Surface dynamics of hexagonal close-packed metals

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Abstract

Theoretical investigations on the dynamics at surfaces of hexagonal close-packed metals are reported. Lattice-dynamical as well as continuum theoretical calculations have been performed using a Green’s function formalism. The lattice-dynamical studies are based on force constant models which are modified in the first layers close to the surface. The calculations presented in this paper refer to the (0001) surface of beryllium, magnesium and zinc. In all cases the results of the lattice-dynamical calculations in the limit of long wavelength are in qualitative agreement with those obtained from elastic theory. For beryllium and magnesium the (0001) surface is found to be very stable against variations of the surface parameters. One should not expect any surface reconstruction. For zinc the ideal (0001) surface is unstable, but there are particular slight changes in the surface parameters which make it stable. These changes correspond with experimental data.

Keywords: Beryllium; Construction and use of effective interatomic interactions; Green’s function methods; Magnesium; Phonons; Zinc

1. Introduction

The bulk states of hexagonal close-packed metals have been studied in great detail by many authors [1–3]. The interatomic forces are found to be rather complex in comparison to e.g. cubic crystals. Force constant models have to be extended to at least sixth or seventh nearest neighbours. Moreover models with axially symmetric or even central forces provide only poor agreement with experimental data. At least three parameters per shell are necessary to describe the dispersion of the bulk states fairly. The present paper starts out from general tensor force models extended to eighth nearest neighbours for zinc and beryllium and sixth nearest neighbours for magnesium, respectively, which provide excellent agreement with data. Due to their large number of parameters these models are not adequate to study the nature of the dynamical forces arising in the crystal. For this purpose particular three- or many-body interatomic potentials in addition to two-body central forces have been discussed recently for hcp metals [4,5]. But this is outside the scope of this paper. It just intends to give a survey of the surface states. While the surface dynamics of cubic lattices and diamond or zincblende type crystals has been investigated thoroughly, little work has been done on hcp structures both theoretically and experimentally so far. The main emphasis is given on the one hand to the occurrence of soft modes and surface reconstructions and on the other hand to the comparison of the lattice-dynamical results in the limit of long wavelength with the results from elastic theory. A rigorous treatment of surface reconstructions of course...
requires the consideration of nonlinear terms in the interaction. But already within the concept of harmonic approximation a zero frequency indicates instability of the surface geometry started from, because the dynamical displacements of the atoms turn to static displacements. The wave vector of the soft phonon gives an idea about the pattern of this static displacement and hence determines the new surface geometry.

First the theory on which the calculations are based is described in short form. Then the results are presented. The investigations are restricted to the surface states outside (particularly below) the projected bulk bands, which are closely related to soft modes and surface reconstructions. A discussion of the results is tried in the light of the available experimental data.

2. Theory

2.1. Lattice dynamics

The equation of motion of the ideal infinite crystal in the harmonic and adiabatic approximation is in matrix notation

\[ M \ddot{u} + \Phi u = 0, \] (1)

that of the semi-infinite crystal (crystal with surface) is

\[ M \ddot{u} + \Phi' u = 0, \] (2)

where \( M \) denotes the mass of the atoms, \( u \) the vector of the displacements of the atoms from their equilibrium positions and \( \Phi, \Phi' \) the matrices of force constants in the unperturbed and the perturbed case, respectively. Introducing the perturbation matrix

\[ J = \Phi - \Phi', \] (3)

one gets

\[ M \ddot{u} + \Phi u = Ju. \] (4)

In the Green’s function method the surface appears as a two-dimensional perturbation of the ideal crystal, which consists of two parts. First the perturbation \( J \) contains all changes in the force constants due to cutting off all couplings between the two semi-infinite crystals which arise from creating a surface. Moreover there are changes in the electronic charge density caused by the surface which are taken into account by variations of the force constants in the layers near the surface. Hence the dimension of the non-zero part of the perturbation \( J \) (and therewith the dimension of the matrices entering in the calculations) is determined by the range of defect. The defect is limited to a few layers. The formal solution of (4) is

\[ u = u_h + GJu \] (5)
or

\[ u = (1 - GJ)^{-1} u_h, \] (6)

with the Green’s function \( G \) of the ideal crystal (i.e. of the homogeneous equation) and a solution \( u_h \) of the unperturbed crystal (of the homogeneous equation). The Green’s function can be expanded with respect to the eigenvectors of the ideal lattice (spectral representation). A Fourier transform with respect to the directions parallel to the surface leads to

\[ \tilde{G}_{ij} \left( \begin{array}{cc} m_x & n_y \\ m_y & n_z \end{array} \right) (k, \omega) = \lim_{\epsilon \to 0} \frac{1}{M} \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} e^{i k \cdot r} \frac{e^{i \omega (k, \omega)} e^{i \omega (q, \omega)}}{\omega^2 (q||, q\perp, \omega) - \omega^2 - i \epsilon} \times \exp[2 \pi i \gamma (n_3 - m_3)] \, dy, \] (7)

with \( q|| = \gamma g, g \) is a reciprocal lattice vector perpendicular to the surface; \( i, j = x, y, z \) denote the Cartesian components; \( m_x, n_y \) the layers; \( \sigma = 1, \cdots, 3s \) the polarization and \( \alpha, \beta = 1, \cdots, s \) the basis indices, \( s \) is the number of atoms in the elementary cell (\( s = 2 \) for hcp structures). \( q|| \) and \( q\perp \) are the components of the wave vector parallel and perpendicular to the surface, respectively. Localized surface modes are characterized by vanishing homogeneous contribution \( u_h \); this yields a condition for their frequencies:

\[ \det(1 - \tilde{G} (q||, \omega) \tilde{J} (q||)) = 0. \] (8)

\( \tilde{J} \) is the Fourier-transformed perturbation. The frequencies of localized states lie outside the projected bulk band. In this case it is \( \epsilon = 0 \) in (7), \( \tilde{G} \) is Hermitian. See Refs. [6–10] for further reference.

To evaluate the formula (7) numerically one introduces mesh points \( \gamma_i; i = 1, \cdots, N \) (\( N \) has to be chosen odd) in the interval \([-\frac{1}{2}, \frac{1}{2}]\) with \( \gamma_1 = -\frac{1}{2}, \gamma_N = \frac{1}{2}, \ldots, \gamma_{N-1} \) such that

\[ \gamma_i - \gamma_{i-1} = \frac{\pi}{N}, \quad i = 1, \cdots, N. \] (9)

The Green’s function \( \tilde{G} \) is calculated at the mesh points \( \gamma_i \) and then interpolated in the bulk region for the evaluation of (7).
\[ \gamma_N = \frac{1}{2}. \] The values of the integrand in (7) are calculated only at the mesh points. The integration is done piecewise. Considering an interval \( [\gamma_i, \gamma_{i+2}] \) the nominator is treated as a constant determined by the value at \( \gamma_{i+1} \), while the denominator is approximated by the interpolation polynomial of second degree, i.e.

\[
\lim_{\epsilon \to 0} \int_{\gamma_i}^{\gamma_{i+2}} \frac{d\gamma}{\omega^2(\gamma, \sigma) - \omega^2 - i\epsilon} = \int_{\gamma_i}^{\gamma_{i+2}} \frac{d\gamma}{a\gamma^2 + b\gamma + c - i\epsilon}
\]

\[
= \left. \frac{1}{\sqrt{b^2 - 4ac}} \ln \left( \frac{2\alpha \gamma + b - \sqrt{b^2 - 4ac}}{2\alpha \gamma + b + \sqrt{b^2 - 4ac}} \right) \right|_{\gamma_i}^{\gamma_{i+2}},
\]

where \( \ln \) has to be taken as a complex function. For localized states 300–500 and close to the band edge 1000 mesh points prove sufficient.

Depending on the point group of the crystal the Green’s function obeys certain symmetry relations. In the case of a hcp structure these are:

\[
\tilde{G}_{ij}(m_3 \ n_3 \ 1 \ 2)(q_\parallel, \omega) = \tilde{G}_{ji}(m_3 \ n_3 \ 1 \ 2)(q_\parallel, \omega),
\]

\[\text{Eq. } (10)\]

\[
\tilde{G}_{ij}(m_3 \ n_3 \ 2 \ 1)(q_\parallel, \omega) = \tilde{G}_{ji}(m_3 \ n_3 \ 2 \ 1)(q_\parallel, \omega),
\]

\[\text{Eq. } (11)\]

\[
\tilde{G}_{ij}(m_3 \ n_3 \ 1 \ 1)(q_\parallel, \omega) = \tilde{G}_{ji}(m_3 \ n_3 \ 1 \ 1)(q_\parallel, \omega).
\]

\[\text{Eq. } (12)\]

2.2. Elastic surface waves

The localized states of semi-infinite elastic media with plane surfaces are the Rayleigh or generalized Rayleigh waves. If they exist (there may be certain surfaces or directions of wave propagation in
anisotropic media without localized states), their frequencies lie below the elastic bulk frequencies. They have exponentially decreasing amplitudes with increasing distance from the surface. The decay constants depend on the elastic properties of the medium and on the wave vector $q_{||}$ parallel to the surface. In general the exponential decrease can be superposed by an oscillatory behaviour (generalized Rayleigh waves). Rayleigh waves always have mixed polarization with a longitudinal and a transverse component perpendicular to the surface. The proportions of the two contributions slightly vary with distance from the surface.

In the limit of long wavelength the results of lattice theory of surface waves have to coincide with those obtained from elastic theory.

The velocities of the surface waves are calculated via the surface Green’s function matching method. The equation of motion in the theory of elasticity is

$$\rho \frac{d^2 u_j}{dt^2} = \sum_{j,k,l} C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l},$$

(13)

if the mass density $\rho$ and the tensor of elastic constants $C$ do not depend on position, and its associated differential operator in the space-representation is

$$L_{ik}(x, t) = \delta_{ik} \rho \frac{\partial^2}{\partial t^2} - \sum_{j,l} C_{ijkl} \frac{\partial^2}{\partial x_j \partial x_l}.$$  

(14)

A Fourier transform with respect to the space directions parallel to the surface leads to

$$L_{ik}(\omega, q_{||}, x_3) = -\delta_{ik} \rho \omega^2 + C_{ik1} k_1^2 - ik_1(C_{ik3} + C_{ik1}) \frac{\partial}{\partial x_3} - C_{ik3} \frac{\partial^2}{\partial x_3^2},$$

(15)

if the $x_3$-axis is perpendicular to the surface and the $x_1$-axis is orientated in the direction of wave propagation $q_{||}$ parallel to the surface. The Fourier-transformed Green’s function is defined by

$$\sum_k L_{ik}(\omega, q_{||}, x_3) \hat{G}_{kj}(\omega, q_{||}, x_3, x'_3) = \delta_{ij} \delta(x_3 - x'_3).$$

(16)

Starting out from the ansatz $\hat{G}_{kj} \sim \exp(\kappa x_3)$ the complex decay constants $\kappa$ are calculated.
face is taken into account by special boundary conditions. See Ref. [11] for further details.

3. Results and discussion

For each metal (beryllium, magnesium and zinc) the investigation starts out from the ideal surface; i.e. the force constant model obtained from the bulk is applied directly to the surface. The physical properties of the real surface are taken into account by variations of the force constants close to the surface. Some changes in the force constants near to the surface are assumed and their influence on the surface states is studied. Since there are no really convincing considerations about the problem which variations of the force constants correspond to the real surface best and almost no experimental data on surface phonons to check against, the discussed changes appear somehow arbitrary. They are just motivated by the available experimental data on the layer spacings at the surface. Hence the present calculations only allow qualitative statements and give a rough idea about the stability of the surfaces and the occurrence of surface reconstructions.

It proves sufficient to consider the two uppermost layers. The couplings in the other layers are found to have only negligible influence on the surface states. They are left unchanged in all calculations. The changes in the force constants between the two uppermost layers or within the uppermost layer always refer to all interatomic couplings contributing to this interplanar and in-plane interaction, respectively.

The calculations make use of general tensor force models extended up to eighth nearest neighbours for zinc and beryllium and up to sixth nearest neighbours for magnesium, which provide excellent agreement with bulk data. The arising tensors of coupling parameters are given in Table 1 for one atom representative of each shell. Note that the sequence of shells refers to beryllium and magnesium and is different with zinc due to the $c/a$ ratio. The bulk

<table>
<thead>
<tr>
<th>$R$</th>
<th>$\Phi(R)$</th>
</tr>
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<tbody>
<tr>
<td>$(0, -\frac{a}{\sqrt{3}}, \frac{c}{2})$</td>
<td>$(\alpha_1, 0, 0)$</td>
</tr>
<tr>
<td></td>
<td>$\beta_1, \delta_1, 0$</td>
</tr>
<tr>
<td>$(a, 0, 0)$</td>
<td>$\alpha_2, \delta_2, 0$</td>
</tr>
<tr>
<td>$(0, \frac{2}{\sqrt{3}}a, \frac{c}{2})$</td>
<td>$\alpha_3, 0, 0$</td>
</tr>
<tr>
<td></td>
<td>$\beta_3, \delta_3, \gamma_3$</td>
</tr>
<tr>
<td>$(0, 0, c)$</td>
<td>$\alpha_4, 0, 0$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_4, 0, 0$</td>
</tr>
<tr>
<td>$(a, \frac{2}{\sqrt{3}}a, \frac{c}{2})$</td>
<td>$\alpha_5, \delta_5, \xi_5$</td>
</tr>
<tr>
<td></td>
<td>$\beta_5, \delta_5, \xi_5$</td>
</tr>
<tr>
<td>$(0, \sqrt{3}a, 0)$</td>
<td>$\alpha_6, 0, 0$</td>
</tr>
<tr>
<td></td>
<td>$\beta_6, 0, 0$</td>
</tr>
<tr>
<td>$(a, 0, c)$</td>
<td>$\alpha_7, \delta_7, \xi_7$</td>
</tr>
<tr>
<td>$(2a, 0, 0)$</td>
<td>$\alpha_8, \delta_8, 0$</td>
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<tr>
<td></td>
<td>$\beta_8, 0, 0$</td>
</tr>
<tr>
<td></td>
<td>$\gamma_8, 0, 0$</td>
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Table 2

Values of the force constants used in the calculations in N/m

<table>
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<tr>
<th></th>
<th>Be</th>
<th>Mg</th>
<th>Zn</th>
<th>Be</th>
<th>Mg</th>
<th>Zn</th>
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<td>1.05</td>
<td>$\alpha_1$</td>
<td>-0.02</td>
<td>-0.07</td>
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<tr>
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<td>-3.52</td>
<td>-2.56</td>
<td>$\beta_1$</td>
<td>-0.36</td>
<td>-0.08</td>
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<td>$\gamma_1$</td>
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<tr>
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<td>0.49</td>
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<td>$\alpha_3$</td>
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</tr>
<tr>
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<td>$\delta_3$</td>
<td>-0.68</td>
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</tr>
<tr>
<td>$\alpha_4$</td>
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<td>-0.22</td>
<td>$\alpha_4$</td>
<td>1.70</td>
<td>0.05</td>
</tr>
<tr>
<td>$\beta_4$</td>
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<td>$\beta_4$</td>
<td>1.86</td>
<td>-0.52</td>
</tr>
<tr>
<td>$\gamma_4$</td>
<td>-1.37</td>
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<td>-0.01</td>
<td>$\gamma_4$</td>
<td>-1.70</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
data used for the least-squares fit to determine the force constants was taken from Refs. [12], [13,14] and [15] for beryllium, magnesium and zinc, respectively. In Table 2 the actual values of the force constants used in the numerical calculations are indicated. With magnesium a fit using couplings up to sixth nearest neighbours is already perfect; the force constants decrease rapidly with increasing order of shell. With beryllium and zinc the couplings in the first three shells are dominating, but inclusion of the seventh and eighth nearest neighbours still improves the quality of the fit. The parameters $\delta_2$, $\delta_3$, and $\zeta_7$ could not be determined with the available bulk data.

To test the dependence of the results upon the special potential model all calculations were repeated using force constant models with an order reduced by one. All results reported below remained qualitatively unaltered; just the changes in force constants have to be modified by a few percent.

As to the number of surface modes and their phase velocities the lattice-dynamical results in the limit of long wavelength are in good qualitative accordance with the results obtained from elastic theory via Green’s function matching method.

### 3.1. Beryllium

For the Be(0001) surface an abnormally large expansion of the first interplanar spacing of 5.8% has been found by Davis et al. [16] using low-energy electron diffraction (LEED). This result suggests stronger in-plane bonding and weaker interplanar bonding at the surface. Moreover in an electron-energy loss spectroscopy investigation Hannon and Plummer [17] observed two modes at the $\overline{M}$-point: a Rayleigh wave at a frequency of 9.55 THz and a shear mode close to the band edge at 12.21 THz.

In the present calculations at the ideal Be(0001) surface in the elastic limit there is one surface mode below the bulk states (Fig. 1). Its phase velocity is about 8180 m/s. Another mode coincides with the bulk band edge at 8570 m/s. Fig. 2 illustrates the results from lattice theory. The frequency of the Rayleigh mode at $\overline{M}$ is 9.44 THz in good agreement with the experimental value. If a weakening of the interplanar interaction between the two uppermost layers is assumed the Rayleigh wave appears at a lower energy. Fig. 3 refers to a weakening by 20% (frequency at $\overline{M}$ 8.56 THz). With a weakening up to

![Fig. 3. Surface phonons at the Be(0001) surface with force constants between the two uppermost layers lowered up to 80%.](image-url)
Fig. 4. Density of surface states (dotted line) for the Mg(0001) surface and of bulk states (solid line) for propagation in $\bar{T}$-direction as a function of the phase velocity.

7% a soft mode at the $\bar{K}$-point occurs. Since such a strong lowering does not seem to be physically realistic the calculations suggest that surface reconstructions do not appear. The strength of the in-plane interaction within the uppermost layer is found to have virtually no influence on the energy of the

Fig. 5. Surface phonons at the ideal Mg(0001) surface within the general tensor force model extended up to sixth nearest neighbours. Bulk phonon bands are shadowed.
Rayleigh mode. It was not possible with any combination of surface parameters to identify a second mode at $\overline{M}$ below the band edge. According to the bulk data the force constant model is based on the band edge lies at a frequency of 11.77 THz. This discrepancy with the experimental results may be
due to the fact that the bulk data refer to a temperature of 80 K whereas the measurements mentioned above have been performed at room temperature. Perhaps a second mode may exist as a resonance in the projected bulk density in continuation of the second dispersion curve below the band edge along the $\bar{\Sigma}$-direction in Figs. 2 and 3, even though it is not clearly visible in the perturbed spectral density.

3.2. Magnesium

As beryllium the Mg(0001) surface also shows an outward expansion. In a LEED analysis Sprunger et
al. [18] found the first interlayer spacing relaxed from the bulk value by 1.9%.

At the ideal surface there exists one Rayleigh mode with a phase velocity of about 2895 m/s at the $\Gamma$-point (Fig. 4). In the lattice-dynamical calculations the mode does not appear so well separated from the band edge (Fig. 5) because the slope of the bulk band is lower than calculated by elastic theory. This may be due to the fact that the available data material on the bulk states was poor (only three directions of high symmetry); hence the force constants could not be determined very precisely. Again a weakening of the couplings between the two uppermost layers (consistent with the layer relaxation) leads to a decrease in frequency of the surface phonon; but the mode does not become soft until a lowering up to 15%. This is a strong indication that the Mg(0001) surface can be regarded as a stable structure.

3.3. Zinc

Using LEED no surface reconstructions have been found at the Zn(0001) surface; the spacing between the two uppermost layers proved contracted from the bulk spacing by as much as 2% at 70 K, which indicates a stronger interaction between them than in the bulk crystal [19].

Both lattice dynamics (Fig. 6) and elastic theory (Fig. 7) provide a Rayleigh wave clearly separated from the bulk band edge. Its phase velocity is 2170 m/s. According to the lattice-dynamical calculations the ideal surface is unstable. At the $\bar{K}$-point a negative square of frequency occurs. This soft mode is related to a $(3 \times 3)$-reconstruction. The surface gets stable if a reinforcement of the couplings between the two uppermost layers is assumed. With a strengthening by 7% the soft mode just vanishes (Fig. 8); with a strengthening by 20% the frequency at $\bar{K}$ increases distinctly (Fig. 9). Such a rather slight reinforcement is possibly in accordance with the mentioned experimental finding of a contracted planar spacing. Moreover with a decrease of the couplings inside the uppermost layer by only 8% the mode gets stable, too (Fig. 10). With a decrease by 15% the frequency at $\bar{K}$ is about 1 THz.

4. Conclusions

Some calculations on the surface states of hcp metals have been reported which have the character of a first survey and are far from being complete. Further investigations, for example using other potential models would be fruitful to check the depen-
dence of the statements upon special models. But the most considerable shortcoming of the present calculations is of course the fact that the force constants close to the surface are not exactly known. Microscopic theory of the changes in the interactions arising in the crystal due to the surface is required to obtain substantial values for them.

References