pendry<sup>c</sup>

<sup>a</sup> *Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany*

<sup>b</sup> *Technische Universität Dresden, Institut für Theoretische Physik, D-01062 Dresden, Germany*

<sup>c</sup> *The Blackett Laboratory, Imperial College, London SW7 2BZ, UK*

Received 30 July 1994; accepted for publication 11 November 1994

### Abstract

We present a new method for the determination of anisotropic (and anharmonic) vibrations by the analysis of temperature dependent LEED intensities using the tensor LEED formalism. The method is applied to the adsorbate system Ni(100) c(2×4)K for temperature dependent data varying between 90 and 200 K. The root mean square displacements parallel to the surface are found to be as large as 0.5 Å. This is about 10 times larger than the value perpendicular to the surface. The inclusion of anisotropic vibrations remarkably improves the experiment-theory fit. So, for  $T = 90$  K the Pendry  $R$ -factor is reduced from 0.26 to 0.19. Though the investigated temperature range of 90–200 K is not large enough to see a strong temperature dependence, the expected trend of increasing vibration amplitudes with increasing temperature is visible.

**Keywords:** Alkali metals; Low energy electron diffraction (LEED); Low index single crystal surfaces; Nickel; Surface structure; Vibrations of adsorbed molecules

### 1. Introduction

It is well known that intensities measured in low energy electron diffraction (LEED) depend on temperature. With increasing temperature the spot intensities weaken in favour of enhanced background intensities. Kinematically this phenomenon can be described by a Debye-Waller factor, which accounts for harmonic vibrations of the scatterers. Whilst this is a good approximation for X-ray diffraction the multiple scattering dominating LEED requires a more sophisticated approach. The standard procedure is to use temperature dependent (complex) phaseshifts [1–4]. Though within this concept only isotropic, harmonic and uncorrelated vibrations can be treated it has been applied

very successfully to a large number of structural analyses.

The isotropy of harmonic vibrations, however, is a simplification which probably does not hold for most adsorbates and surface atoms. In spite of this only a few attempts have been undertaken to go beyond isotropic vibrations [5–8]. One reason for this is the fact that anisotropic vibrations destroy the spherical symmetry of the scattering problem which leads to non-diagonal  $t$ -matrices and therefore a large increase of the necessary computational efforts. Fortunately, however, with *tensor LEED* there is a formalism at hand which is designed to produce and treat non-diagonal  $t$ -matrices. Originally, the non-diagonality was introduced by static displacements of atoms off some reference positions [9–11], but recently vibrational isotropic displacements could be simulated in

\* Corresponding author. Fax: +49 9131 858400.

this way [12]. Moreover, an efficient way to calculate atomic t-matrices for anisotropic and even anharmonic vibrations has been suggested only recently [13]. Here we present this new method and apply it to the adsorbate system K/Ni(100) whose structure has been investigated earlier [14,15].

## 2. Theory

### 2.1. The treatment of anisotropic vibrations by tensor LEED

Within the formalism of tensor LEED [9-11] the diffraction amplitude  $A$  of a certain structure deviating from a reference structure with amplitude  $A_0$  is calculated by perturbation,  $A = A_0 + \delta A$ . The amplitude change  $\delta A$  is written as  $\delta A = \sum_i \hat{T}_i \delta \hat{t}_i$ , where the quantities  $\hat{T}_i$  are tensors depending only on the reference structure. The  $\delta \hat{t}_i$  represent the change in scattering strength of a certain atom  $i$ , i.e. the change of the atomic t-matrix of that atom. This change may be due to geometrical displacements (*geometrical tensor LEED*, the case for which tensor LEED has been developed in the first place [9-11]), to the substitution of an atomic scatterer by a different one (*chemical tensor LEED*), with  $\delta \hat{t} = \hat{t}(\text{new atom}) - \hat{t}(\text{old atom})$  [16-19] or to isotropic thermal vibrations with  $\delta \hat{t} = \hat{t}(T) - \hat{t}_0$  [12]. In the latter case the t-matrix of the vibrating atom is calculated straightforward using the concept of temperature dependent phaseshifts [1-3].

In the present paper we choose a more powerful approach which allows the treatment of anisotropic and even anharmonic vibrations [13]. With concentration to anisotropic but still harmonic vibrations, the complexity of the theory is considerably reduced. The extension to anharmonicity will be published separately. We start with the atomic t-matrix of an atom displaced by a distance  $u$  off its reference position. This writes as

$$\hat{t}(u) = \hat{J}(-u) \hat{t}^0 \hat{J}(u), \quad (1)$$

with  $\hat{J}(u)$  the free space propagator and  $\hat{t}^0$  the scattering matrix in the reference system. Now a set of matrices  $\hat{M}^\alpha$  can be found such that

$$\hat{J}(u) = \exp \left( ik \sum_{\alpha} u_{\alpha} \hat{M}^{\alpha} \right). \quad (2)$$

The index  $\alpha$  represents the real space dimensions  $x, y$  and  $z$ . It immediately follows from Eqs. (1) and (2) that

$$\hat{t}(u) = \exp \left( -ik \sum_{\alpha} u_{\alpha} \hat{M}^{\alpha} \right) \hat{t}^0 \exp \left( ik \sum_{\alpha} u_{\alpha} \hat{M}^{\alpha} \right). \quad (3)$$

Using the Baker-Hausdorff lemma we find the following exponential series which can be calculated recursively [13,20]:

$$\begin{aligned} \hat{t}(u) &= \exp \left( -ik \sum_{\alpha} u_{\alpha} [\hat{M}^{\alpha}, \bullet] \right) \hat{t}^0 \quad (4) \\ &:= \hat{t}^0 - ik \sum_{\alpha} u_{\alpha} [\hat{M}^{\alpha}, \hat{t}^0] \\ &\quad + \frac{(-ik)^2}{2!} \sum_{\alpha, \beta} u_{\alpha} u_{\beta} [\hat{M}^{\alpha}, [\hat{M}^{\beta}, \hat{t}^0]] + \dots \quad (5) \end{aligned}$$

Let us assume  $u$  to be the time-dependent amplitude of an harmonic vibration around a mean value ( $\langle u \rangle = 0$ ). We apply the same averaging procedure as used for isotropic vibrations [1,21].

$$\begin{aligned} \langle \hat{t} \rangle_u &= \left\langle \exp \left( -ik \sum_{\alpha} u_{\alpha} [\hat{M}^{\alpha}, \bullet] \right) \hat{t}^0 \right\rangle_u \\ &= \exp \left( -\frac{1}{2} k^2 \sum_{\alpha} \langle u_{\alpha}^2 \rangle [\hat{M}^{\alpha}, [\hat{M}^{\alpha}, \bullet]] \right) \hat{t}^0. \quad (6) \end{aligned}$$

In this equation it has been assumed that the principal axes of the symmetric tensor  $\langle u_{\alpha} u_{\beta} \rangle$  coincide with the axes of the coordinate system so that  $\langle u_{\alpha} u_{\beta} \rangle = 0$  for  $\alpha \neq \beta$ . Again  $\langle \hat{t} \rangle$  can be obtained by recurrence. The matrix  $\langle \hat{t} \rangle$  is diagonal for  $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$  but becomes non-diagonal for anisotropic vibrations [13].

If there is an additional static atomic displacement  $\delta r$  the total change of the t-matrix  $\delta \hat{t}$  is

$$\delta \hat{t} = \hat{J}(-\delta r) \langle \hat{t} \rangle_u \hat{J}(\delta r) - \hat{t}^0. \quad (7)$$

Here we can profit from the fact that Eq. (4) holds for both diagonal and non-diagonal matrices  $\hat{t}^0$ , where  $\delta r$  plays the role of the static displacement  $u$  in Eq. (4).

## 2.2. Validity of the method

Some tests of the new method were performed using the  $c(4 \times 2)\text{K}/\text{Ni}(100)$  adsorbate system. As starting point we used the same reference structure as described in Refs. [12,14,15], i.e. the potassium atom residing in the fourfold hollow site  $d_{01} = 2.68 \text{ \AA}$  above the top nickel layer and with nickel interlayer distances of the bulk value ( $1.76 \text{ \AA}$ ). We chose this structure as a reference because the tensors  $\hat{T}_i$  were still available from earlier work. In the reference Ni and K atoms were assumed to vibrate isotropically according to Debye temperatures  $\Theta_{\text{Ni}}=440 \text{ K}$  and  $\Theta_{\text{K}}=200 \text{ K}$ , respectively.

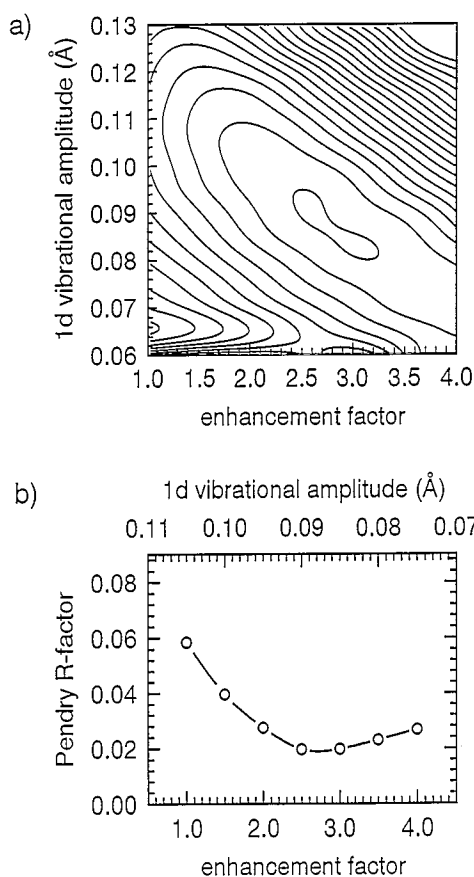


Fig. 1. Fit of the *anisotropic thermal tensor LEED* data with pseudo-experimental data for a vibration amplitude of  $0.095 \text{ \AA}$  and an enhancement factor 3. (a) Contour Pendry  $R$ -factor map (inner line  $R_p = 0.02$ , increment:  $\Delta R_p = 0.01$ ), (b) cut along a diagonal line of the map in (a).

First we made sure that our new method yields

the same results as the use of temperature corrected phaseshifts if only isotropic vibrations are allowed. A second test was to check the validity of the method for anisotropic vibrations. Of course, a fully reliable test could only come by comparison with exact results which, however, are not available because an exact theory for the handling of anisotropic vibrations is lacking. Therefore, we use a Debye–Waller-factor like approximation proposed by Van Hove and Tong (chapter 3.5 in Ref. [2]). We assume the potassium atoms to vibrate with different amplitudes  $u_{\parallel}^2 := \langle u_x^2 \rangle = \langle u_y^2 \rangle$  and  $u_{\perp}^2 := \langle u_z^2 \rangle$  in plane and normal to the surface, respectively. Kinematically this can be described by the Debye–Waller-factor

$$\exp \left[ -\frac{1}{2} \left( |\Delta k_{\parallel}|^2 u_{\parallel}^2 + |\Delta k_{\perp}|^2 u_{\perp}^2 \right) \right], \quad (8)$$

with  $\Delta k_{\parallel}$  and  $\Delta k_{\perp}$  being the momentum transfers parallel and vertical to the surface. For the higher-order intralayer scattering events it is assumed that the atoms vibrate isotropically with an averaged amplitude. We point out that our method is more accurate in this respect: It considers full multiple intra- and interlayer scattering of the anisotropic vibrating scatterer with other atoms, though for the latter only the isotropically vibrating parts of the scatterers enter the multiple scattering events. This is a good approximation because the use of temperature corrected phase shifts in the reference calculation accounts already for full multiple scattering between isotropically vibrating atoms.

Using Eq. (8) we produced a set of pseudo-experimental data. For the adlayer vibration we used  $u_{\perp} = 0.095 \text{ \AA}$  and  $u_{\parallel} = n \cdot u_{\perp}$  with the anisotropic enhancement factor  $n = 3$  (the value  $u_{\perp} = 0.095 \text{ \AA}$  was chosen because it corresponds to the one-dimensional (1D) vibration amplitude  $u_{1D} = 0.095 \text{ \AA}$  fitting the potassium Debye temperature  $\Theta_{\text{K}} = 200 \text{ K}$ ). All other parameters were taken from the reference calculation described above. They were fitted using our new method where  $u_{\perp}$  and  $n$  were varied in the ranges  $0.06 \text{ \AA} \leq u_{\perp} \leq 0.13 \text{ \AA}$  and  $1 \leq n \leq 4$ , respectively. As displayed in Fig. 1a, a broad minimum results with  $R_p = 0.02$ . If we cut along a diagonal line in Fig. 1a we can extract a shallow minimum for  $u_{\perp} \approx 0.087 \text{ \AA}$  and  $n \approx 2.7$  (Fig. 1b). These values fit within the limits of error to those of the pseudo-experiment, though they are slightly shifted towards smaller vibrational amplitudes. This is reasonable because our

method accounts more realistically for anisotropic vibrations whilst their influence on intralayer scattering is neglected in the Debye-Waller-factor approach.

### 3. Application to experimental data of Ni(100) $c(2 \times 4)K$

At coverage of  $\frac{1}{4}$  potassium exhibits a well ordered  $c(2 \times 4)$  superstructure on Ni(100) [14]. Since this ordering takes place even at liquid nitrogen temperature, the potassium atoms must be quite mobile at the surface. In a simplified picture there is a weakly corrugated binding potential with energetically favored hollow sites and diffusion between them. Therefore we expect larger root mean square (rms) vibrational amplitudes parallel to the surface than perpendicular to it. This should show up in the analysis of intensities, in particular of temperature dependent data. Therefore,  $I(E)$  spectra for integer and fractional order spots were taken at 90, 125, 150, 175 and 200 K. The experimental set-up and video data acquisition method is described in detail elsewhere [14,22-24]. The data used in the present paper are slightly different from those published earlier [15] because the temperature control involved some different mode of measurement.

An anisotropic harmonic vibration can be described by an ellipsoid or shortly by its three principal axes. In our case we chose these principal axes to coincide with the cartesian coordinate axes. The values of the rms vibrational amplitude along those axes, i.e.  $\sqrt{\langle u_x^2 \rangle}$ ,  $\sqrt{\langle u_y^2 \rangle}$  and  $\sqrt{\langle u_z^2 \rangle}$  must be varied in the course of the intensity analysis. For isotropic vibrations we find  $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$  and therefore  $u_{3D}^2 = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle = 3\langle u_x^2 \rangle$ . With the formula given in Ref. [2]

$$\left(u_{3D}^{\text{Debye}}\right)^2 := \langle u^2 \rangle = \sqrt{\left(\frac{9\hbar^2}{4mk_B\Theta_D}\right)^2 + \left(\frac{9\hbar^2 T}{mk_B\Theta_D^2}\right)^2} \quad (9)$$

the one-dimensional (1D) vibration amplitude  $u_{1D} = \sqrt{\langle u_x^2 \rangle} = \sqrt{\langle u_y^2 \rangle} = \sqrt{\langle u_z^2 \rangle} = \frac{1}{\sqrt{3}}u_{3D}^{\text{Debye}}$  may be calculated from the Debye-temperature  $\Theta_D$  and the measurement temperature  $T$ . As pointed out in Ref. [14] a potassium Debye-temperature of about 200 K has been found in the course of the fitting procedure. Using

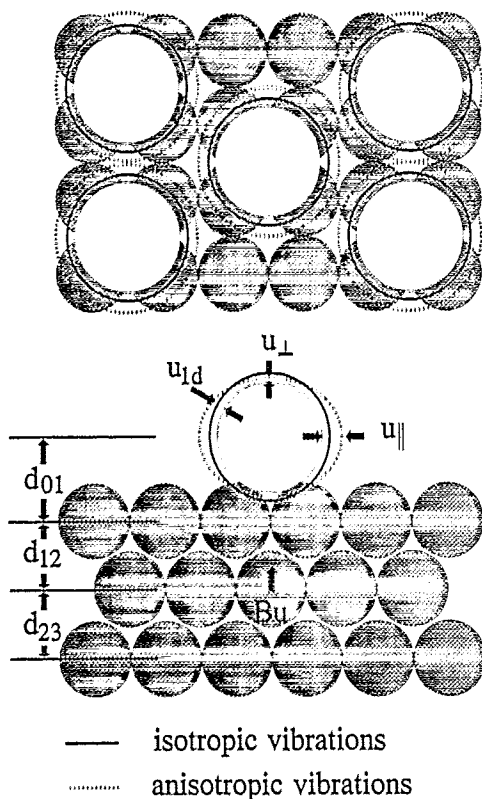


Fig. 2. Vibrational and structural parameters of  $c(4 \times 2)K/Ni(100)$  in on-top view (top) and side view (bottom).

isotropic, harmonic vibrations, *thermal tensor LEED* confirmed that result within the limits of error yielding vibration amplitudes corresponding to  $\Theta_D = 180$  K [12]. This leads to an 1D vibration amplitude  $u_{1D} \approx 0.1 \text{ \AA}$  for  $\Theta_D = 180$  K and  $T = 90$  K.

In the present paper we allow for different vibration amplitudes parallel and perpendicular to the surface, i.e. vibrational isotropy is reduced to in-plane vibrations ( $\langle u_x^2 \rangle = \langle u_y^2 \rangle = u_{\parallel}^2$ ,  $\langle u_z^2 \rangle = u_{\perp}^2 \neq u_{\parallel}^2$ ).

Since a change of the vibrational properties of an atom changes its scattering behavior, it can easily influence the resulting best fit geometrical structure. We therefore varied both the vibrational parameters of the K-atom and the geometrical positions of atoms in the substrate as well as in the adlayer. The best fit results for 90 and 175 K are given in Tables 1 and 2, respectively.  $\bar{R}$ ,  $R_i$  and  $R_f$  denote the Pendry  $R$ -factors as averaged over all, integer order and fractional order beams, respectively. The quantities  $\Delta d_{01}$ ,  $\Delta d_{12}$  and  $\Delta d_{23}$  are the deviations of the layer distances from the

Table 1  
Best fit parameters for isotropic and anisotropic vibrations using 90 K data

*	Isotropic vib.	Anisotropic vib.
$\bar{R}$	0.26	0.19
$R_i$	0.24	0.23
$R_f$	0.28	0.16
$\Delta d_{01}$	+0.015 Å	+0.045 Å
$\Delta d_{12}$	-0.015 Å	+0.00 Å
$\Delta d_{23}$	0.00 Å	-0.015 Å
Bu	0.030 Å	0.075 Å
$u_{1D}$	0.135 Å ± 0.06 Å	-
$u_{\perp}$	-	0.05 Å <sup>+0.07Å</sup> (-0.05Å)
$u_{  }$	-	0.4 Å ± 0.12 Å

Table 2  
Best fit parameters for isotropic and anisotropic vibrations using 175 K data

*	Isotropic vib.	Anisotropic vib.
$\bar{R}$	0.30	0.21
$R_i$	0.24	0.19
$R_f$	0.34	0.22
$\Delta d_{01}$	+0.02 Å	+0.065 Å
$\Delta d_{12}$	+0.00 Å	+0.00 Å
$\Delta d_{23}$	+0.00 Å	-0.015 Å
Bu	-0.015 Å	0.045 Å
$u_{1D}$	0.15 Å ± 0.05 Å	-
$u_{\perp}$	-	0.05 Å <sup>+0.09Å</sup> (-0.05Å)
$u_{  }$	-	0.5 Å ± 0.15 Å

reference structure. The parameter Bu indicates the buckling in the second layer as shown in Fig. 2. On the left hand side of the table only isotropic vibrations were allowed, on the right hand side the vibrations were allowed to be anisotropic as described above.

The inclusion of anisotropic vibrations leads to a considerable  $R$ -factor improvement for both the 90 and the 175 K data. Particularly the fractional order  $R$ -factor,  $R_f$ , improves drastically from 0.28 to 0.16 (90 K) and from 0.34 to 0.22 (175 K). It should be noted that the variance of the Pendry  $R$ -factor is as low as 0.05 for both data sets. So, the improvements of the total  $R$ -factor from 0.26 to 0.19 and from 0.30

to 0.21 are significant.

For the 90 K data full dynamical intensity analyses assuming isotropic vibrations were carried out earlier [12,14,15]. However, they cannot be compared to the present results in a straightforward manner because they correspond to slightly different experimental data [12,14,15] and either lack to consider a buckling of the substrate [14] or additionally include some scattering from the surface dipole caused by potassium [15]. Nevertheless, the results for the geometrical parameters agree within the limits of error given by the variance of the Pendry  $R$ -factor. However, it is worth noting that by allowing for anisotropic vibrations both the buckling in the second layer and the adsorption height of potassium can shift considerably, i.e. of the order of 0.05 Å. Clearly, the proper consideration of vibrational anisotropy is of importance not only for the quality of the theory-experiment fit but also – what is even more important – for the values of structural parameters determined by LEED intensity analysis.

As apparent from Tables 1 and 2 the vibrational amplitudes parallel to the surface can be 10 times larger than normal to the surface. This is corroborated by the high mobility potassium atoms exhibit even at low temperatures and fits well to the hard core radii as shown in Fig. 2. The absolute values of  $u_{||} \approx 0.4$  Å compare well to the results ( $u_{||} = 0.3$  Å) obtained with the concept of split positions found for K on Al(111) [8]. The surface parallel amplitude is higher at 175 K than at 90 K as it should but we should keep in mind the large error bars involved and inherent to LEED for surface parallel parameters. Nevertheless we evaluated the intensities also for the other temperatures of measurement given above. From the results we calculate  $u_{3D} = \sqrt{\langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle}$  and compare it to  $u_{3D}^{\text{Debye}}$  for isotropic vibrations according to the Debye model (Eq. (9)). The results are displayed in Fig. 3 where the lines correspond to  $u_{3D}^{\text{Debye}}$  for the Debye temperature given.

Unfortunately it was not possible to measure experimental data for temperatures higher than 200 K since the K-atoms start to disorder such that the  $c(4 \times 2)$  structure becomes unstable. Since the measured temperatures lie in the same range as the Debye temperatures and the range of 90–200 K is relatively small we do not see a clear  $\sqrt{T}$  dependence as expected from the high temperature limit. Instead of this we

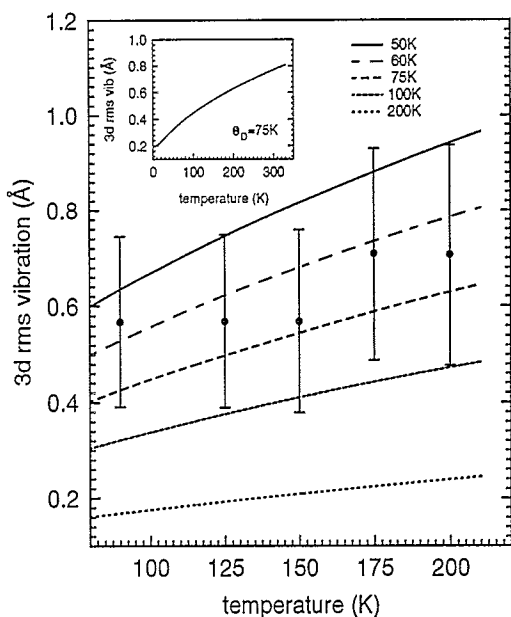


Fig. 3. Temperature dependence of vibration amplitudes. Data points: 3D vib. amplitudes  $u_{3D}$ ; lines: 3D vib. amplitude  $u_{3D}^{\text{Debye}}$  using isotropic Debye model.

observe only a section of the larger temperature scale depicted in the upper left of Fig. 3, where the well known features as zero point vibrations and the high temperature limit are visible. Since the lateral vibrations are the main contributions to  $u_{3D}$  calculated from our data, the errorbars are relatively large. Nevertheless, the temperature dependence fits reasonably well to the  $u_{3D}^{\text{Debye}}(T)$  trend for an effective Debye temperature of about 70 K. This comparatively low  $\Theta_D$  takes account for the large lateral vibration amplitudes (up to 0.5 Å for  $T = 200$  K) and may not be mixed up with the best fit  $\Theta_D$  of about 200 K found for isotropic vibrations, where particularly the strong influence of the vibrations perpendicular to the surface dominates.

### Acknowledgements

We gratefully acknowledge support by the German Research Foundation (SFB 292), the Leibniz-Rechenzentrum München and by the Höchstleistungsrechenzentrum (HLRZ) Jülich.

### References

- [1] J.B. Pendry, *Low Energy Electron Diffraction* (Academic Press, London, 1974).
- [2] M.A. Van Hove and S.Y. Tong, *Surface Crystallography by LEED* (Springer, Heidelberg, 1979).
- [3] M.A. Van Hove, W.H. Weinberg and C.-M. Chan, *Low-Energy Electron Diffraction* (Springer, Heidelberg, 1986).
- [4] M.M. Nielsen, J. Burchhardt, D.L. Adams, E. Lundgren and J.N. Andersen, *Phys. Rev. Lett.* 72 (1994) 3370.
- [5] M. Uehla and H. L. Davis, *J. Vac. Sci. Technol.* 15 (1978) 642.
- [6] J.B. Pendry and K. Heinz, *Surf. Sci.* 230 (1990) 137.
- [7] H. Over, W. Moritz and G. Ertl, *Phys. Rev. Lett.* 70 (1993) 315.
- [8] C. Stampfl, M. Scheffler, H. Over, J. Burchhardt, M. Nielsen, D.L. Adams and W. Moritz, *Phys. Rev. B* 49 (1994) 4959.
- [9] P.J. Rous, J.B. Pendry, D.K. Saldin, K. Heinz, K. Müller and N. Bickel, *Phys. Rev. Lett.* 57 (1986) 2951.
- [10] P.J. Rous and J.B. Pendry, *Surf. Sci.* 219 (1989) 355, 373.
- [11] P.J. Rous, *Progr. Surf. Sci.* 39 (1992) 3.
- [12] U. Löffler, R. Döll, K. Heinz and J.B. Pendry, *Surf. Sci.* 301 (1994) 346.
- [13] V. Fritzsche, *Phys. Rev. B* 50 (1994) 1922.
- [14] U. Muschiol, P. Bayer, K. Heinz, W. Oed and J.B. Pendry, *Surf. Sci.* 275 (1992) 185.
- [15] V. Fritzsche, J.B. Pendry, U. Löffler, H. Wedler, M.A. Mendez and K. Heinz, *Surf. Sci.* 289 (1993) 389.
- [16] R. Döll, M. Kottcke and K. Heinz, *Phys. Rev. B* 48 (1993) 1973.
- [17] R. Döll, M. Kottcke and K. Heinz, *Surf. Sci.* 304 (1994) 309.
- [18] R. Döll, M. Kottcke, K. Heinz, L. Hammer, K. Müller and D.M. Zehner, *Surf. Sci.* 307–309 (1994) 434.
- [19] K. Heinz, *Surf. Sci.* 299/300 (1994) 433.
- [20] W. Oed, P.J. Rous and J.B. Pendry, *Surf. Sci.* 273 (1992) 261.
- [21] A.A. Maradudin, E.W. Montroll and G.H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation*, Solid State Physics, Supplement 3 (Academic Press, New York, 1963).
- [22] K. Heinz, K. Müller, in: *Structural Studies of Surfaces*, Vol. 91 of Springer Tracts in Modern Physics, Ed. G. Höhler (Springer, Berlin, 1982).
- [23] K. Heinz, *Prog. Surf. Sci.* 27 (1988) 239.
- [24] U. Muschiol, *Diplomthesis*, Erlangen, 1992.