# Surface–surface phonon scattering by surface inhomogeneities

A Khater†‡, N Auby† and D Kechrakos§

† Service de Recherche sur les Surfaces et l'Irradiation de la Matière, CEN Saclay, 91191 Gif sur Yvette Cédex, France
‡ Laboratoire de Physique des Matériaux CNRS Unité de Recherche Associé No 807, Université du Maine, 72017 Le Mans Cédex, France
§ Department of Physics, University of Exeter, Exeter EX4 4QL, UK

**Abstract.** A one-dimensional model is presented for surface phonon scattering into surface phonon channels by atomic inhomogeneities along a high symmetry direction in a solid surface. The model yields characteristic resonances over the full Brillouin zone of the model linear chain, for a monoatomic step and an adatom, at the limit of low concentrations where the approximation of an isolated inhomogeneity holds. Additional resonances are found near the step edges for a symmetric double step, these indicate weak localization of surface phonons on a slightly disordered surface. The theoretical results can, in principle, be tested by electron energy loss spectroscopy and He atom surface scattering.

## 1. Introduction

The phonon structure of low-index surfaces has been studied extensively using electron energy loss spectroscopy (EELS) [1], and helium atom scattering [2]. Theoretical models typically employ the model of nearest and next-nearest-neighbour force constants in the harmonic approximation [3–5]. Although extensive, this study of surface phonons has been limited to ideal surfaces.

Interest in disordered surfaces is a more recent development [6–11]. This type of disorder concerns random steps and terraces, and inhomogeneities on the surface such as adsorbates and substitutional impurities. It concerns a more general situation than the vicinal surfaces usually characterized by periodic steps, and terraces.

The analysis of phonons in the neighbourhood of isolated inhomogeneities differs from that on ideal surfaces, and is more complicated. Surface inhomogeneities modify the vibrational properties of the system in two ways; firstly, they can give rise to new modes localized in their neighbourhood, and secondly they scatter the bulk and surface phonons.

The vibrational states in a disordered surface have been studied for an isolated step in the surface of a simple cubic lattice with nearest-neighbour interactions [6]. This is an idealized system as the lattice is unstable, and exhibits no surface phonons. There are also calculations for localized states, and phonon scattering into surface and bulk channels [7–9], using elasticity theory in the acoustic limit for the phonon wave vector domain $\leqslant l^{-1}$, where $l$ is a measure of the average distance between successive peaks and
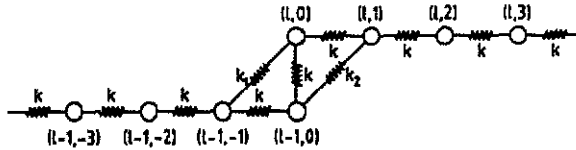
**Figure 1.** Schematic representation of one-dimensional model for an isolated step in a given symmetry direction on the surface.

valleys in a surface with a small degree of roughness [7], or the width of an isolated ridge [9], or island [8].

The study of localized states and phonon scattering by atomic inhomogeneities needs to consider processes for wavevectors out to the Brillouin zone boundary, $\geqslant l^{-1}$. This has been discussed for localized states on steps in an FCC surface [10]; the model, however, considers wide terraces separated by periodic monoatomic steps. This situation has been investigated using similarly imposed periodic boundary conditions [11]. Atomic scale approximations can also be used to study phonon scattering in surfaces with random adsorbates [12], in surface alloys [13], and alloy interfaces [14]. A complete treatment of these processes involves the scattering of surface phonons into both surface and bulk channels.

One-dimensional models have long been of theoretical interest as hypothetical systems with simple mathematical properties which can yield useful information (e.g. Lieb and Mattis [15]). We have recently used a one-dimensional model for phonon scattering in bulk AgBr:I, to calculate the scattering cross section of coherent phonons generated on an excited iodine impurity I* along a direction that is slightly off a high symmetry axis and is reflected at a non-excited impurity I [16]. It can be shown that the weak localization of phonons in the bulk semiconductor contributes to the increase in photoluminescence intensity, above a threshold concentration of the impurities which corresponds to an average distance between I* and I that is smaller than the bulk phonon coherence length.

The high-symmetry direction for phonons in a surface is a weaker diffractive system than the off-symmetry axis encountered in bulk AgBr, and, furthermore, Rayleigh modes are more localized than the bulk phonons. Consequently the one-dimensional model [16] can be extended to a high-symmetry direction in the surface, along which a Rayleigh phonon propagates. The model accounts for phonon scattering into surface channels and neglects scattering into bulk channels. Detailed results obtained over the full Brillouin zone can be tested experimentally by EELS and He atom scattering.

The analysis presented is for surface–surface phonon scattering by an isolated surface inhomogeneity such as a monoatomic step (figure 1), an adsorbate atom (figure 4), and a symmetric double step (figure 8). This is done using a one-dimensional model in a given symmetry direction in the surface and the matching technique [5] to calculate the scattering cross section at the inhomogeneities. The one-dimensional model yields detailed results for the displacement eigenvectors of the atoms on, and away from, the inhomogeneity. It does so for given configurations of the force constants which simulate the strain field of the inhomogeneity. In the matching approach we are able to deal with both localized phonons and the scattering of phonons by surface inhomogeneities, within the same mathematical framework. In this paper only the scattering results are presented. In general, they show resonant behaviour on the dispersion curve of the Rayleigh surface phonons.

In particular we find that at low concentrations, where the approximation of an isolated inhomogeneity holds, a characteristic resonant behaviour exists when Co adatoms on Cu(001) scatter the Rayleigh phonon in the (110) direction, at a frequency that is approximately 75% of its maximum value. It is also found that for a surface with a weak degree of disorder, characterized by a relatively small density of atomic steps, strong oscillatory resonances can exist on the steps due to the exchange of coherent surface phonons between the steps. These resonances should disappear with decreasing step densities when the average distance between the steps becomes larger than the phonon coherence length. Such effects should be measurable using EELS and He atom surface scattering.

## 2. Single surface step

This case is modelled (figure 1), by two linear chains $l$ and $l - 1$, joined by a step. There is experimental evidence that the frequencies of the localized vibrational states on the step can be either greater than the maximum frequency of the bulk phonon spectrum [17], or smaller than the frequency of the surface phonon mode [18] of the flat terraces. This has been modelled by attributing stiffened [19] or loosened [18] force constants in the neighbourhood of the step.

The stiffening or loosening of the force constants in the neighbourhood of a step is simulated (see figure 1) by two additional interactions, $k_1$ on the outside of the step between the $(l, 0)$ and $(l - 1, -1)$ atoms, and $k_2$ on the inside of the step between the $(l, 1)$ and $(l - 1, 0)$ atoms. The force constants between the atoms are otherwise equal to $k$, and $k \neq k_1 \neq k_2$ in general. It is convenient to define the dimensionless quantities $r_1 = k_1/k$ and $r_2 = k_2/k$.

The dynamics of a localized longitudinal vibrational state on the step can be characterized by the equation:

$$\mathbf{A}u = 0 \tag{1}$$

where $\mathbf{A}$ is a dynamical matrix, in this case reduced to six rows and eight columns. The matrix elements are given as:

$$A_{11} = \Omega^2 - (1 + r_1/2) \qquad A_{22} = \Omega^2 - (1 + r_2/2)$$

$$A_{33} = \Omega^2 - (2 + r_2/2) \qquad A_{44} = \Omega^2 - (2 + r_1/2)$$

$$A_{55} = A_{66} = \Omega^2 - 2$$

$$A_{14} = A_{41} = r_1/2 \qquad A_{23} = A_{32} = r_2/2 \tag{2}$$

$$A_{13} = A_{24} = A_{35} = A_{46} = A_{57} = A_{68} = A_{31} = A_{42} = A_{53} = A_{64} = 1.$$

All other elements $= 0$.

In equations (1) and (2) the dispersion of longitudinal surface Rayleigh phonons on the flat terraces corresponds to the linear chain modes. This is an adequate approximation for this model. The column vector $u$ groups the components of the longitudinal displacements of the atoms in the neighbourhood of the step, and is given by:

$$u = [u(l, 0), u(l - 1, 0), u(l, 1), u(l - 1, -1), u(l, 2),$$

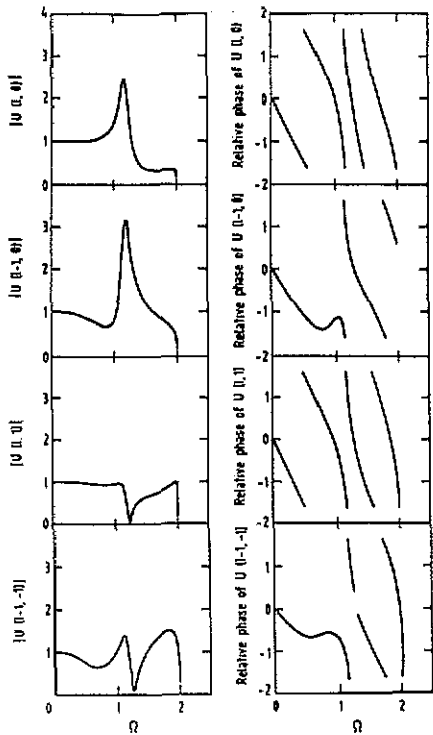$$\times u(l - 1, -2), u(l, 3), u(l - 1, -3)]^T. \tag{3}$$

**Figure 2.** Relative moduli and phases of the longitudinal displacements of the $(l, 0)$, $(l - 1, 0)$, $(l, 1)$, and $(l - 1, -1)$ atoms, as a function of the dimensionless frequency $\Omega$. (See text for details.)
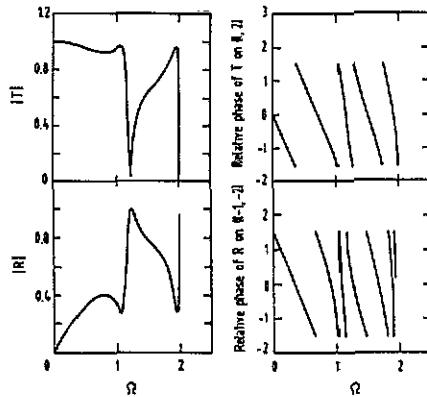
**Figure 3.** As in figure 2 for the transmission $(T)$ and reflection $(R)$ coefficients on $(l, 2)$ and $(l - 1, -2)$ atoms, respectively.

The scattering of chain phonons by the step is studied by the matching technique, with reference to an incident phonon, which is split into its transmitted and reflected parts. Equation (1) becomes inhomogeneous, and is solved to yield the displacement eigenvectors. The results presented in this section are obtained with reference to a phonon incident from the left in figure 1, of unit amplitude, and of zero phase on the $(l - 1, -2)$ atom.

The numerical analysis is carried out for values of $r_1 = 0.8$ and $r_2 = 1.2$, which are reasonable values for a case study. In figure 2, the relative moduli and phases of the respective longitudinal displacements $u(l, 0)$, $u(l - 1, 0)$, $u(l, 1)$, and $u(l - 1, -1)$, are presented as a function of the dimensionless frequency $\Omega$ in the interval $0 \leqslant \Omega \leqslant 2$ of the phonons energy band. There is resonant behaviour on the four step atoms $(l, 0)$, $(l - 1, 0)$, $(l, 1)$, $(l - 1, -1)$, where pronounced maxima on the first pair correspond to pronounced minima on the last pair. The four atoms oscillate in phase at this frequency, which is characteristic of the given $r_1$ and $r_2$ values.

The absolute moduli of the transmission $T$ and reflection $R$ coefficients, and the relative phases of $T$ and $R$ on the $(l, 2)$ and $(l - 1, -2)$ atoms, respectively, are given in figure 3. $T$ and $R$ serve to construct the displacement amplitudes $u(l, n)$ and $u(l - 1, -n)$ for all $n \geqslant 2$. The condition that

$$|R|^2 + |T|^2 = 1 \tag{4}$$

for each $\Omega$, is used as a check on the calculation. The $u(l, 1)$ displacement amplitude is
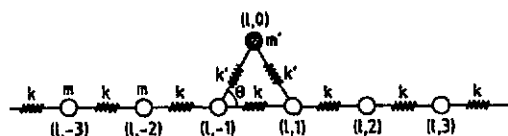
Figure 4. Schematic representation of one-dimensional model for an adsorbate atom along a given symmetry direction on the surface.

the same as the amplitude of the transmission coefficient $T$, although they have different phase structures over the frequency range of the surface Rayleigh phonons. In contrast, the $u(l-1, -1)$ displacement eigenvector differs significantly from the reflection coefficient $R$ in amplitude and phase over this $\Omega$ range.

## 3. Isolated adsorbate atom

Adsorbate atoms present on the flat terraces of a solid surface in small concentrations, are modelled in figure 4. A given symmetry direction in the surface describes a linear chain of host atoms. The adsorbate is physisorbed by additional force constants $k'$, to the two nearest-neighbour host atoms. In general the adatom mas $m'$ is different from the mass $m$ of chain atoms, and $\theta$ is the angle which it subtends on its two nearest neighbours.

The scattering of the chain phonons by the adsorbate is characterized by the possibility of longitudinal and transverse polarizations for the displacement eigenvectors on the adatom and the chain atoms in its neighbourhood. However, the present work is concerned with the case when no mode-mixing occurs due to the scattering process, and the chain atoms are kept away from the inhomogeneity to propagate a single polarization. It is convenient to define the following quantities:

$$a_1 = r\cos^2\theta \qquad a_2 = r\sin^2\theta$$
$$b = r\sin\theta\cos\theta \qquad (5)$$
$$m' = m(1+\varepsilon) \qquad r = k'/k.$$

The dynamics of this inhomogeneity are characterized by equation (1), where $\mathbf{A}$ is now the appropriate dynamical matrix, and the column vector $u$ groups the components of the longitudinal $x$ and transverse $z$ components of the atomic displacements:

$$u = [u_x(0), u_z(0), u_x(-1), u_z(-1), u_x(1), u_z(1), u_x(-2), u_z(2), u(-3), u_x(3)]^T. \qquad (6)$$

The scattering of longitudinal chain phonons by the adsorbate is analysed, with reference to a phonon of unit amplitude, and of zero phase on the $l = -2$ atom. The calculation considers the particular case of an isolated Co atom on the Cu(001) surface, thus figure 4 models the adsorbate viewed along the (110) direction. Numerical values for the quantities are $\theta = 1.028$ rad, $\varepsilon = 0.07$, and $r = 1.179$ [20, 21].

The relative moduli and phases of the Co adsorbate, the neighbouring Cu atoms, and the $T$ and $R$ coefficients, are presented in figures 5–7, respectively, as a function of $\Omega$. The presence of the adsorbate modifies the transmission properties of the Rayleigh phonon, and induces strong resonances on and in the neighbourhood of the adsorbate, which should be susceptible to experimental measurement. The $z$ component resonance of the Co atom which is perpendicular to the surface, and which is usually sensitive to a helium scattering experiment, has a pronounced maximum, and occurs at a definite
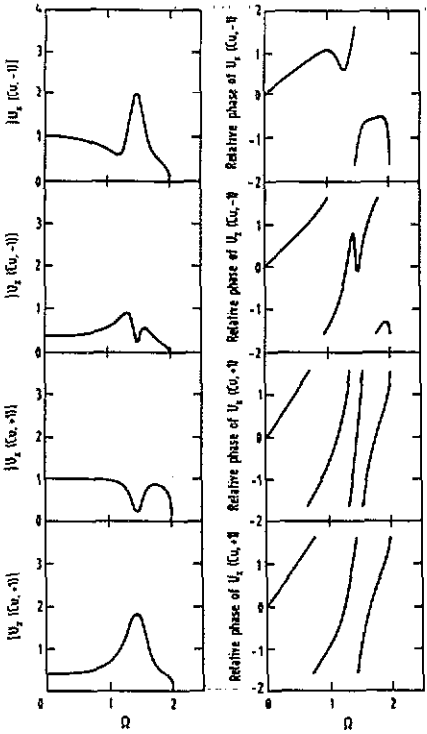
**Figure 5.** Relative moduli and phases of the longitudinal and transverse displacement of the Co adatom on a Cu (100) surface, in the (110) symmetry direction. (See text for details.)
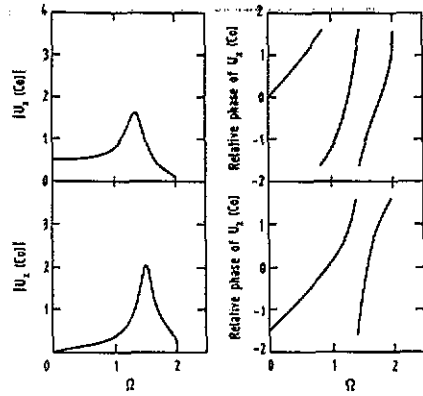
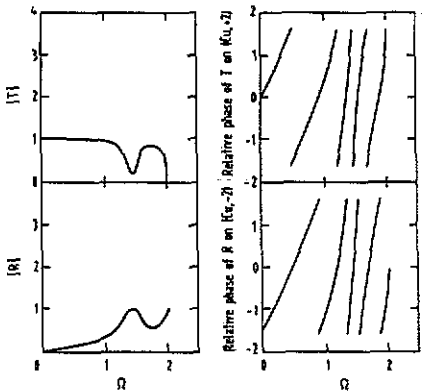**Figure 6.** As in figure 5 for the (Cu, −1) and (Cu, +1) atoms.

**Figure 7.** As in figure 5 for the transmission ($T$) and reflection ($\bar{R}$) coefficients, on the (Cu, +2) and (Cu, −2) atoms respectively.

change of phase from $+\pi/2$ to $-\pi/2$. This resonance also occurs at a frequency which is a characteristic fraction (0.75) of the maximum of the Rayleigh mode along the (110) direction in the Cu(100) surface.

Comparing figures 2, 5 and 6, we note similar resonant behaviour for phonon scattering by isolated steps and adsorbate atoms. This implies that it may be more
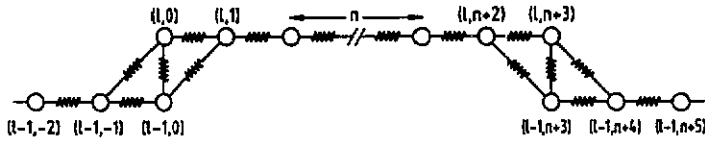
**Figure 8.** Schematic representation of the one-dimensional model for double steps in a given symmetry direction on the surface.

difficult to differentiate between step and adsorbate phonon scatterings than the helium atom scattering technique had led us to assume.

## 4. Isolated double step

The surface–surface phonon scattering is now considered for double steps (figure 8), where the two step edges are sufficiently far apart to justify decoupling the dynamics of the two edges. There exists a domain where the two edges are still sufficiently close ($n$ corresponds to a distance smaller than the surface phonon coherence length) where the two steps interact by exchanging coherent surface phonons. The calculation is done to test the weak localization of surface phonons in a surface with a small degree of disorder.

$T$ and $R$ denote the transmission and reflection amplitudes, respectively, on the step edge of figure 1, and $\hat{T}$ and $\hat{R}$ are defined by:

$$\hat{T}(r_2, r_1) = T(r_1, r_2) \tag{7}$$

$$\hat{R}(r_2, r_1) = R(r_1, r_2). \tag{8}$$

Assuming that $n \leqslant$ the surface phonon coherence length, an infinite series of transmissions and reflections at the two step edges can be summed analytically to yield standing wave modes.

It is relatively easy to show that the displacements of the $(l-1, n+5)$ and the $(l-1, -2)$ atoms can be represented within the coherence approximation by:

$$u(l-1, -2) = 1 + R + T\hat{T}R(1 - \hat{R}^2)^{-1}$$
$$u(l-1, n+5) = T\hat{T}(1 - \hat{R}^2)^{-1} \tag{9}$$

with reference to a phonon incident from the left of unit amplitude and zero phase on the $(l-1, -2)$ atom.

For most solids at room temperature the bulk phonon coherence length is $\approx 80$ Å. The requirement is consequently that for a lattice parameter $a$, the distance, $na$ satisfies the condition:

$$8 \text{ Å} \leqslant na \leqslant 80 \text{ Å}$$

assuming equivalent coherence lengths for surface and bulk phonons.

The amplitude of the atoms on the plateau between the two step edges can be similarly obtained within the coherence approximation in the form:

$$u(l, 1+s) = \exp(-is\varphi) \, T(1 - \hat{R}) \tag{10}$$

where $s = 0, 1, \ldots n$ on the plateau, and $\varphi = qa$ is the phonon phase angle.

The numerical analysis is carried out for $r_1 = 0.8$ and $r_2 = 1.2$. It is instructive to calculate the standing-wave displacements $u(l-1, -2)$ and $u(l-1, n+5)$ in the
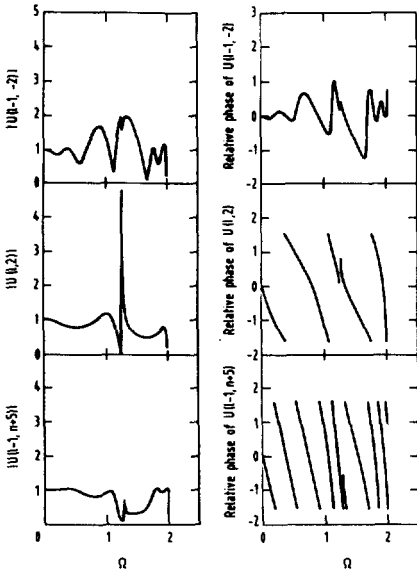
**Figure 9.** The relative moduli and phases of the longitudinal displacements which characterize phonon scattering by the double step, at $(l-1, -2)$ and $(l-1, n+5)$ atoms in the neighbourhood of the step edges, and at $(l, 2)$ on the plateau. (See text for details.)

neighbourhood of the step edges, which characterize backward and forward scattering by the double step. These results, and the displacement $u(l, 2)$ which characterizes the vibrational states of the plateau atoms, are presented in figure 9.

The surface–surface phonon scattering induces a pronounced resonance on the plateau atoms of the double step. This additional structure corresponds to standing wave resonant states within the step. The backward and forward scattering are characterized in the step edge regions, by additional structure which is absent from the single isolated step. The only comparison we can make in this context is with previous work by Lahee *et al* [22] on helium atom scattering from step edges on a Pt(111) surface. The main feature of their result is the strong oscillatory behaviour, with additional superstructure near the Bragg positions. These oscillations were first explained as the diffraction pattern of the step edge which was assumed to be a static half-cylinder hard boss. Hinch [23] has used a more realistic shape, but his use of the Eikonal approximation is questionable for such a large corrugation. Owing to the simplicity of our model we have not attempted a detailed comparison with the experimental data for Pt(111). Nevertheless it should be noted that we observed similar oscillatory behaviour for the spectral intensity of atomic displacements in the neighbourhood of the step edges of double steps.

## 5. Conclusions

A one-dimensional model for the analysis of surface–surface phonon scattering by isolated surface inhomogeneities, is presented, for a given high symmetry direction in the surface, neglecting surface–bulk phonon scattering.

The matching technique is used to calculate the eigenvectors of the atomic displacements on surface inhomogeneities and away from them, using plausible configurations of force constants, to simulate the strain field of the inhomogeneity. In particular the Rayleigh mode scattering by isolated steps, adatoms (Co on Cu), and

symmetric double steps, are investigated, in the limit of small concentrations where the approximation of an isolated inhomogeneity holds.

This leads to a number of quantitative conclusions. Firstly, characteristic resonant behaviour is found for the atomic displacements on the inhomogeneity which, in principle, should be detectable by helium atom scattering and EELS, scanning along the Rayleigh dispersion curve. In particular we find characteristic resonances for Co on Cu(100) along the (110) direction for frequencies which are approximately 75% of the maximum Rayleigh mode frequency.

Secondly, comparing the theoretical results for isolated steps and adatoms, it may be difficult using present experimental techniques to distinguish between a single atomic step and an adatom, since their resonant spectra bear strong similarities.

The third conclusion concerns helium atom scattering from step edges as in Pt(111), which has been ascribed to diffraction effects from a static structure modelling the inhomogeneity. Analysing the double step, we have found that strong oscillatory behaviour occurs on the steps, for a range of step concentrations, owing to the exchange of coherent phonons.

Experimentally it should be possible to distinguish between whether the strong oscillations are a diffraction pattern due to a static structure, or whether they arise dynamically owing to the exchange of coherent Rayleigh phonons, by going to the limit of low concentrations of step edges when the coherence criteria breaks down.

## Acknowledgments

## References

[1] Ibach H and Mills D L (eds) 1982 *Electron Energy Loss Spectroscopy and Surface Vibrations* (New York: Academic)
[2] Brusdeylins G, Doak R B and Toennies J P 1983 *Phys. Rev.* B **27** 3662
[3] Maradudin A A and Melngailis J 1964 *Phys. Rev.* A **133** 1188
[4] Wallis R F 1964 *Surf. Sci.* **2** 146
[5] Szeftel J and Khater A 1987 *J. Phys. C: Solid State Phys.* **20** 4725
[6] Masri P, Allan G and Dobrzynski L 1972 *J. Physique* **33** 85
[7] Equiluz A G and Maradudin A A 1983 *Phys. Rev.* B **28** 728
[8] Khater A 1986 *Europhys. Lett.* **2** 539
[9] Maradudin A A, Ryan P and McGurn A R 1988 *Phys. Rev.* B **38** 3068
    Maradudin A A and McGurn A R 1989 *Phys. Rev.* B **39** 8732
[10] Knipp P 1989 *Phys. Rev.* B **40** 7993
[11] Armand G and Masri P 1983 *Surf. Sci.* **130** 89
[12] Fabre F, Armand G, Manson J R and Lapujoulade J 1990 *Vacuum* **41** 424
[13] Khater A, Auby N and Wallis R F 1989 *Surf. Sci.* **217** 563
[14] Kechrakos D 1990 *J. Phys.: Condens. Matter* **2** 2637
[15] Lieb E H and Mattis D C (eds) 1966 *Mathematical Physics in One Dimension* (New York: Academic)
[16] Khater A and Czaja W 1990 *Physica* B **167** 33
[17] Ibach H and Bruchmann D 1978 *Phys. Rev. Lett.* **41** 958
[18] Wuttig M, Oshima C, Aizawa T, Souda R, Otami S and Ishizawa Y 1988 *Surf. Sci.* **193** 180
[19] Mostoller M and Landmann U 1979 *Phys. Rev.* B **20** 1755
[20] Roubin P, Chandersis D, Rossi S, Lecante J, Desjonqueres M C and Reglia G T 1986 *Phys. Rev. Lett.* **56** 1272

[21] Desjonqueres M C and Treglia G 1986 *Phys. Rev.* B **34** 6662
[22] Lahee A, Manson J R and Toennies J P 1986 *Phys. Rev. Lett.* **57** 471
[23] Hinch B J 1985 *Phys. Rev.* B **31** 2551