Vibrational Raman spectroscopy on adsorbate-induced low-dimensional surface structures

Eugen Speisera, Norbert Essera,b,∗, Benedikt Halbigc, Jean Geurts c, Wolf Gero Schmidt d, Simone Sanna e

a Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Interface Analytics Department, Schwarzschildstr. 8, D-12489, Berlin, Germany
b Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstr. 36, D-10623, Berlin, Germany
c Physikalisches Institut, Universität Würzburg, Am Hubland, D-97074, Würzburg, Germany
d Theoretische Physik, Universität Paderborn, Warburger Str. 100, D-33090, Paderborn, Germany
e Institut für Theoretische Physik and Center for Materials Research (LaMa), Justus-Liebig-Universität, Heinrich-Buff-Ring 16, D-35392, Gießen, Germany

K EYWORDS:
Surface Raman spectroscopy
2D surface structures
1D surface structures
Surface vibrations
Semiconductor surfaces
Electron-phonon coupling
Phase transition
Peierls transition
ab initio calculations
DFT

A B S T R A C T
Low-dimensional self-organized surface structures, induced by (sub)monolayer metal adsorbates on semiconductor surfaces may give rise not only to a variety of emergent electronic properties, but also to a multitude of specific localized vibronic features. The focus of this review is on the analysis of these novel surface vibration eigenmodes. The application of in situ surface Raman spectroscopy under UHV conditions on clean semiconductor surfaces and those with self-ordered adsorbates, in close conjunction with the calculations of Raman spectra, based on the first-principles determination of the structural, electronic and vibronic properties, allows a consistent determination of the vibration eigenfrequencies, symmetry properties, and elongation patterns of the systems of interest. The localized nature of the surface eigenmodes determines the surface sensitivity, independent of the large penetration depth of light. The surface contribution can be selectively enhanced by employing resonance conditions to surface electronic transitions. Moreover, surface and bulk contributions can be separated by taking differences spectra between various stages of surface preparation. The relevant surfaces are Ge and especially Si with different orientations ((111) and vicinal (hhk)), on which the adsorption of various metals (Au, Sn, Pb, or In) gives rise to two- and quasi-one-dimensional structures (e.g. Au-(5 × 2)/Si(111)) with a variety of vibration modes. The Raman analysis of these modes not only enables the distinction between different proposed structural models (e.g. for Au-(√3 × √3)/Si(111)), but also gives access to the role of electron-phonon coupling in structural phase transitions (e.g. for In-(8 × 2)-(4 × 1)/Si(111)).

© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

For various metal elements, their deposition in the monolayer range onto semiconductor surfaces gives rise to a spontaneous structural order, which typically includes not only the adsorbed metal atoms, but also implies a relocation of the uppermost substrate atoms and a rearrangement of their bond orbitals. A broad spectrum of options is available for the adsorbate material (e.g. Au, Pt, Sn, Pb, In, or Sb), the choice of the substrate (e.g. Si, Ge, InP, or GaAs), its surface orientation (e.g. (111), (001), (110), or vicinal (hhk)), and the adsorbate coverage. This multitude of alternatives allows the realization of a broad variety of one- or two-dimensional structural order patterns, such as e.g. nanowires with widths in the single-atom range.

These self-organized low-dimensional metal adsorbate structures have advanced to a very topical subject in modern physics in the fields of experiment as well as theory, because they constitute a versatile playground for tuning and studying electron correlation effects and many-body physics. The combination of competing interactions in these systems may result in the emergence of new phenomena, such as correlation-induced metal-insulator transitions, heavy fermion physics, spin chains and spin liquid phases, low-dimensional superconductivity, Tomonaga Luttinger liquids, etc. [1–7].

https://doi.org/10.1016/j.surfrep.2020.100480
0167-5729/© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
found interplay between the structural and electronic properties of the self-ordered adsorbates is illustrated by the occurrence of metal-insulator phase transitions, which may be displacive or have order/disorder character, as well as by spin- and charge density waves (CDWs) and Peierls transitions [8].

At this stage the atomic vibration dynamics also comes into play, because phase transitions are often preceded by the frequency reduction (softening) of a specific vibration mode, whose elongation pattern is subsequently frozen to give the new atomic arrangement. The explanatory power of the atomic vibration dynamics, however, by far exceeds this special aspect. The vibration modes are not only determined by the atomic positions and masses, but likewise by the atomic bonds, notably by their number, strengths, and directions. Therefore, a thorough high-accuracy spectroscopic analysis of the vibration frequencies and symmetry properties in conjunction with first-principles calculations of eigenmode elongation patterns and eigenfrequencies can offer a substantial contribution to a more profound understanding of the interplay of the positioning and bonding of the adatoms with the relocation and bonding rearrangement of the uppermost substrate atoms in self-ordered systems of metal atoms on semiconductor surfaces. Usually, these adsorbate-induced surface-confined vibration modes appear in the frequency range below the domain of the bulk optical phonons of the substrate, because of the surface-inherent absence of restoring forces from the external side, and moreover by the involvement of the metal adsorbate atoms, whose masses clearly exceed those of the substrate atoms.

Traditionally, the frequency analysis of surface vibration modes has been performed by energy loss spectroscopy, employing as probes either low-energy electrons or He atoms. These probes are eligible for this purpose because of their intrinsic surface selectivity, since penetration depths of only a few atomic layers or even less are achievable. Concomitantly, the electron- and atom-based spectroscopy methods, high-resolution electron energy loss spectroscopy (HREELS) [9–11] and Helium atom scattering (HAS) [12,13], imply certain limitations concerning spectral range and resolution. Furthermore, they offer only limited information about the vibration mode symmetries. Therefore, an alternative method with an extended spectral range and a superior resolution seems highly desirable.

A very promising alternative in all these aspects has been established by the employment of a photon-based energy loss spectroscopy in the visible range, also denoted as inelastic light scattering or Raman spectroscopy (RS). This is a versatile and widely employed experimental method for the analysis of vibration modes, and well-known for applications in a broad range of domains, such as (bio)chemistry, material science, physics, biomedicine, etc. Its impressive advancement during the past decades has been paved by equipment progress in many aspects, such as laser light sources of improved efficiency, high-performance spectrographs, ultra-steep spectral edge- and notch filters, and extremely sensitive multichannel detector arrays (Charge-Coupled Devices, CCDs), which altogether have enabled versatile, small, moderate-budget Raman setups with high spectral resolution and strongly improved sensitivity. In the field of fundamental research in solid-state physics many studies are focused on optical phonon modes of the crystal lattice. The basics of this application of RS are outlined in Section 2.

Simultaneously, RS has achieved a great success in the field of solid-surface studies by analyzing their surface vibration modes. The application is referred to as Surface Raman Spectroscopy (SRS) and is the subject of this review article. Focus material systems for this application are clean semiconductor surfaces with various reconstruction superstructures, e.g., Si(111), Si(hhk), Ge(111), and Ge(001), and moreover the above-mentioned one- and two-dimensional self-ordered atomic arrangements which are induced by the (sub)monolayer adsorption of metal atoms.

The long-standing application of phonon RS on solid semiconductors, comprising, apart from bulk materials, also layer systems and nanostructures, is based on the versatile information depth, which for many material systems is tunable by the appropriate choice of the photon energy. While it covers the total depth of the sample in the transparent range, i.e., for light frequencies below the fundamental electronic energy band gap, it is only in the range of 10 nm in the spectral region of strongest absorption, as illustrated in Fig. 1 for the relevant substrate materials Si, Ge, and GaAs. On the other hand, this obviously implies that RS is by no means an intrinsically surface-selective method, since its minimum depth of information by far exceeds the in-depth extent of the surface vibration modes, i.e., for adsorbate/substrate systems the scattering volume essentially covers the substrate bulk phonons. Therefore, for the case of a comparable scattering efficiency of the surface vibration modes and the bulk phonons, the Raman intensity spectrum is expected to be dominated largely by the latter, while the surface- and/or adsorbate vibration signals will only give a weak contribution due to additional modes and possibly also structural changes at the surface.

For a more detailed consideration of the intensity ratio, it has to be taken into account that many material systems allow a specific tuning of the scattering efficiency by employing a resonant enhancement of the Raman efficiency upon matching the laser photon energy with an electronic transition energy. In bulk material studies this feature, which is referred to as Resonant Raman Scattering (RRS) [16,17], has been exploited since several decades for boosting the Raman intensity, as well as for a layer- and interface-selective intensity enhancement in heterostructures [18–20].

Along the same line, for the study of surfaces and adsorbate/substrate systems the distinct electronic band structure of the surface and adsorbate with respect to the bulk may allow a surface-specific intensity enhancement for an appropriate light frequency. This is denoted as Surface Resonant Raman Scattering (SRRS) (see Section 2.4). However, this effect is mostly insufficient to break the strong dominance of the bulk-phonon intensity contribution. The delicate issue of the disentanglement of the surface contribution and the bulk phonon signal can be tackled by considering that the surface vibrations and the bulk phonons usually have different eigenfrequencies, symmetry selection rules, and Raman resonance behavior. This distinction originates from the surface-specific atomic and electronic structure. Moreover, a deliberate quenching of the surface reconstruction, e.g., by controlled oxidation has proven to be a
very successful approach. In this case the vibration signature of the surface is derived from the difference between the Raman spectra before and after the quenching (see e.g. Section 2.6). Additionally, in the analysis of the remaining features it has to be considered that besides novel adsorbate-induced vibration modes slight adsorbate-induced modifications of bulk vibration frequencies and their Raman efficiencies may also occur and the surface-specific Rayleigh wave of the substrate may be modified.

Furthermore, it should be noted that this review article focuses on surface phonons, i.e., vibration modes with a surface confinement within a few atomic layers. Surface and interface modes, which arise in polar materials due to the electromagnetic boundary conditions of the electric fields, are not included in this compilation (for a review see Ref. [18]). For the sake of completeness it should be mentioned here that a fundamentally different surface-to-bulk intensity ratio is achieved in Surface Enhanced Raman Scattering (SERS) or Tip Enhanced Raman Scattering (TERS), whose extremely strong surface Raman signal is based on an extraordinarily strong local electrical field enhancement at the metal tip or metal islands at the surface (see Refs. [21,22]).

The suitability of SRS for the analysis of (sub)monolayer coverages on semiconductor surfaces has been demonstrated on Sb-monolayer-terminated III-V(110) surfaces, e.g., in extensive studies on InP (110) in the 1990s [23–25]. Besides surface vibration analysis, Raman studies of electronic band bending were also performed by electric-field induced Raman scattering (EFIRS) (for reviews see Refs. [19,26]). Since then, the new field of Raman analysis of surface vibration modes has successfully developed and resulted in a variety of studies on clean reconstructed semiconductor surfaces as well as with such as with self-ordered one- and two-dimensional adsorbate terminations. In the last decade, self-organized one- or two-dimensional structures of (sub)monolayer metal adsorbates like In, Au, Pb, and Sn on Si(111) or Ge(111) substrates have been the focus of SRS, and the present review report is addressed to this area.

In parallel with these experimental achievements, significant progress has been obtained in the field of the theory for describing the structural and electronic properties, as well as the vibration dynamics of clean surfaces and adsorbate-induced surface structures. Based on sophisticated modelling and increased computing power, detailed descriptions of the atomic arrangement and band structure are achieved by ab initio density functional theory (DFT) calculations of surface slabs, containing also several sub-surface atomic layers. Besides a comparison of formation energies and stability of various structural models, also vibration dynamics can be calculated, yielding eigenmode elongation patterns and eigenfrequencies. While the frozen phonon approach is confined to the Brillouin zone center, arbitrary phonon wave vectors can be accessed by density functional perturbation theory (DFPT). In the next stage, the impact of each eigenvibration on the optical properties is calculated, which manifests itself as a modulation of the dielectric susceptibility in the visible spectral range. This procedure allows the evaluation of the Raman scattering efficiency of each surface vibration eigenmode, and results in a quantitative predictive power for full vibrational Raman spectra.

This review of experimental and theoretical achievements in the field of vibrational RS on adsorbate-induced low-dimensional surface structures starts with a treatment of the fundamentals of RS in Section 2, with special reference to photon-phonon interaction mechanisms, resonance effects, and the impact of symmetry considerations. At the end of this chapter, in Section 2.6 exemplary results are discussed for Sb-adsorbed GaAs (110) and InP (110) surfaces.

Subsequently, in Section 3 a survey is presented of the calculation of surface vibrations and their Raman scattering efficiencies. The current development status in the ab initio determination of equilibrium geometries and the corresponding electronic band structures is covered, which enables the determination of surface vibration modes (Section 3.4), including their frequencies, elongation patterns and symmetry, and finally their Raman scattering efficiency and its resonance behavior (Section 3.7), i.e., an ab initio simulation of surface Raman spectra.

After these chapters with a tutorial aspect, the presentation and discussion of the results on various material systems, which constitute the main part of this article, are topical sorted according to (i) clean surfaces (Section 4), (ii) two-dimensional adsorbate systems (Section 5), and (iii) the tuning from two- to quasi-one-dimensional adsorbate systems (Section 6).

In Section 4, the Raman studies of the Si(111)-(7 × 7)- and the Ge(111)-(2 × 8) surface (Section 4.1 and 4.2, respectively) are not only motivated by the vibration dynamics of these clean surfaces, but also act as references for the metal-covered surfaces in the following chapters. For the clean Ge(001) surface (Section 4.3) a main focus is on the impact of the thermally induced phase transition between the disordered dynamical (2 × 1) and the ordered static (4 × 2) reconstruction.

The two-dimensional adsorbate systems in Section 5 involve 1/3 monolayer (ML) Pb on Si(111), and 1/3 ML Sn on Ge(111) or Si(111). While Pb/Si(111) (Section 5.1) is characterized by an extremely sharp interface with a very low adsorbate binding energy, the interest for Sn on Ge (111) (Section 5.3), essentially originates from its thermally induced structural phase transition between (√3 × √3) and (3 × 3), which does not occur for Sn-(√3 × √3)/Si(111) (Section 5.2).

As an example for tuning from two- to quasi-one-dimensional adsorbates in Section 6, Au on Si substrates is presented, comprising the two-dimensional Au-(√3 × √3)/Si(111) reconstruction (Section 6.1), Au-ribbons on Si(hhk) (Section 6.2), and the quasi-one-dimensional Au-(5 × 2)/Si(111) (Section 6.3). One-dimensional In chains on Si(111) and their thermally induced structural phase transition are treated in Section 6.4. Finally, special reference to electron-phonon coupling in metallic chains is given in Section 6.5.

2. Fundamentals of Surface Raman Spectroscopy

2.1. Basics

In an inelastic light scattering process, upon the incidence of a photon, a certain amount of energy ΔE is transferred between the incident photon and the sample for the creation or annihilation of an elementary excitation, e.g., a vibration mode. The process is completed by the emission of a scattered photon, which consequently has a deficit or excess energy ΔE with respect to the incoming one, which implies a corresponding frequency shift. The term Raman spectroscopy is applied for the frequency analysis of the inelastically scattered light whose photon energy shift is at least about 1 meV. In terms of the light wavelength this energy shift corresponds to a shift of 8.0655 cm⁻¹. Inelastic light scattering with an energy transfer below this approximate threshold is referred to as Brillouin scattering.

The energy conservation in the scattering process is quantitatively described by the expression

\[ E_\text{in} = E_\text{out} = h\omega_i = h\omega_{\text{in}} + h\omega_{\text{ouv}}, \]

which correlates the frequencies ω of the incident photon “i”, the scattered photon “s”, and the phonon mode “n”. The “minus” sign denotes the case of phonon creation, referred to as Stokes process, and the “plus” sign gives the phonon annihilation, which is called anti-Stokes process. The frequency difference ω_i − ω_s is denoted as Raman shift, and commonly measured in units of cm⁻¹. Beside Raman scattering due to a single phonon, also e.g. a combination of two phonons may be involved, or a phonon may occur twice in the scattering process. These Raman processes are referred to as two-
phonon scattering. As a higher-order effect, two-phonon scattering generally has a strongly reduced probability, and gives rise to much weaker spectral features than first-order Raman scattering from a single phonon.

The probability of the anti-Stokes process is proportional to the phonon occupation density, while the Stokes process comprises spontaneous as well as stimulated phonon creation. Therefore, the intensity ratio of the Stokes- and anti-Stokes Raman signals of a given phonon mode reflects its temperature-dependent occupation density according to Ref. [27].

\[
\frac{I_{\text{Stokes}}}{I_{\text{Anti-Stokes}}} = \left(\frac{\omega_I - \omega_m}{\omega_I + \omega_m}\right)^4 \cdot \exp\left(\frac{-\hbar \omega_m}{k_B T}\right).
\] (2)

For most optical phonons this ratio is distinctly larger than one, especially at low temperatures. Therefore, the vast majority of experimental Raman studies concerns the recording of the more intense Stokes scattering branch. In suitable cases the recording of both the Stokes and the anti-Stokes branch may allow a temperature determination or be helpful for unambiguously distinguishing a phonon signature from the background.

Besides energy conservation, a second constraint for the inelastic light scattering process is established by momentum conservation, which determines the wave vector $\mathbf{q}_m$ of the involved phonon mode $m$ for a scattering process with light wave vectors $\mathbf{q}_i$ (incident) and $\mathbf{q}_s$ (scattered) by

\[
h\mathbf{q}_i = h\mathbf{q}_s = h\mathbf{q}_m.
\] (3)

For an estimation of the phonon wave vector range which may be probed in Raman scattering experiments, it must be considered that (i) the wave vectors of visible light are several orders of magnitude below the extent of the Brillouin zone (BZ), and (ii) the experiments are performed in quasi-backscattering. For the systems of interest in this article, the backscattering configuration is imposed as a natural restriction due to the opaqueness of the substrate materials in the relevant spectral range. This backscattering configuration implies nearly vanishing $\mathbf{q}_i$-components. Therefore only surface phonons in the vicinity of the Brillouin zone center are accessible. The simultaneous fulfillment of energy- and quasi-momentum conservation implies that RS allows the analysis of optical phonon modes. For Raman scattering on surface phonons, the wave vector conservation is confined to the in-plane components. Therefore, here Eq. (3) only applies to the two-dimensional $q_{\parallel}$-vectors. Furthermore, in case of two-phonon Raman scattering the phonon wave vector $\mathbf{q}_m$ in Eq. (3) is substituted by the vector sum of the involved phonons wave vectors. Therefore, two-phonon scattering is not confined to phonons from the BZ center, and the multitude of possible $q_m$ values with different phonon frequencies $\omega_m$ results in broad spectral bands, in contrast to the sharp peaks from one-phonon Raman scattering.

These considerations on momentum conservation strictly apply only for samples with a perfect structural periodicity. In reality, the in-plane translational invariance may be disturbed by surface steps, structural defects, domain boundaries, adsorbate-induced distortions, and thermal fluctuations. These effects weaken the wave vector conservation, which should imply the appearance of a broadening of the phonon signatures in the Raman spectrum. Disorder on the surface may give rise to the observation of the phonon density of states rather than the zone center phonon mode. A quantitative evaluation of broadening and damping effects may be hampered by the often very low intensity of the surface Raman peaks. Nevertheless, in the following examples are given where surface phonon scattering from the whole Brillouin zone (BZ) or BZ boundary is contributing.

### 2.2. Instrumental aspects

The instrumental requirement for SRS is the combination of a Raman setup with an ultra-high vacuum (UHV) vessel, which comprises sample preparation facilities (surface preparation and adsorbate deposition) and a standard surface analysis chamber with optical access. Thus the combination of a Raman setup with an UHV setup is rather uncomplicated since just the suitable optical ports need to be incorporated in the UHV vessel. For achieving a high aperture angle, the collection window should be positioned rather close to the sample surface. This geometry can be realized by employing a re-entrant window.

The Raman setup essentially consists of a laser light source, a high-resolution spectrometer and a multichannel detector. As we will explain in Section 2.4, an important aspect for optimizing the Raman scattering efficiency is the application of a laser light source with a photon energy which matches an electronic resonance of the (surface/adsorbate related) electronic band structure as closely as possible. Therefore, the availability of a set of laser lines of different photon energies is very important. Traditionally gas lasers (He–Ne, Ar+, and Kr+) with a variety of lines in the visible spectral range were mostly employed. Since recently, compact diode-pumped solid-state lasers with a strongly enhanced efficiency are available, offering single lines in a wide spectral range from the near infrared (NIR) to ultraviolet (UV). Alternatively, a tunable laser source would be most adequate.

A crucial part of each Raman equipment is the spectrometer. For SRS, the already very high optical performance requirements are even enhanced. The most relevant requirements are (i) a spectrally resolved imaging of the Raman frequency range on the detector, (ii) an extremely strong suppression of the laser frequency, together with a high transmission of immediately adjacent frequencies of the Raman light. One established effective setup is a triple grating spectrometer, in which the first and second stage subtractively act as a spectral bandpass filter for laser suppression, and the third stage as a spectrograph for the spectrally resolved imaging of the Raman frequency range on the detector plane. The essential merit of this concept is the detectability of frequencies very close to the laser line (down to below 20 cm$^{-1}$). Moreover, the triple grating spectrometer is also necessary if a tunable laser is used.

Exploiting the triple spectrograph scheme with an additional laser line blind allows a simultaneous recording of Stokes and anti-Stokes contributions in the low-energy range. In Fig. 2, surface Raman spectra from In-(8 × 2)/Si(111) are shown, demonstrating an efficient control of inelastically scattered laser light in two main polarization configurations (for details of the polarization notation see Section 2.5). The comparison of Stokes and anti-Stokes parts of the spectra can be used for the confirmation of the origin of appearing lines, since light scattering on phonons generates contributions in both parts, and it can be employed for an in situ temperature measurement according to Eq. (2). Moreover, changes of the local surface roughness can be verified by monitoring of the residual elastically scattered laser light during the experiment.

Alternatively, a single grating spectrometer may be employed, combined with a suppression filter for the elastically scattered laser light. For blocking the laser frequency, either an ultrastep long-pass edge filter may be applied (allowing Raman light transmission on the Stokes side down to 40 cm$^{-1}$ from the laser line) or in case of extremely high-quality sample surfaces a (preferably double) Bragg notch filter (transmission down to 25 cm$^{-1}$ from the laser line on both the Stokes and anti-Stokes side). The main merit of the single-spectrometer concept is its high throughput of the Raman light. For all these spectrometer concepts, the spectral resolution (full width at half maximum (FWHM)) is between 1.0 and 3.0 cm$^{-1}$, and a spectral accuracy better than 0.5 cm$^{-1}$ is achieved for the determination of Raman peak positions.
Stokes and anti-Stokes Raman spectra from Si(111):In(8x2) at 40K

Fig. 2. Raman measurements of Stokes and anti-Stokes contributions from In- 
(8 x 2)/Si(111) at 40 K for z(x) (black line) and z(xy) (red line) polarization con-
figurations. The spectral range near the excitation laser line filtered by the laser blind 
filtering shows up at 0 cm⁻¹ (from Ref. [28]). (For interpretation of the references 
to color in this figure legend, the reader is referred to the Web version of this article.)

cooled backside-illuminated CCD arrays are employed, which combine a nearly ideal photon conversion efficiency with an extremely low electronic noise level.

The combination of all these beneficial factors has resulted in SRS setups, which allow the recording of almost noise-free Raman spectra within a feasible acquisition time, and the subsequent disentan-
glement of the surface Raman features from the bulk peaks even if these exceed them by three to four orders of magnitude.

2.3. Generalized dielectric susceptibility

Within the framework of classical electrodynamics, Raman scattering is described in terms of a higher-order extension of the common dielectric susceptibility \( \chi(\omega) \), which determines the induced polarization \( \mathbf{P}(\omega) \) as the linear response of a material on an incident electric field \( \mathbf{E}(\omega) \). In the NIR-VIS-UV spectral range \( \chi(\omega) \) is essen-
tially governed by electronic excitations. The extended higher-order dielectric susceptibility tensor \( \tilde{\chi}(\omega_1, \omega_2) \) gives rise to a polarization with an altered frequency \( \omega_s \), and consequently a scattered field with this frequency, upon incidence of a field with frequency \( \omega_i \) (here the laser light frequency) in the presence of a phonon with frequency \( \omega_m = \omega_i - \omega_s \). The tensor character of \( \tilde{\chi}(\omega_1, \omega_2) \) considers the phonon symmetry properties. This concept results in the equation

\[
\tilde{\mathbf{P}}(\omega_i) = e_0 \tilde{\chi}(\omega_i, \omega_s) \mathbf{E}(\omega_i). \tag{4}
\]

Here, \( \mathbf{P}(\omega_i) \) is the oscillating polarization, whose dipole radiation gives rise to the scattered light wave with frequency \( \omega_s \) and \( \mathbf{E}(\omega_i) \) is the oscillating electric field of the incident light wave. The tensor \( \tilde{\chi}(\omega_i, \omega_s) \) is commonly referred to as Raman tensor, and also denoted as \( \mathbf{R} \).

Now, for an incident light intensity \( I_0 \), the intensity \( I_s \) of the Raman-scattered light which is emitted from the oscillating polarization \( \tilde{\mathbf{P}}(\omega_0) \) can be deduced by employing the Raman tensor \( \tilde{\chi}(\omega_i, \omega_s) \) as [16,27].

\[
I_s = I_0 \frac{\alpha_0 V}{(4\pi e_0 e_c)^2} |\mathbf{e}_s \tilde{\chi}(\omega_i, \omega_s) \mathbf{e}_i|^2, \tag{5}
\]

where \( \mathbf{e}_s \) and \( \mathbf{e}_i \) denote the polarization directions of the incident and scattered light, respectively, and \( V \) is the scattering volume. For Raman scattering on bulk phonons \( V \) is limited in transparent sam-
ples only by their thickness, and in opaque ones by the light penetra-
tion depth, usually distinctly beyond 10 nm (see Fig. 1). For Raman scattering on surface vibrations, however, the scattering volume \( V \) is limited for each vibration mode individually by its decay depth.

Thus, the Raman scattering efficiency is expressed as

\[
S_{\alpha\beta} = \frac{dI_s}{dI_0 d\Omega} = |\mathbf{X}_{\alpha\beta}(\omega_i, \omega_s)|^2 \frac{\alpha_0 V}{c^4}. \tag{6}
\]

where \( \mathbf{X}_{\alpha\beta}(\omega_i, \omega_s) \) is the Raman tensor element which corre-
sponds to the polarization directions of the incident and scattered light, denoted as \( \beta \) and \( \alpha \), respectively. The vanishing or non-
vanishing of the Raman tensor component for given polarization combinations \( \alpha \beta \) directly reflects the symmetry constraints which arise from the symmetry properties of the sample (point group), and its possible symmetry reduction by the distortion due to the consid-
ered phonon. Thus, the tensor-element values indicate whether for a particular vibration mode Raman scattering in a given polarization configuration of incident and scattered light is allowed or forbidden. Reciprocally, Raman scattering experiments with a systematic varia-
tion of the polarization directions along the principal symmetry axes may be applied for probing the individual components \( \mathbf{X}_{\alpha\beta}(\omega_i, \omega_s) \) of the Raman tensor and assigning the symmetry character of the respective vibration mode.

The treatment of the lattice vibrations as small perturbations of the crystal structure allows the expression of the generalized suscepti-
bility tensor \( \tilde{\chi}(\omega_i, \omega_s) \) as a Taylor expansion of the linear suscepti-
bility \( \chi(\omega) \), primarily in terms of the lattice deformation by a vibra-
tion mode or a combination of vibration modes, but if relevant also in terms of additional parameters, which may be involved in the modu-
lation of the electronic susceptibility, such as an electric field, a finite phonon wave vector, etc. When considering single vibration modes as well as mode pair combinations, within the adiabatic approxima-
tion one obtains the equation

\[
\mathbf{X}_{\alpha\beta}(\omega_i, \omega_s) = \chi^0_{\alpha\beta}(\omega_i) + \sum_m Q_m \frac{\partial \chi^0_{\alpha\beta}(\omega_i)}{\partial Q_m} + \frac{1}{2} \sum_{m,m'} Q_m Q_m' \frac{\partial^2 \chi^0_{\alpha\beta}(\omega_i)}{\partial Q_m \partial Q_m'} + \ldots \tag{7}
\]

Here \( Q_m \) denotes the amplitude of phonon mode \( m \) in terms of a 
generalized coordinate. The first-derivative term describes one-
phonon scattering, the second-order derivative terms correspond to 
two-phonon scattering, and further derivative terms may be consid-
ered if required [16,27].

2.4. Resonance effects

Because in the NIR-VIS-UV spectral range the dielectric response is essentially determined by the electron band structure, i.e., energy gaps and wave functions, the derivative terms in Eq. (7) describe the modula-
tion of energy and wave function of the interatomic bonding states by the periodic phonon-induced crystal deformation. This har-
monic deformation induces an oscillating additional contribution to 
the crystal potential. Therefore, the corresponding Raman scattering mechanism is called deformation potential (DP) scattering. Usually this is the predominant scattering mechanism in semiconductors. Its impact is maximum when the light frequencies \( \omega_i \) and \( \omega_s \) closely match an electronic transition frequency, i.e., when the photon ener-
gies are in the vicinity of an electronic energy gap. The resulting DP-induced Resonant Raman scattering (RRS) has been discussed in 
great detail for bulk phonon Raman scattering in Refs. [16,27].

In a microscopic quantum-mechanical framework, RRS is appropriately described by a time-dependent perturbation theory approach. Here, the dominant one-phonon contribution to the gen-

\[
S_{\alpha\beta} = \frac{dI_s}{dI_0 d\Omega} = |\mathbf{X}_{\alpha\beta}(\omega_i, \omega_s)|^2 \frac{\alpha_0 V}{c^4}. \tag{6}
\]
eralized dielectric susceptibility reads [16,17]:

$$X_{ab}(\omega_i, \omega_s) = \frac{e^2}{m_0\alpha_s V} \sum_{p_s} \left\langle 0 | p_\alpha | e' \right\rangle \left\langle e'H_{E_s-L} | e \right\rangle \left\langle e | p_\beta | 0 \right\rangle \left( E_{e'} - \hbar \omega_s \right) \left( E_e - \hbar \omega_i \right),$$

(8)

where $m_0$ is the electron mass, $V$ the scattering volume, $p_\alpha, p_\beta$ the $\alpha$- and $\beta$- component of the momentum operator, $E_e$ and $E_{e'}$ the energies of two electron-hole pair states, and $H_{E_s-L}$ the electron-phonon interaction Hamiltonian. Descriptively, in a coherent three-step process the incident photon is transformed into an electron-hole-pair state (transient exciton) $|e\rangle$ which is scattered into another electron-hole pair state (transient exciton) $|e'\rangle$ by interaction with the phonon, and is finally annihilated while generating the scattered photon. The coherence of the Raman scattering process implies that the intermediate electron-hole-pair states $|e\rangle$ and $|e'\rangle$ are not real excitonic eigenstates of the material, they are referred to as virtual excitation states.

But if the incident or scattered photon energy closely matches an excitonic transition energy $E_e$ or $E_{e'}$ in the sample material, the numerators tend to zero and the Raman cross section is resonantly enhanced. This refers to the generalized susceptibility model: At electronic resonances the polarizability of the material becomes largely referring to a large Raman cross section. It has been shown that the quantum mechanical perturbation theory result for $\chi(\omega, \omega)$ can be approximated by the derivative of the linear dielectric susceptibility $\chi(\omega)$ with respect to the phonon coordinates $[16,27]$. If the same pair of electronic bands applies for both transient exciton states $|e\rangle$ and $|e'\rangle$ (two-band Raman scattering process), within this approximation the first order term can be formulated as:

$$X_{ab}(\omega_i, \omega_s) = D_m \frac{\partial X_{ab}(\omega)}{\partial (\hbar \omega)},$$

(9)

where $D_m$ denotes the DP which applies for the involved electronic band pair due to the vibration mode $m$. A presumption for this expression is a constant electron-phonon coupling strength for all electronic transitions. If this does not apply, an individual consideration of the deformation-induced energy modulation is required for each transient exciton state.

From Eqs. (8) and (9) the Raman scattering cross section may be derived by calculations, which may be based on the derivative of the experimentally determined susceptibility or rest upon more sophisticated quantum mechanical considerations. In the latter case, $\chi(\omega_i, \omega_s)$ may be derived from the difference of the dielectric function for the ground state and the phonon-distorted one $[16,29–31]$. We would like to note that a quantitatively reliable $ab$ $initio$ calculation of the dielectric function requires to include the Coulomb correlation of the excited electron-hole pairs $[32,33]$. Thus the electronic band structure and corresponding independent-particle approach are not sufficient to describe the interaction of photons with the solid. Rather, local effects like dielectric screening (quasiparticles) and Coulomb-correlation (transient excitons) must be taken into account additionally. In practice, however, these corrections may be often omitted due to the large calculation effort, and related discrepancies partially compensated by a shift of the energy scale.

From the available experimental results it can be concluded that the order of magnitude of the Raman scattering cross section for the surface vibrations equals the DP-induced Raman scattering from bulk phonons in Si, Ge, and III-V materials $[29–31]$. Raman scattering from surface vibrations is expected to occur generally at solid surfaces, governed by the DP strength of the individual vibrations.

In the Raman scattering process, the predominance of the modulation of the electronic band structure by the lattice DP applies for scattering from surface vibrations as well as from bulk phonons. However, it should be noted that the impact of the surface vibrations is confined to just near-surface atomic layers. The electronic band structure in this region is usually quite different from the bulk, and surface-specific electronic transition energies occur. Therefore, a specific resonant enhancement of the surface-vibration scattering efficiency may be achieved when the photon energy closely matches an energy gap of the surface band structure. It is referred to as Resonant Surface Raman Scattering and can be employed for a partial compensation of the weakness of the surface-vibration signal as compared to the bulk.

2.5. Symmetry selection rules

The results of the above-mentioned considerations about the vanishing and non-vanishing elements $X_{ab}$ of the generalized susceptibility tensor $\chi$, or equivalently Raman tensor $R$, are referred to as Raman selection rules. They determine whether Raman scattering from a certain phonon mode is allowed or forbidden for given polarization directions of the incident and scattered light with respect to the high-symmetry axes of a crystal. The selection rules can be derived from group theory by utilizing the symmetry properties of the undisturbed crystal lattice and the considered phonon. For all irreducible representations of the 32 crystallographic point groups of three-dimensional lattices the Raman tensors are listed, e.g., in Refs. [16,27,34].

If a surface is taken into account, symmetry operations are greatly reduced, which implies fewer restrictions for the Raman selection rules for surface vibration modes than for bulk phonons. In practice, for backscattering geometry as usually employed, the polarization directions of incident and scattered light are oriented within the surface plane directions. Therefore, two-dimensional Raman tensors have to be considered, which represent a subset of the three-dimensional ones.

The focus of this review on SRS is on the vibration modes of a variety of clean-surface reconstructions and one- and two-dimensional self-ordered adsorbate structures, based on (001), (110), and (111) surfaces of cubic crystals. A general distinction with regard to symmetry properties concerns the rectangular 2D translation lattice of (001) and (110) surfaces and the trigonal one of (111) surfaces, if ordered, commensurate surface structures are considered. The surface structures may have different symmetry properties depending on the atomic arrangement and belong to different point groups. But in all those cases the possible vibration modes may be classified into symmetric ones, denoted as $A'$- or $A_1$-modes, and non-symmetric ones, denoted as $A''$, $A_2$, or $E$ modes. For symmetric vibration modes the original symmetry of the non-vibrating system is conserved, while a symmetry reduction is induced by non-symmetric ones. The according 2D Raman tensors in the rectangular mesh denote to:

$$R_{A' A_1} = \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix},$$

(10)

$$R_{A' A_2} = \begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix},$$

(11)

and in the trigonal one:

$$R_{A_1} = \begin{pmatrix} a & 0 \\ 0 & a \end{pmatrix},$$

(12)

$$R_{A_2} = \begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix},$$

(13)

The appropriate choice of the light polarization configurations allows the distinction between symmetric and non-symmetric modes, and moreover the determination of the tensor components $a$, $b$, and $c$. Thus, for parallel polarization of the incident and scattered light along a principal axis of the 2D structure, only the symmetric
surfaces, which represents a simple rectangular \((1 \times 1)\) structure, while the in-plane surface directions span the \((x, y)\) plane. Note, however, that the unambiguous classification of the in-plane axes according to light polarization directions is only possible in case of a unique orientation of all surface reconstruction domains.

### 2.6. Vibrational Surface Raman spectra

In order to understand how surface sensitivity is achieved in spite of the high light penetration depth, i.e., to illustrate the origin of a surface Raman spectrum and to show how to extract it in practice from an experimentally recorded Raman spectrum, we will consider a “model system”, the Sb monolayer structure on \((110)\) surfaces of III-V semiconductors \([36]\). This example will demonstrate how the surface contribution may be extracted from the difference between the Raman spectra from various stages of surface preparation and underscore the power of using surface resonant Raman conditions. Our “model system” is structurally very well defined and simple. Moreover, it has been very intensively studied both experimentally and theoretically in the past. Thus the atomic and electronic structure as well as the surface optical and surface vibrational properties are very well known, and the Sb monolayer structure on III-V\((110)\) has been used to demonstrate the principles of SRS \([31,37,38]\). This delivers the basic understanding required for the Raman applications on the structurally complex surfaces which are in the focus of the current review.

In the following we will at first consider the surface atomic structure and electronic band structure before we turn to the Raman scattering process on surfaces and its experimental observation. Sb forms a so-called epitaxially continued layer structure (ECLS) on III-V\((110)\) surfaces, which represents a simple rectangular \((1 \times 1)\) structure with only two Sb atoms in the 2D unit cell (see Fig. 3). The interface is atomically abrupt, i.e., there is no intermixing of the Sb with substrate atoms. Moreover, the monolayer structure is well ordered and the Sb atoms form strong covalent bonds to the substrate atoms, in a similar way as the covalent bonds in the substrate. Due to the electronic configuration of Sb (group V), the monolayer passivates the surface and there are no metallic surface states (see band structure in Fig. 4). In the picture of a laterally periodic 2D structure the substrate atoms below the rectangular Sb unit cell are attributed to the in-depth extended unit cell of the two-dimensional lattice, i.e., the number of atoms within the unit cell depends on the number of substrate layers which are taken into account in addition to the Sb monolayer. Consequently, when discussing surface properties such as electronic states or vibrational modes, a certain interaction with the substrate layers is always present, and the degree of surface confinement needs to be considered in detail for each electronic state, vibration, etc. This is very important for the physical/microscopic understanding of the surface excitations and also for any \textit{ab initio} calculation depending on a slab geometry. Therefore, the coupling between surface and bulk is an essential issue of the following discussions and examples.

The electronic band structure of Sb on III-V\((110)\) is shown in Fig. 4 for InP\((110)\), derived from DFT calculations. We would like to note that the atomic as well as electronic structure on other III-V\((110)\) substrates is almost the same. Due to the covalent bonds between Sb and the group-III or -V atoms in the second layer two pairs of bonding/antibonding-state-related surface bands develop \((S_6/S_7; S_8/S_{5} : Sb-V, S_8/S_5 : Sb-III)\). The surface bands denoted with \(A_6\) and \(A_5\) belong to the electronic states localized at the anion or cation in the second layer. This tight-binding picture is in full agreement with the result of the charge density distribution from DFT calculations \([31,37]\). The charge density distribution related to the electronic states of the surface bands gives the degree of confinement, i.e., it indicates how many substrate layers are involved in an electronic state. In general, those parts of the surface bands which lie in the bulk band gap are surface confined, whereas the parts overlapping with the bulk bands are surface resonances extending into the bulk.

The optical properties of the monolayers and the substrate have been analyzed in detail both experimentally and by theoretical calculations to relate the spectral features to the electronic structure of the surface and bulk \([29,31,37,39]\). In Fig. 5 the surface optical properties are shown, on the one hand as derived from ellipsometry in terms of
the surface excess function (SEF), which corresponds to the product of the surface dielectric function and the effective surface layer thickness \([40]\), and on the other hand as reflected from the surface optical anisotropy. Obviously, the surface electronic states discussed above give rise to strong surface-optical absorption structures. The surface bands, which are related to the bonding of the Sb to the InP substrate, lead to a surface-optical absorption at 2.7 eV for light polarized along the [001] direction. Electronic transitions involving the \(A_\Gamma\) electronic state in the substrate layer, to the contrary, lead to optical absorption at 2.1 eV for light polarized along the [1\,1\,0] direction. Strong optical absorption in the substrate (bulk) arises around the \(E_1/\Delta_1\) gap, i.e., at 3.15/3.3 eV (here \(\Delta_1\) implies the effect of spin-orbit coupling). Thus it is possible to perform surface RRS via one of the surface excitations around 2.1 and 2.7 eV (also taking into account the polarization direction), spectrally well separated from the bulk \(E_1\) gap transition at 3.15 eV [29,31,37]. We would like to note that the polarization dependence of the surface optical absorption bands is related to the orbital picture of the involved surface states. The two optical absorption bands are related to distinct surface bonds with allowed optical transitions for \(E\)-field orientations either along the [1\,1\,0]- or the [001] direction.

We now turn to the experimental Raman spectra. As a first example we consider Sb on InP(110). When Sb is deposited on InP(110), new Raman modes develop in the spectrum, in addition to the bulk-related ones, notably the transverse optical (TO) and the longitudinal optical (LO) phonon, which are observed at the clean surface. This is shown in Fig. 6 for Sb deposition up to 1 ML [41]. For Sb coverage beyond 1 ML the intensity of the related Raman peaks does not increase any more. Apparently the change in the Raman spectrum observed between 0 ML Sb and 1 ML Sb is related to the formation of the monolayer structure and the according modification of vibrational properties, i.e., surface vibration modes of the Sb-terminated InP(110) crystal. Six surface vibration Raman modes were identified as marked by the dash-dotted lines. The surface contribution of the Raman spectrum may be understood as the difference between the Raman spectra with and without Sb termination. However, one has to take into consideration that also the clean InP(110) surface has particular vibration properties distinct from the bulk modes [23]. These surface modes are quenched upon surface termination, however the related Raman spectrum is not visible here since the contribution of the clean surface is too weak with respect to the bulk signal. In general a controlled modification (such as the deliberate surface oxidation, quenching of surface reconstruction by adsorbates) of the surface is a good choice to separate the bulk and surface-related Raman scattering. Since the surface Raman signal is very strong in the particular case shown here (the intensity scale is normalized to the transverse optical (TO) phonon scattering from bulk InP, thus the surface modes reach 70% intensity of the bulk TO mode), the surface-related part is evident without further processing of the original spectra.

The monolayer structure belongs to point group \(C_\Gamma\), having a mirror plane symmetry element as indicated in the top view of Fig. 3 (dashed-dotted line). Accordingly, vibration modes can be classified as \(m\)-symmetry conserving \((A')\) and \(m\)-symmetry breaking \((A'')\) ones. It corresponds to two Raman tensors \(R\): \(R_{A'}\), with two different diagonal elements, and \(R_{A''}\) with two equal off-diagonal elements (see Eqs. (10) and (11)). The Raman selection rules can be probed by choosing the polarization vector of incident and scattered light along the principal axes of the 2D structure, i.e. the [1\,1\,0] and [001] crystal axes within the surface plane [31,41]. As shown in Fig. 7, different subsets of Raman modes are observed depending on the polarization configuration, i.e., \(A'\) and \(A''\) modes can be identified from the polarization selection rules. The existence of surface localized \(A'\) and \(A''\) modes was confirmed by first-principles surface dynamics calculations for Sb/III-V(110) [42,43]. The elements \(a\) and \(b\) of the \(R_{A'}\) Raman tensor are different, due the anisotropic structure of the Sb monolayer. \(A'\) modes appear weak in the [001],[001] polarization configuration (\(a\)-component), whereas they are strong in the ([1\,1\,0],[1\,1\,0]) configuration (\(b\)-component). This reflects the
Polarization selection rules for 1 ML Sb on InP(110). Excitation energy was 2.41 eV. \( A' \) and \( A'' \) modes can be identified by choosing the appropriate polarization configuration. The polarization notations parallel and perpendicular denote the direction with respect to the Sb chain direction [110]. The intensity scale is normalized to the Raman line of the bulk TO phonon of InP (from Ref. [41]).

The fact that the surface Raman lines have almost the same intensity as the bulk modes is related to resonance enhancement of the surface part. The Raman spectra shown in Fig. 6 were recorded with 2.41 eV laser excitation, i.e., in resonance to the electronic transitions between the \( S_{1/2} \) and \( S_{3/4} \) surface bands, but well separated from the \( E_1 \) bulk transition (3.15 eV for InP). Due to the resonance dependence of the Raman cross section, the surface Raman spectra depend strongly on the choice of the laser excitation line. In Fig. 8, a compilation of Raman spectra for laser excitations between 1.8 and 3.05 eV is shown [44]. The experimental finding is that those Raman peaks related to surface vibration modes become very prominently visible in the spectrum under surface resonant conditions, i.e., for excitation between 1.9 and 2.7 eV. By evaluating the intensity of the surface Raman lines as a function of photon excitation energy, as shown in Fig. 9, it becomes evident that the Raman resonance cross section differs strongly for the various surface vibration modes. In particular, strong resonances occur for the \( 1A'' \) mode around 2 eV, for the \( A' \) mode around 2.6 eV, and the \( 3A' \) mode follows rather closely the bulk InP TO resonance. This shows that the coupling with the electronic states depends strongly on the displacements pattern of the individual surface mode: The \( 1A'' \) mode couples to Sb-substrate bond related states, the \( 1A' \) mode to subsurface anion related states and the \( 3A' \) to bulk related states [31]. The first two modes are thus surface confined modes, and the third one is a surface resonance. The distinct electron-phonon coupling of the modes depending on their displacement patterns has been worked out for Sb/InP(110) in detail [29].

We now turn to the related Sb/GaAs(110) case. The monolayer structure is the same as in the InP case, however due to slight differences in the electronic band structure the surface resonance enhancement of the Raman cross section is less pronounced. Therefore it is of more general relevance for the following examples in this review. For the corresponding Raman spectra of Sb on GaAs(110), see Fig. 10 [38]. Shown are the three sets of spectra for different polarization configurations, referring to the a, b, and c Raman tensor elements. Each set consists of a spectrum of the clean GaAs(110) substrate, the Sb monolayer covered one, and the difference spectrum of both. The subtraction allows to extract the surface Raman spectrum, by elimination of the bulk part. Surface phonon modes of the
clean GaAs(110) surface are not considered, since the 2.41 eV laser excitation is non-resonant to the surface electronic states of clean GaAs(110). Thus, the Raman spectrum of the clean GaAs shows the well-known second-order acoustic phonon spectrum of GaAs bulk, which of course is also present after Sb-monolayer termination in terms of a superposition of bulk and surface scattering.

This subtraction procedure works indeed very well for the configuration ([001],[001]) and the crossed polarization configuration. For the ([110],[110]) configuration, the second-order bulk phonon background however is enhanced in intensity upon Sb monolayer termination. This means that the surface resonance enhancement also enhances to some extent the bulk acoustical modes, since those modes are associated with atomic displacements in the upper layers (near surface region) as well. According to the DP scattering picture, all vibration modes with displacements in the Sb layer and the underlying few substrate layers, which define the surface electronic bands, may benefit from the surface resonance enhancement. As known from the discussion of the surface optical properties, at 2.41 eV the surface excitation involves the \( A_2 \) subsurface state for light polarization along [110]. For polarization along [001], on the contrary, the surface states \( S_L-S_0 \) related to the Sb-substrate bonds are involved. Consequently, the subsurface excitation may lead to an enhancement of the acoustic multiphonon bands, while the surface excitation does not. Accordingly, the subtraction of spectra to extract the surface contribution must be taken with care. A careful inspection of the reference spectrum with respect to possible surface modes and bulk mode enhancement is required [38].

After subtraction of the bulk part the surface-mode related Raman spectra are obtained individually for each polarization configuration. This allows to identify eigenfrequencies and symmetries of the surface vibration modes, as highlighted by the dashed lines in Fig. 10. A very clear surface Raman spectrum is obtained, larger in intensity than the second-order bulk scattering. The surface spectrum shows partly sharp and intense peaks, such as the \( A' \) mode at 166 cm\(^{-1}\), and partly broad and asymmetric bands, such as the \( A''_3, A''_4 \), and \( A''_5 \) bands [38].

For the interpretation of the surface Raman spectrum it is very useful to consider the DFPT simulation of the surface dynamical properties [38,46]. As will be outlined in the next chapter, by DFPT the structure and force constants of the Sb monolayer structure are firstly calculated by DFT within a repeated-slab geometry of nine atomic layers. Thereafter, in order to compute the dynamical properties properly, a thick slab of 25 layers is constructed by adding additional bulk GaAs layers to the slab using force constants of the bulk structure [46]. This procedure allows to compute realistic displacement patterns, to analyze the degree of surface confinement of the modes and to compute the full two-dimensional dispersion of the phonon modes. The result of the computation is shown in Figs. 11 and 12.

In Fig. 11 the shaded areas represent bulk phonon modes, the continuous lines are surface phonon modes. The + “ and − “ signs denote \( A' \)– \( A'' \) symmetry of the phonon branches. The filled and open symbols denote the peak position and symmetry of the modes observed in the surface Raman spectrum. From \( \vec{q} \)-conservation it should be expected that all Raman peaks are related to phonons from the \( \Gamma \) point of the surface BZ. By comparison with the DFPT-calculated modes it turns out that indeed some of the Raman modes refer to confined surface modes, and some others to surface resonances, similar as we already concluded above from considering the mode resonance behavior. This becomes evident from the phonon displacement patterns shown in Fig. 12. Strongly localized to the surface Sb layer is the \( A' \) mode at 159 cm\(^{-1}\) in DFPT, corresponding to 166 cm\(^{-1}\) in the Raman spectra. It has a very flat surface dispersion and produces a strong and sharp Raman peak. The \( A' \) modes are less confined to the surface and show, apart from the Rayleigh wave (RW) at 76.6 cm\(^{-1}\), mostly significant dispersion. They refer to broad and asymmetric structures in the Raman spectra (see branches
at 170–185 cm\(^{-1}\) and 210–220 cm\(^{-1}\).

Moreover, at low frequency two modes show up which refer to the Rayleigh wave frequencies at the BZ boundary. This demonstrates that the \(\vec{q}\)-conservation law is not fulfilled. Defects on the surface, such as preparation-related atomic steps and defects in the cleaved (110) substrate plane, as well as structural inhomogeneities in the Sb monolayer, residual gas adsorption, etc., may lead to a relaxation of the \(\vec{q}\)-conservation rule. Under such conditions the surface Raman spectrum reflects the density of states of the surface phonon branches rather than \(\Gamma\)-point modes. Due to the large density of states of the flat Rayleigh wave dispersion close to the BZ boundary the peaks \(A'_1\) and \(A'_2\) are generated. The \(\vec{q}\)-relaxation, moreover, is also important for the line shape of the optical surface modes. Only those optical branches showing a flat dispersion curve should give rise to sharp Raman peaks, while branches with significant dispersion yield a broad and asymmetric Raman band, according to the related density of vibrational states. Exactly this behavior is found in the Raman spectrum, as, e.g., the sharp \(A''_1\) mode at 166 cm\(^{-1}\) belongs to a flat dispersion branch while the broad bands \(A'_3, A'_4\) and \(A''_5, A''_6\) originate from dispersive branches.

We would like to note that the same argument holds also for Sb/InP(110). The surface Raman peaks are asymmetric due to the dispersion of the surface phonon branches. The Raman peaks are narrower than in the GaAs case due to lower dispersion of the related surface modes. Moreover, the surface resonances are sharper and lead to a higher surface Raman cross section than in the GaAs case [38]. Thus, the bulk acoustic background is much less prominent than in the GaAs case and the surface Raman peaks appear sharper and more intense than in the case of GaAs.

Ordering effects are also observed in the examples discussed in the following chapters. Apart from structural inhomogeneities, also backfolding due to changes in surface reconstruction and thermal fluctuations of the surface atomic positions lead to such effects and are useful indicators of surface structural phase transitions.

In summary, RS from surface phonons is related to DP scattering by surface vibration modes. Due to the surface confinement of the respective vibration modes, the deformation-related modulation acts only on the chemical bonds within the according surface layer. Therefore, the SRS depends on the atomic and electronic structure of the surface layer, i.e., few atomic layers with an atomic and electronic structure distinct from the bulk, irrespective of the much larger light penetration depth. By choosing the excitation laser in resonance with a surface transition, corresponding to an electronic transition within the surface band structure, only the surface-related Raman signal is enhanced, making this particular part of the signal more prominent.

Due to the low symmetry of surface structures, the resonance enhancement of the cross section is specific for a particular surface vibration mode and may differ significantly for different eigenmodes. This is due to the displacement pattern of each eigenmode which determines the coupling with the electronic structure of the involved atomic layers.

If non-resonant conditions apply and the Raman scattering cross sections of the surface and bulk scattering are similar, the signal from the surface is present, but as a very weak intensity superimposed on the bulk Raman signal.

In the presence of structural imperfections or thermal fluctuations on the surfaces, the surface Raman spectrum may reflect the density of surface phonon states rather than particular surface modes at the \(\Gamma\) point of the surface BZ. Sharp SRS peaks are associated with modes showing a flat dispersion branch, and the line shape of the surface modes should depend on structural perfection of the surface. Moreover, phonon modes from the Brillouin zone boundary may appear as Raman features due to the large density of states.

3. Calculation of surface vibrations and scattering efficiencies

The last few decades have witnessed a rapid progress in computational materials science. On the one hand, theoretical foundations have been laid to explain and to predict properties of real materials using \textit{ab initio} theory, i.e., based solely on the fundamental principles of electrostatics and quantum mechanics which are applied using well-controlled simplifications and approximations, but without any empirical parameters [47]. On the other hand, high-performance computing has come into its own, allowing for the application of \textit{ab initio} theory even to complex materials and for truly predictive simulations of spectroscopic properties based on information on the individual atoms constituting these materials [48]. Materials excitation properties such as probed by RS provide deep insight into the interplay of atomic and electronic degrees of freedom and can as well be used to determine or verify the geometry of specific structural models. The full potential of techniques such as RS, however, can often only be exploited when the experimental data are supplemented with numerical simulations. DFT [49–51] has proven frequently to be a particularly suitable starting point for the simula-

![Fig. 12. Displacement patterns of surface localized eigenmodes typical for Sb monolayers on III-V(110). The notations \(A'\) and \(A''\) indicate the mode symmetry. RW denotes the Rayleigh wave (see Ref. [46]).](image-url)
tion of Raman spectra for a wide range of systems [52–55]. In order to calculate Raman spectra, the phonon eigenvalues and eigenvectors as well as the dielectric tensor of the investigated system are required. They are usually computed in separate steps. In the following, we will outline the procedure used to explore and explain the Raman signatures for the surface systems discussed in the present review. Additionally, we discuss methodological challenges as well as potential extensions. Thereby we focus on the state-of-the-art \textit{ab initio} techniques which have by now almost completely replaced earlier semi-empirical approaches such as tight-binding models for electronic-structure calculations or the adiabatic bond charge model for the lattice dynamics [56,57].

3.1. Density-functional theory for equilibrium geometries and single-particle band structures

Precise knowledge of the surface structure is a prerequisite for the calculation of Raman spectra. In particular for large and complex surface structures DFT is the \textit{ab initio} method of choice for determining the surface geometry [32]. It has led to many breakthroughs in the understanding of clean [58–62] and adsorbed surfaces [63–66] as well as thin films [67], and has also been successfully used to address the dynamic entanglement of surface structural and electronic degrees of freedom subsequent to excitations [68,69]. Since the general aspects of density-functional theory have been reviewed in several excellent articles (see, e.g. Refs. [51,70–73]), we restrict the general aspect to the presentation of the models relevant for the modelling of surfaces and their Raman signatures.

DFT [49] in the Kohn-Sham approach [50] maps the electronic N-particles problem onto an easier to solve set of single-particle equations. Many-body effects are accounted for by the so-called exchange-correlation functional. Following Hohenberg and Kohn, the total energy of a system of N electrons in an external potential \(V_{\text{ext}}\) can be expressed as a functional of the electronic charge density \(\rho\)

\[E[\rho] = T_\rho[\rho] + V_H[\rho] + V_{\text{ext}}[\rho].\]

In this expression, \(T_\rho[\rho]\) is the kinetic energy of a non-interacting electron gas with density \(\rho\), \(V_H[\rho]\) is the Hartree energy and \(V_{\text{ext}}[\rho]\) is the exchange-correlation functional.

Within the approach proposed by Kohn and Sham [50], the minimization of the energy functional \(E[\rho]\) leads to a set of single-particle equations for a system of non-interacting particles moving in the effective potential

\[v_{\text{eff}}(\vec{r}) = v_0(\vec{r}) + v_u(\vec{r}) + v_{\text{ext}}(\vec{r}).\]

These so-called Kohn-Sham equations

\[-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{eff}}(\vec{r})\] \(\phi_n(\vec{r}) = \epsilon_n \phi_n(\vec{r})\]

are solved self consistently, as the effective potential \(v_{\text{eff}}(\vec{r})\) depends on the electronic charge density, given by

\[\rho(\vec{r}) = \sum_n \phi_n^\ast(\vec{r}) \phi_n(\vec{r})^2.\]

where \(\phi_n\) are the occupations of the Kohn-Sham orbitals \(\phi_n\). Solution of the Kohn-Sham equations leads to the single-particle electronic wavefunctions \(\phi_n(\vec{r})\) and the Kohn-Sham eigenvalues \(\epsilon_n\).

Following the Hellmann-Feynman theorem [74], the forces acting on the ions can be obtained from the ground-state wavefunctions

\[\vec{F}(\vec{r}) = - \frac{\partial}{\partial \vec{r}} \left\langle \phi \left| \frac{\partial H}{\partial \vec{r}} \right| \phi \right\rangle.\]

The expression above is easily evaluated [75], provided a plane-wave basis is used to expand the electronic wavefunctions. By adjusting the atomic positions according to the Hellmann-Feynman forces, and recalculating both the electronic charge density \(\rho\) and the external potential for the new atomic positions, a step-by-step structural optimization can be performed [70]. This will eventually lead to the structurally relaxed ground state, or at least a local minimum on the potential energy surface of the nuclei. Typically a few hundred up to roughly thousand atoms can be routinely handled in this way. This allows to address many complex surface structures as well as long-range surface reconstructions. Temperature effects on the surface structure can be accounted for by free-energy calculations [76–78]. This leads very often to calculated surface structures which are in excellent agreement with experiment [32].

More problematic – as will be discussed below – is typically the description of the surface electronic structure within DFT [79]. Nevertheless, the Kohn-Sham eigenvalues \(\epsilon_n\), although not identical to quasiparticle energies, can be employed together with the single-particle orbitals \(\phi_n(\vec{r})\) to obtain the dielectric tensor from DFT: The macroscopic dielectric tensor can be calculated in the long-wavelength limit \(q \to 0\), with or without local-field effects, e.g., following the approach of Adler and Wiser [80–82]. Labeling cartesian directions by \(\alpha, \beta\), valence and conduction states with \(v, c\), respectively, the corresponding Kohn-Sham eigenvalues at the reciprocal-space point \(\vec{q}\) with \(\epsilon_{\nu \alpha}\) and \(\epsilon_{\nu \alpha}^{*}\), as well as the periodic part of the Bloch orbitals \(\psi_{\nu \alpha}(\vec{r})\) with \(u_{\nu \alpha}\), the imaginary part of the frequency dependent dielectric tensor for a unit cell with the volume \(\Omega_0\) is given by

\[
\epsilon^\text{im}_{\nu \alpha}(\omega) = \frac{4\pi e^2}{\Omega_0} \lim_{q \to 0} \frac{1}{q} \sum_{\nu \alpha \nu \alpha'} 2\omega_k \delta(\epsilon_{\nu \alpha} - \epsilon_{\nu \alpha'} - \omega) 
\times (u_{\nu \alpha}^{*} + u_{\nu \alpha}^{\prime} + u_{\nu \alpha}^{*} u_{\nu \alpha}^{\prime} + u_{\nu \alpha}^{\prime} u_{\nu \alpha}^{*}) 
\times (u_{\nu \alpha} + u_{\nu \alpha}^{\prime} + u_{\nu \alpha}^{*} u_{\nu \alpha}^{\prime} + u_{\nu \alpha}^{\prime} u_{\nu \alpha}^{*}).
\]

Iterative techniques, based on DFTP [83], even allow to avoid the explicit calculation of virtual electronic states for obtaining the dielectric tensor. The real part of the frequency dependent dielectric function can be obtained from the imaginary part by a Kramers-Kronig transformation

\[
\epsilon^\text{re}_{\nu \alpha}(\omega) = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{\epsilon^\text{im}_{\nu \alpha}^{\prime}(\omega') \omega'}{\omega^2 - \omega'^2} \, d\omega'.
\]

3.2. Quasiparticle bands and electron-hole attraction

While DFT is typically very reliable concerning the determination of the structurally relaxed ground state, the use of DFT as a theoretical tool for the study of physical properties other than the ground state, as in the calculation of electronic spectra, e.g., photoluminescence, inverse photoemission, electron-energy loss- or optical spectra, e.g., luminescence, absorption, reflectance anisotropy, is an \textit{a priori} not justified: The Kohn-Sham eigenvalues of the effective, non-interacting single particles of the DFT can neither be interpreted as electron removal or addition energies nor as energies of neutral electronic excitations, such as electron-hole pairs [79]. In particular, the Kohn-Sham band gap often dramatically underestimates the measured band gap in semiconductors, and, in some cases, gapped systems are even predicted to be metallic. This problem can be overcome in part by applying constrained DFT, which can be used to determine reliably ionization potentials, electron affinities, or quasiparticle gaps [84,85] as well as for electron-hole pair energies or excited-state potential energy surfaces [68,69].

A systematic approach to excited-state properties is referred to as propagator or Green’s function method [86,87]. It starts from the screening of the electronic system after electronic or opti-
interaction. Accordingly, the dynamically screened or shielded Coulomb interaction $W$ is the central quantity used in these methods. The excitation energies correspond to the poles of single- and two-particle Green's functions [86–88] that are obtained by means of a many-body perturbation theory [79]. By evaluating the one-electron Green's function $G$, single-particle excitations, e.g., ionization energies and electron affinities are derived that can be measured in photoemission and inverse photoemission spectroscopies. Two-particle Green's functions of the electronic system, e.g., the irreducible polarization propagator or the density-density response function, allow one to access electron-hole pair energies and collective excitations, e.g., plasmons, which may be observed in optical spectroscopies or electron-energy loss spectroscopy. The Lehmann representation of the single-particle Green's function leads to an eigenvalue problem for the quasiparticles

$$
\left( -\frac{\hbar^2 \nabla^2}{2m} + V_c(r) + V_{p}(r) \right) \phi_{n_k}(r) + \int d\vec{r}\, \Sigma(\vec{r}, \vec{r}'), E_{n_k} \delta_{n_k n_k} \phi_{n_k}(\vec{r}') = \epsilon_{n_k} \phi_{n_k}(\vec{r}),
$$

which can be considered a formal replacement of the Kohn-Sham equation [16].

The self-energy $\Sigma$ is typically approximated within the so-called $GW$ approximation [86,89,90], i.e., as convolution of the single-particle Green's function $G$ and the dynamically screened Coulomb interaction $W$

$$
\Sigma(\vec{r}, \vec{r}', \omega) = -\frac{i}{2\pi} \int d\omega' \, G(\vec{r}, \vec{r}', \omega + \omega') W(\vec{r}, \vec{r}', \omega').
$$

It turns out that in many instances the quasiparticle wave functions $\phi_{n_k}(\vec{r})$ are very similar to the Kohn-Sham wave functions $\phi_{n_k}(\vec{r})$. This allows for a perturbative determination of the quasiparticle energies as

$$
\epsilon_{n_k}^{QP} = \epsilon_{n_k} - \Delta_{n_k}^{\text{exc}},
$$

where $\Delta_{n_k}^{\text{exc}}$ is the state and $\vec{k}$-point dependent self-energy correction. The $GW$ approximation has been shown to improve in many instances the DFT description of the electronic structure of clean and adsorbed surfaces, see, e.g., Refs. [91–96]. In short, the $GW$ quasiparticle energies $\epsilon_{n_k}^{QP}$ account for electron-electron self-energy effects, which leads to an improved description, e.g., of the electronic fundamental gap in semiconductors and, correspondingly, of the dielectric tensor. In the case of the silicon substrates investigated in this review, many-body effects enlarge the Kohn-Sham gap by about 0.5 eV, leading to a very good agreement with the experimental value. Due to the band gap opening, a blue shift with respect to the original DFT calculations is observed.

While the thus resulting quasiparticle gaps are in excellent agreement with the gap energies obtained from photoemission and inverse photoemission experiments (electronic or transport gap), some deviation is still observed when they are compared with optically determined fundamental gaps, where electron-hole attraction effects may reduce the transition energy. The onset of the optical absorption as calculated on the $GW$ level of theory is typically overestimated in comparison with the experimentally determined values. This is due to the fact that the single quasiparticle formalism does not account for the electron-hole interaction and thus does not model correctly charge-neutral excitations. In fact, in particular surface localized electronic states often give rise to very large exciton binding energies [97,98].

In order to account for these effects one has to go beyond the single-quasiparticle approximation and to solve the Bethe-Salpeter equation (BSE) for the two-particle polarization function of the macroscopic dielectric function [88,99–102]. The BSE can be formulated as an effective eigenvalue problem in electron-hole basis

$$
\hat{H}^{\text{eff}} \psi_j = \epsilon_j \psi_j,
$$

where $\epsilon_j$ are the exciton energies and the electron-hole Hamiltonian is given by

$$
\hat{H}^{\text{eff}}_{\psi\psi'} = (\epsilon_c - \epsilon_v) \delta_{\psi\psi'} \delta_{\psi\psi'} + (\phi_\psi \phi_\psi \hat{V}_{\psi\psi'} \phi_v \phi_v - (\phi_\psi \phi_\psi \hat{W} \phi_v \phi_v),
$$

where $\hat{V}_{\psi\psi'}$ is the bare Coulomb potential without the long-range part and $\epsilon_{n_k}^{QP}$ are the quasiparticle conduction-band and valence-band energies associated to the eigenfunctions $\phi_{n_k}$. Finally, indicating with $\hat{W}$ the dipole operator, the imaginary part of the macroscopic dielectric function can be described as

$$
e^{\text{im}}(\omega) = \frac{8\pi \varepsilon_0 \hbar^2}{\Omega_0 m^2} \sum_n \sum_{\nu \nu'} \sum_{\psi \psi'} \sum_{\psi' \psi''} \epsilon_{\psi \psi'} \delta(\omega - \epsilon_n),
$$

where $\Omega_0$ is the volume of the unit cell.

3.3. Supercell method for surface modelling

While several approaches allow for the numerical modelling of surfaces, such as cluster [106,107], transfer matrix [108,109], or scattering methods [110,111], the method of choice in many instances is given by the supercell or slab method. It allows for exploiting the advantages of periodical boundary conditions, e.g., the usage of Bloch functions, even for surfaces, where the translational symmetry is broken in one direction. Thereby, the surface is modeled by a three-dimensional supercell consisting of a material slab, i.e., bulk material with surface termination and a vacuum layer. Obviously, the supercell method suffers from finite-size effects. Therefore, both the vacuum region which separates the two surface terminations as well as the slab thickness have to be large enough to decouple upper and lower surface terminations and to mimic semi-infinite crystals, respectively. Typically, 5 to 20 atomic layers embedded in a vacuum region of 10–20 Å are sufficient to reproduce bulk behavior in the center of the slab, and minimize interactions between the surfaces through the vacuum layer [32,112].

In the slab method, two surfaces per unit cell on opposite sides are created (see Fig. 13(a), illustrating a symmetric supercell used to model a Au-$\sqrt{3} \times \sqrt{3}$ monolayer at the Si(111) surface). Only for centrosymmetric slabs can the two faces be made equal. In other cases it is often preferable to consider the front end of a slab containing the surface of interest, and suitably passivate the bottom surface, e.g., with (pseudo-)hydrogen atoms with appropriate valence charges [113]. Thereby, the charge is chosen such as to doubly occupy the surface hydrogen bonds. This is exemplarily shown for the Au-$\sqrt{3} \times \sqrt{3}$ monolayer at the Si(111) surface in Fig. 13(b).

After passivation, the bottom of the slab corresponds ideally to a perfect, neutral semiconducting surface with electronic states well below and above the fundamental bulk band gap. However, two problems remain. At first, it is not possible to directly calculate the surface formation energy, as the slab contains two different surfaces.
This issue can be tackled, e.g., by the energy density formalism [114]. A second problem is due to the fact that two inequivalent slab surfaces will in general give rise to electric fields both in the material slab and in the vacuum region. While this problem is a minor issue for non-polar surfaces modeled by thick slabs separated by large vacuum layers, it becomes critical in the case of strongly polar surfaces.

Perpendicular to polar surfaces – as well as many adsorbate covered surfaces – there exists an electric field, the modelling of which requires additional care [59, 115, 116] as it may have a pronounced influence on, e.g., the surface Raman scattering [117]. The periodic boundary conditions are applied within the supercell approach to both the geometry and the electrostatic (or Hartree) potential \( V_H \).

This results in a zero macroscopic internal field \( \vec{E} \), independently from the presence (or from the exact value) of a spontaneous bulk polarization \( \vec{P}_S \) of the modeled material. This situation is illustrated in Fig. 14(a). However, a non-vanishing electrical dipole orthogonal to a surface modeled within a supercell approach will give rise to an electrostatic potential as shown in Fig. 14(b). As previously discussed, the net dipole moment will be in general the sum of a contribution due to the bulk polarization and a contribution due to the surface: A non-polar crystal with two non-equivalent surface terminations will result in a net dipole moment as well. This situation corresponds to a surface modeled within a supercell approach to both the geometry and the electrostatic (or Hartree) potential \( V_H \).

Indeed, by increasing the thickness of the slab or of the vacuum region the artificial fields become smaller, vanishing in the limit of a slab of infinite thickness, eventually recovering the bulk behavior (Fig. 14(a)).

The error introduced by the artificial field in finite slabs can be accounted for by specifically developed dipole corrections [118, 119]. The correction consists in the application of an external electric dipole in the vacuum region of the supercell, and yields to the scenario sketched in Fig. 14(c), in which the external electric field \( E_{\text{EXT}} \) vanishes. The electrostatic potential is now a continuous function, with a slope determined by the magnitude of the supercell. Hence, neither the internal nor the external field have a direct physical meaning. Indeed, by increasing the thickness of the slab or of the vacuum region the artificial fields become smaller, vanishing in the limit of slabs of infinite thickness, eventually recovering the bulk behavior (Fig. 14(a)).

It should be mentioned that none of the above illustrated periodic boundary conditions for the electrostatic potential is inherently correct and universally applicable. Vanishing internal field boundaries represent the correct conditions far from the surface and are hence appropriate to model the bulk of thin films. In contrast, vanishing external field conditions are the proper boundaries to model the surface itself. Thus, the proper choice of the suitable boundary conditions as discussed above is related to the system properties that have to be simulated. For the calculation of vibrational properties vanishing external field conditions are usually the method of choice.

### 3.4. Zone-center phonons from the frozen-phonon approach

The so-called frozen-phonon approach [83, 120] is an obvious method to determine phonon modes at high-symmetry points of the Brillouin zone, which was earlier applied to surfaces [121]. There a monochromatic perturbation is frozen with a finite amplitude in the system. Labeling the wave-vector dependent eigenfrequencies by \( \omega(q) \) and the displacement pattern of atom \( n \) of mass \( M_n \) in the cartesian direction \( \alpha \) by \( U_{\alpha n}^n(q) \), the secular equation for the calculation of the normal modes in a crystal is given by

\[
\sum_{n',\beta} \left( \delta_{\alpha n'} - M_n \omega^2(q) \delta_{n\alpha} \delta_{n'\beta} \right) U_{\alpha n'}^{n'}(q) = 0.
\]
Thereby the matrix

\[ C_{\text{nm}}^{\text{ab}} = \frac{\partial^2 E(\mathbf{R})}{\partial R_{\alpha}^n \partial R_{\beta}^m} = -\frac{\partial F_n^a(\mathbf{R})}{\partial R_{\alpha}^m} \]

of the second derivatives of the energy with respect to atomic displacements (Hessian matrix) and its Fourier transform

\[ C_{\text{nm}}^{\text{ab}}(\mathbf{q}) = \sum_{\mathbf{R}_l} e^{-i\mathbf{q} \cdot \mathbf{R}_l} C_{\text{nm}}^{\text{ab}}(\mathbf{R}_l) \]

must be calculated to gain access to the vibrational frequencies and displacement patterns. These are obtained diagonalizing the dynamical matrix

\[ D_{\text{nm}}^{\text{ab}}(\mathbf{q}) = \frac{1}{\sqrt{M_n M_m}} \sum_{\mathbf{R}_l} e^{-i\mathbf{q} \cdot \mathbf{R}_l} C_{\text{nm}}^{\text{ab}}(\mathbf{R}_l), \]

where \( \mathbf{R}_l \) is a lattice vector and the index \( l \) labels the \( l \)-th unit cell. For the calculation of the Hessian matrix finite differences are used, i.e., the \( i \)-th atom is displaced in each cartesian direction, and the forces caused on every atom are obtained using the Hellmann-Feynman theorem, Eq. (36).

Within the frozen-phonon approach, the calculation of the dynamical matrix \( D_{\text{nm}}^{\text{ab}}(\mathbf{q}) \) for an arbitrary point \( \mathbf{q} \) of the BZ is not straightforward. This becomes clear by writing the elements of the dynamical matrix as second derivative of the energy with respect to a lattice distortion of wave vector \( \mathbf{q} \)

\[ C_{\text{nm}}^{\text{ab}}(\mathbf{q}) = \frac{1}{N_{\text{uc}}} \frac{1}{\partial U_n^{*a}(\mathbf{q})} \frac{\partial^2 E}{\partial R_{\alpha}^m(\mathbf{q})}. \]

where \( N_{\text{uc}} \) is the number of unit cells in the crystal and \( U_n^{*a}(\mathbf{q}) \) is the amplitude of the lattice distortion. Let \( \mathbf{R}_l \) be a lattice vector. Any distortion \( U_n(\mathbf{q}) \), displacing atom \( n \) in the \( l \)-th unit cell by the amplitude

\[ U_n(\mathbf{q}) = U_n(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_l} \]

affects the original periodicity, unless \( \mathbf{q} = 0 \). In this case the distortion is commensurate to the unit cell (lattice periodical phonons). Otherwise, larger supercells (i.e., multiples of the unit cell) must be employed, for which \( \mathbf{q} \) corresponds to a reciprocal lattice vector. As the computational demand rapidly grows with the number of considered atoms (typically as \( N^3 \) in plane wave codes), the frozen-phonon calculations are de facto limited to high-symmetry \( \mathbf{q} \) points.

This is not problematic, if the calculated phonons have to be compared with single-phonon RS. As a result of wavevector conservation, the wave vector \( \mathbf{q} \) of phonons studied by one-phonon Raman scattering is limited for most semiconductors and typical laser frequencies to values corresponding to about 1/100 of the size of the BZ. Hence one-phonon Raman scattering probes only zone-center phonons and \( \mathbf{q} \) can usually be assumed to be zero. This exactly corresponds to the lattice-periodical (\( \mathbf{q} = 0 \)) phonons calculated with the frozen-phonon approach.

However, for comparison with the overtone Raman spectrum, which is in first approximation a measure of the phonon density of states, computational methods yielding the whole phonon dispersion must be employed. These will be discussed in the next section.

In case of polar materials, the force constants matrix \( C_{\text{nm}}^{\text{ab}}(\mathbf{q}) \) can be modified to account for the polarization induced by a longitudinal phonon [122,123]. This can be done in different ways, either following the approach of Gonze based on Ewald summation techniques [124], or adding a non-analytical contribution as proposed by Wang [125]. These corrections for polar materials are, however, not discussed in detail in this review.

Although the frozen-phonon approach is computationally very efficient, large supercells are in principle required to accurately calculate the force constant matrix. Due to the periodic boundary conditions, the displacement of one atom in a small unit cell gives rise to spurious forces on the periodic images of the supercells, limiting the accuracy of the method.

3.5. Phonon dispersion from density-functional perturbation theory in linear response

DFPT (see, e.g., Ref. [126]) in the linear response allows for direct calculation of second-order derivatives of the energy and thus yields the force constants matrix in a rather direct way. Assuming that the external potential depends on a parameter \( \lambda \), which we will later identify with the phononic distortions, the external potential \( V \), the electronic charge density \( \rho \) and the energy functional \( E \) can be expanded in powers of \( \lambda \). Evaluating the derivatives at \( \lambda = 0 \)

\[ V_\lambda(\mathbf{r}) \approx V(\mathbf{r}) + \lambda \frac{\partial V(\mathbf{r})}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} + \ldots \]

\[ \rho_\lambda(\mathbf{r}) \approx \rho(\mathbf{r}) + \lambda \frac{\partial \rho(\mathbf{r})}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 \rho(\mathbf{r})}{\partial \lambda^2} + \ldots \]

\[ E_\lambda \approx E + \lambda \frac{\partial E}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 E}{\partial \lambda^2} + \ldots \]

Due to the Hellmann-Feynman theorem, the first-order derivative \( \frac{\partial E}{\partial \lambda} \) does not depend on any derivative of \( \rho(\mathbf{r}) \)

\[ \frac{\partial E}{\partial \lambda} = \int \rho_\lambda(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d^3 r. \]

Similarly, the second-order derivative \( \frac{\partial^2 E}{\partial \lambda^2} \) depends on the first-order derivative of the charge density

\[ \frac{\partial^2 E}{\partial \lambda^2} = \int \frac{\partial V(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d^3 r + \int \rho_\lambda(\mathbf{r}) \frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} d^3 r \]

and

\[ \frac{\partial^2 E}{\partial \lambda \partial \mu} = \int \frac{\partial V(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d^3 r + \int \rho_\lambda(\mathbf{r}) \frac{\partial^2 V(\mathbf{r})}{\partial \lambda \partial \mu} d^3 r. \]

As previously discussed, the Fourier transform of force constants at \( \mathbf{q} \) can be expressed as the second-order derivatives of the energy with respect to the atomic displacements, which now play the role of the perturbations \( \lambda \) and \( \mu \)

\[ C_{\text{nm}}^{\text{ab}}(\mathbf{q}) = \frac{1}{N_{\text{uc}}} \frac{1}{\partial U_n^{*a}(\mathbf{q})} \frac{\partial^2 E}{\partial R_{\alpha}^m(\mathbf{q})}. \]

This expression can be readily calculated with the knowledge of the linear response

\[ \frac{\partial \rho(\mathbf{r})}{\partial R_{\alpha}^m(\mathbf{q})} \]

and diagonalized to get access to the phonon eigenfrequencies and eigenvectors.

The advantage of this approach is that the linear response has the same wave vector \( \mathbf{q} \) of the perturbation and thus allows to calculate the phonon modes at arbitrary \( \mathbf{q} \) without employing any supercell. This methodology was applied, e.g., to obtain the surface phonon dispersion of clean and Sb-adsorbed III-V surfaces [46,127].
are that the Hessian matrix does not need to be calculated and that

calculation see, e.g., Refs. [130,131] – and focus on the first-principles

gy are in agreement, some uncertainty might result in experi-

tion of the displacement patterns and, if applicable, on the mode degener-

rations. In calculations the symmetry is directly assigned on the basis

symmetry properties are determined differently in calculations and

acterized by a smaller degree of surface localization.

appropriate. Both surface-localized phonon modes and bulk reso-

vibrations have energies above or below the corresponding bulk val-

The susceptibility tensor \( \tilde{\alpha} \) is calculated according to

\[ a_{\alpha\beta}^{m} = \sqrt{\delta_{\alpha\beta}} \sum_{n,\beta} \frac{\partial^{2} \phi_{n,\beta}^{(1)}}{\partial U_{m,n}^{(\beta)}} \]

where \( \phi_{n,\beta}^{(1)} \) are the elements of the electronic linear dielectric susceptibility tensor, which are related to the frequency dependent

dielectric permittivity by \( \epsilon_{\alpha\beta}(1) = 1 + \phi_{\alpha\beta}^{(1)} \). The latter is calculated, e.g., in independent-particle or independent-quasiparticle approximation [139]. The zone center phonon frequencies \( \omega_{m} \) as well as the
gendisplacements \( U_{m,n}^{(\beta)} \) are calculated within the frozen-phonon method or by DFPT in linear response. \( U_{m,n}^{(\beta)} \) represents the displacement of atom \( n \) in direction \( \beta \) within phonon \( m \).

The comparison of the calculated Raman spectra with the experimental ones requires great care because the calculated Raman scat-
tering efficiencies of each eigenmode turn out to depend individu-

ally and strongly on the chosen excitation wavelength. As an exam-
ples, we show in Fig. 15 the calculated Raman spectra of the Au-
ally and strongly on the chosen excitation wavelength. As an exam-

3.7. Calculation of Raman scattering efficiency

In the following we neglect second-order effects – for their cal-
culation see, e.g., Refs. [130,131] – and focus on the first-principles calculation of Raman scattering efficiencies of zone center optical phonons [132–135]. For non-resonant Raman processes, the Placzek
aproximation described in the following can be applied. In the case of exact resonance of the Raman process, described by the Albrecht

toric theory [136], the excitation must match the energy of an electronic interband transition or of an exciton. This requires the

knowledge of excited-state Born-Oppenheimer surfaces, which are

expensive to calculate. However, Walter and Moseler have demon-

strated that Placzek polarizability theory can be considered as the semi-classical limit of the more exact Albrecht formulation, which

yields results remarkably similar to Albrecht vibronic theory also in

resonance regions, unless multiple excitations are involved [137].

Raman coefficients are third-order derivatives of the electron transition energy that can be calculated by different approaches.

Lazzeri et al. have suggested to compute them as a second-order response to an electric field [54]. However, the Raman intensity can also be calculated via finite differences of the dielectric tensor with a phonon frozen in. The main equations derived in Refs. [27,138,139] are briefly summarized in the following. We label the polarization of the incoming photon by \( \vec{e}_{i} \) and its frequency by \( \omega_{i} \). The incoming photon is scattered to an outgoing photon of polarization \( \vec{e}_{r} \) and frequency \( \omega_{r} = \omega_{m} \), while a phonon of frequency \( \omega_{m} \) is created.

The differential scattering efficiency of phonon \( m \) with respect to the collection angle \( \Omega \) of the scattered photons is given by

\[ \frac{\partial \sigma_{m}}{\partial \Omega} = |\vec{e}_{r} \cdot \vec{R} \vec{m} \cdot \vec{e}_{i}|^{2} = \frac{(\omega_{i} - \omega_{m})^{4}}{(4\pi\epsilon_{0})^{2}} |\vec{e}_{r} \cdot \vec{m} \vec{m} \cdot \vec{e}_{i}|^{2} \frac{\hbar}{2\omega_{m}(n_{m} + 1)}. \]  

In this equation, \( \vec{R} \vec{m} \) represents the Raman tensor, and \( c \) the speed of light in vacuum. The phonon occupation numbers \( n_{m} \) are given by the Bose-Einstein distribution

\[ n_{m} = \frac{1}{\exp \left( \frac{\hbar \omega_{m}}{k_{B} T} \right)} - 1. \]

The susceptibility tensor \( \tilde{\alpha} \) is calculated according to

\[ a_{\alpha\beta}^{m} = \sqrt{\delta_{\alpha\beta}} \sum_{n,\beta} \frac{\partial^{2} \phi_{n,\beta}^{(1)}}{\partial U_{m,n}^{(\beta)}} \]

photon of frequency \( \omega_{m} \) is created.

3.6. Atomistic simulations and surface phonons

Surface phonon modes can have very different dispersions. Surface phonon branches can be completely bound within the bulk phonon dispersion or be localized outside these bands. In the first case, they are called phonon resonances, while in the second case they are referred to as surface localized phonon modes. Similarly, surface phonons can be divided into two groups, depending on their origin. Indeed, there are surface modes which can only exist in the surface termination, and surface modes which are the counterpart of bulk vibrations in the presence of a surface. Surface-modified bulk vibrations have energies above or below the corresponding bulk values, as the surface relaxation may lead to the contraction or expansion of the surface termination. Whether a phonon mode is surface localized or not can be quantitatively investigated by calculating the contribution of the single atomic surface layers to the absolute value of the phonon eigenvalues. As SRS is typically sensitive to vibrations of a few topmost surface layers, vibrations which are dominantly localized on the outermost atomic layers are usually considered surface localized phonon modes. The precise classification must be handled with caution. On the one hand, many quantities involved in the Raman scattering process, such as the penetration depth of the exciting radiation or the extent of the region considered as a surface termination are strongly system dependent, thus the localization threshold should be chosen as system dependent. On the other hand, the degree of localization of a given phonon eigenvector depends on the physical and numerical approximations that enter the calculations. Therefore, a sharp localization threshold is not appropriate. Both surface-localized phonon modes and bulk resonances are in principle detectable in RS, although the latter are characterized by a smaller degree of surface localization.

Phonon modes are classified with respect to their symmetry, which eventually determines the Raman selection rules. However, symmetry properties are determined differently in calculations and experiments. In experiments the mode symmetry is assigned on the basis of the selection rules, which allow only modes of certain displacement patterns to be detectable within given scattering configurations. In calculations the symmetry is directly assigned on the basis of the displacement patterns and, if applicable, on the mode degeneracy. Although experimentally and theoretically assigned mode symmetry are in agreement, some uncertainty might result in experiment by spurious polarization components of the exciting radiation field or by surface imperfections relaxing the selection rules.
vibrations with elongation patterns which are compatible with the symmetry of the reconstruction pattern. Especially for complex surface structures such as Si(111)-(7 \times 7) and Ge(111)-(c(2 \times 8)) a multitude of eigenmodes may be expected.

In Section 4.1 vibration modes of the Si(111)-(7 \times 7) surface are discussed. Subsequently, Ge(111)-(c(2 \times 8)) is in the focus of Section 4.2. Finally, in Section 4.3 results for the clean Ge(001)-(2 \times 1) and -c(4 \times 2) surfaces are presented.

### 4.1. Clean Si(111)-(7 \times 7)

The investigation of the surface vibration modes of the clean Si(111)-(7 \times 7) surface is motivated by several aspects: (i) its surface reconstruction is intriguing by its very large unit cell with a complex atomic structure, from which a rich variety of surface vibration modes may be expected, (ii) the knowledge of the vibration modes of the clean surface is a prerequisite for the subsequent assignment of potential vibration signatures upon coverage with metal atoms, (iii) from detailed studies over many years [see, e.g., Ref. [144]] the atomic structure of the complex unit cell is known in great detail, which should facilitate the identification of surface vibration signatures.

The commonly accepted Si(111)-(7 \times 7) surface structure is denoted as the dimer-adatom-stacking-fault (DAS) model. This model describes a rhombooidal surface, consisting of a faulted and an unfaulted part. The topmost Si layer comprises twelve adatoms, six rest atoms, and one corner-hole atom. Its symmetry is threefold and corresponds to the point group C_{3v}, with three vertical mirror planes. Calculations on Si(111)-(7 \times 7) surface vibration eigenmodes have been performed by several groups, essentially employing molecular-dynamics simulations [145–148]. Experimental studies have been reported, applying HREELS [149] and HAS [150]. In these studies several eigenmodes have been identified, but from investigations by SRS a significantly enhanced spectral resolution is expected, and moreover a symmetry assignment of the individual modes. According to the point group C_{3v}, the symmetry of the Raman-active vibration eigenmodes may be either A_{1} or E, which implies either only diagonal Raman tensor elements (a, b) or only off-diagonal ones (c), respectively. Therefore, for Raman backscattering geometry with polarization of the incoming and scattered light in a principal in-plane direction \( x = [112] \) or \( y = [\bar{1}10] \), \( A_{1} \) modes should appear in configurations with parallel polarization, and \( E \) modes in crossed ones.

#### 4.1.1. Surface Raman spectra of the Si(111)-(7 \times 7) surface

A detailed analysis of the Si(111)-(7 \times 7) surface vibration eigenmodes by polarized SRS at room temperature (RT), as well as at T \approx 40 K, has been reported in Ref. [151]. Here, after preparation of the (7 \times 7) reconstruction of the clean surface by flash annealing in UHV and its quality check by Low-Energy Electron Diffraction (LEED), several distinct Raman peaks were observed. Their surface-mode origin was confirmed subsequently by their disappearance upon quenching of the (7 \times 7) reconstruction by a controlled residual-gas exposure.

Fig. 16 shows the Raman spectra of the (7 \times 7)-reconstructed surface and the aged one for comparison for both polarization configurations z(\hat{y}y\hat{z}) and z(\hat{x}y\hat{z}). The spectra are clearly dominated by the first-order Raman peak of the degenerate longitudinal and transverse optical (LTO) phonon of bulk Si at 520.7 cm^{-1}, which by far exceeds the ordinate scale (Fig. 16(a)). It is accompanied by a very broad structure which is about two orders of magnitude weaker, and originates from second-order Raman scattering from acoustic bulk phonons. Its maximum is at 303 cm^{-1}, belonging to 2TA(X), i.e., second-order scattering from two transverse acoustic phonons at X-points of the BZ edge. For distinguishing the surface-vibration...
peaks, a further upscaling of the intensity by a factor of 10 is required (Fig. 16(b) and (c)). Then, six structures become observable in the spectra of the (7 × 7)-reconstructed surface, marked by blue vertical lines. They obviously have disappeared in the spectra after the quenching of the reconstruction by aging of the surface. This justifies their assignment to surface-vibration modes. Their net contributions are plotted in Fig. 16(d) as the Raman-intensity difference ΔI between the (7 × 7) reconstruction and the same surface after aging. In detail, the surface-vibration signatures appear as four peaks at 62.5, 136.1, 250.9 and 420.0 cm⁻¹, and two further weaker features in the range between 110 and 140 cm⁻¹. Among the four peaks, those at 62.5 and 136.1 cm⁻¹ occur for parallel polarization, corresponding to A₁ symmetry, and those at 250.9 and 420.0 cm⁻¹ for crossed polarization, which implies E-symmetry configurations (Table 1). Additional spectra at T ≈ 40 K showed narrower peaks and allowed the identification of modes at 115.3 and 130.0 cm⁻¹. In accordance with calculation results [145–148] the Ramap peak at 250.9 cm⁻¹ is assigned to out-of-plane adatom vibration modes, which had been predicted between 220 and 280 cm⁻¹. The same assignment had been made by HREELS [149].

The E-symmetry peak at 420.0 cm⁻¹ is attributed to a collective mode, in which the adatoms as well as the atoms underneath in the first and second full Si layer are involved. It should be noted that this mode, which was predicted theoretically between 400 and 460 cm⁻¹, is outside the frequency range which is accessible for HAS. The three peaks between 110 and 140 cm⁻¹, two of which were only resolved at low temperature, were modeled as in-plane wagging oscillations of the adatoms and the subjacent atoms with additional contributions of Si atoms down to the third layer. Their polarization dependence indicates for the 136.1 cm⁻¹ mode, in which the adatoms as well as the atoms underneath in the first bulk-like Ge layer and furthermore one Ge atom vertically underneath in the second layer. Besides, the surface energy is further reduced by a shift of two atoms of the first layer, which are referred to as restatoms [155]. Finally, the adatoms and restatoms induce static displacements of further atomic positions, reaching several layers deep into the bulk. The Ge(111)-c(2 × 8) reconstruction allows no point symmetry operations. In particular, it has no mirror planes, due to the non-equivalence of the adatoms and restatoms [156,157].

4.2. Clean Ge(111)-c(2 × 8)

The clean Ge(111) surface is characterized by a c(2 × 8) reconstruction [152], which features two additional Ge adatoms per primitive surface unit cell, compared to the unreconstructed Ge(111) surface. These adatoms are located at T₃p positions [153,154], which implies for each adatom three next-neighbor atoms in the first bulk-like Ge layer and furthermore one Ge atom vertically underneath in the second layer. Besides, the surface energy is further reduced by a shift of two atoms of the first layer, which are referred to as restatoms [155]. Finally, the adatoms and restatoms induce static displacements of further atomic positions, reaching several layers deep into the bulk. The Ge(111)-c(2 × 8) reconstruction allows no point symmetry operations. In particular, it has no mirror planes, due to the non-equivalence of the adatoms and restatoms [156,157].
Table 1
Summary of the surface phonon mode properties of the Si(111)-(7 × 7) surface: frequencies at 300 K, preferential polarization configuration for Raman observation (if applicable), corresponding theoretically derived frequency range, mode assignment, and experimental observation by a different experimental technique (if applicable) (from Ref. [151]).

| Raman position (cm⁻¹) | dominant pol. config. | theoretical results [146, 148, 149] | mode assignment | other experimental techniques |
|-----------------------|-----------------------|-------------------------------------|-----------------|---------------------------|
| 62.5                  | z(yy) \( \tilde{z} \) | 60 - 100                            | Rayleigh wave   | HAS [151]               |
| 115.3                 | z(yy) \( \tilde{z} \) | 110                                 | in-plane wiggling modes | (adatom - atom underneath) |
| 130.0                 | z(yy) \( \tilde{z} \) | 140                                 |                 |                          |
| 250.9                 | z(px) \( \tilde{z} \) | 220 - 280                           | localized at adatomic sites | HREELS [150] |
| 420.0                 | z(yz) \( \tilde{z} \) | 400 - 460                           | collective mode | (adatoms, 1⁴/2⁵ layer atoms) |

4.2.1. Surface Raman spectra of the Ge(111)-c(2 × 8) surface

The Raman spectra of Ge(111)-c(2 × 8) surfaces for both polarization configurations z(xy) \( \tilde{z} \) and z(xy) \( \tilde{z} \) at T \( \approx 40 \) K are depicted in Fig. 17. Especially the spectrum with diagonal polarization configuration z(xy) \( \tilde{z} \) shows a rich variety of peaks, some of which appear exclusively for this polarization, while others also occur in the z(xy) \( \tilde{z} \) configuration. The low temperature induces a narrowing of the peaks, which allows the resolution of additional structures with respect to RT spectra, and for some peaks a substructure is observed. The peak frequencies for 40 K are listed together with those for RT in Table 2. The temperature-induced frequency shifts are attributed to anharmonic effects. According to a molecular dynamics simulation, based on local-density-functional calculations (MD-LDF) [155], the majority of these modes originate from Ge adatoms or restatoms and other atoms in this layer. The most prominent peak in the spectrum for the z(xy) \( \tilde{z} \) configuration is located at 121.7 cm⁻¹. Its much weaker intensity in the z(xy) \( \tilde{z} \) configuration suggests the A' symmetry. After its observation in HAS, this feature has been attributed to an optical surface phonon with a flat dispersion [158], which is consistent with its rather narrow Raman peak width. Following the outcome of the MD calculations, this Raman peak is attributed to adatoms. The same applies for the higher one of the double peaks at \( \approx 135 \) cm⁻¹, which interestingly was not observed in HAS experiments. Note the twin-peak maxima at 132.1 and 135.4 cm⁻¹ that are clearly resolved in the z(xy) \( \tilde{z} \) spectrum. This peak splitting might point to inequivalent roles of the Ge adatoms due to the above-mentioned lack of surface symmetry. Two further optical phonon peaks appear at 161.3 and 189.7 cm⁻¹, which have also been identified by HAS. According to the calculations, these modes belong to adatoms and atoms in the first complete Ge layer, respectively. The latter peak is accompanied by a pendant on the low-frequency side at 182.4 cm⁻¹, which is distinguishable by its different polarization characteristics. The Raman peak at 221.5 cm⁻¹, which is beyond the frequency range which was investigated by HAS, is also attributed to the restatoms on the Ge(111) surface. It forms a twin-peak structure together with the stronger partner at 227.6 cm⁻¹, better resolved in the z(xy) \( \tilde{z} \) spectrum. The peak at 244.1 cm⁻¹, which appears in both polarization configurations, is not predicted by MD-LDF. Finally, at the low-frequency edge of the bulk Ge LTO phonon (\( \omega_{\text{LTO}} = 300 \) cm⁻¹), three distinct peaks are observed at 260.2, 274.8, and 285.7 cm⁻¹. These peaks might originate from the LO and TO branch, and appear as a result of disorder or backfolding at the surface with respect to the bulk phonon dispersion [160,161]. Note that the upper peak shows a polarization behavior that is different from the other two.

The two Raman peaks at 61.6 and 83.6 cm⁻¹ are associated with disorder-induced or backfolded RWs, in accordance with HAS [158].

The high-intensity Raman peak at 69.9 cm⁻¹ is identified with a feature which is observed also in HAS between the RWs. For the low-lying RW, the MD-LDF simulations concordantly predict a mode localized mainly at the ad- and restatoms. The higher RW and the mode in between also have counterparts in the calculations. Also note the additional small peaks at 64.9 and 77.3 cm⁻¹, that were not observed in HAS.

All Raman peaks of the Ge(111)-c(2 × 8) reconstruction together with vibration frequencies calculated by MD-LDF and HAS measurements are also summarized in Table 2. The reported HAS data give the same values for 300 K and for 170 K, which may be partially due to its reduced spectral resolution. Overall, the comparison of the different experimental techniques and the calculation results shows a consistent picture and a very good agreement. The Raman data allow, besides the enhanced frequency accuracy also the identification of several vibration modes which are not detectable in HAS.

4.3. Clean Ge(001)-(2 × 1) and -(4 × 2)

The clean Ge(001) surface has found widespread interest for several decades, because the temperature dependence and the temporal dynamics of its reconstruction allow the analysis of the interplay between a strong short-range interaction of Ge surface dimers and a
The Ge(001) surface reconstructions are based on [110]-aligned rows of [110] Ge dimers, giving a \((2 \times 1)\) superstructure, which was experimentally established for 300 K by LEED [163,164] and He diffraction [165]. In more detail, the dimers are asymmetrically buckled with an antiferromagnetic buckling order within each row due to a rather strong short-range interaction. This pattern doubles the surface unit cells to a \((2 \times 2)\) reconstruction, as confirmed by time-resolved STM results [162,166–168]. The seeming contradiction with the apparent \((2 \times 1)\) reconstruction was resolved by the perception of a dynamical periodic flip-flop between the two possible dimer buckling orientations in the \((2 \times 2)\) unit cells, which makes them appear averaged as \((2 \times 1)\) for time-integrating probing methods. Additionally, a weak long-range interaction induces a trend to a row-to-row dimer buckling ordering, which is locally observed already at 300 K and establishes a global \((c(4 \times 2)\) reconstruction below 100 K [169–171].

The surface vibration modes which are expected for these reconstructions are intriguing not only with respect to the different reconstructions themselves, but also from the viewpoint of the possible impact of the dimer flipping and the coexistence of \((2 \times 1)\) and \((c(4 \times 2)\) reconstructed areas at 300 K. The rectangular surface unit cell of the \((2 \times 1)\) reconstruction belongs to the point group \(Pm\) (monoclinic), which enables eigenmodes with symmetry \(A_{1}\) and \(A_{2}\). The point group of the \((2 \times 2)\) reconstruction is \(P2_{1}mg\) (orthorhombic), which may give rise to \(A_{1}, A_{2}, B_{1},\) and \(B_{2}\) eigenmodes. Finally, the plane and point group of the diamond-shaped \((c(4 \times 2)\) unit cell are \(c2mm\) and \(2\overline{2}m\), respectively, which gives eigenmode symmetries identical with the \((2 \times 2)\) reconstruction. Each of these three symmetries allows altogether DP Raman scattering in parallel as well as perpendicular polarization configuration [27]. Surface phonon calculations have been performed with DFPT and local-coupling transfer [165,172], and within the adiabatic bond charge model [173].

On the experimental side, in the late 1990s the Rayleigh wave and optical surface modes in the energy range up to 7 meV have been studied by inelastic He atom scattering at 300 K for the mixed \((2 \times 1)(c(4 \times 2)\) phase [165]. A few years ago, the observation of several Ge(001) surface vibration modes by SRS was reported for 300 K, i.e., for the \((2 \times 1)\) reconstruction with flipping dimers and \((c(4 \times 2)\) admixture, as well as for 40 K, where the static \((c(4 \times 2)\) superstructure occurs [174]. These surface vibration modes are the subject of the next sections with special emphasis to their eigenfrequencies and their assignment according to their displacement patterns.

### 4.3.1. Raman spectra of Ge(001)

In Fig. 18, polarized Raman spectra of Ge(001) by Räthel et al. [174] are shown, which were recorded in situ in UHV at 300 K after a flash annealing preparation of the \((2 \times 1)\) Ge(001) reconstruction with \((c(4 \times 2)\) admixture (black curves). For comparison also the spectra which were recorded before annealing are plotted, i.e., with thermal surface oxide (red curves). For both symmetry configurations \(A_{1}\) (panel (a)) and \(A_{2}\) (panel (b)), the oxidized Raman signature represents the expected two-phonon features and one-phonon LO flank from the bulk, while the reconstructed surface yields distinct additional peaks, which are attributed to surface vibration modes. The net surface contributions are plotted at the bottom of each panel as the intensity difference \(\Delta I\) between the reconstructed and the oxidized surface. Note also the grey marking of the range below 40 cm\(^{-1}\), which is omitted in the further evaluation because of hampering by increasing laser background.

The difference spectra feature surface vibration peaks at 46, 62, 122, and 227 cm\(^{-1}\) (i.e., 5.70, 7.69, 15.13, and 28.15 meV), which are denoted as \(S_{1}\) to \(S_{6}\). The additional bracketed indications \(\Gamma, K\) represent their location in the surface \(BZ\), which will be discussed in Section 4.3.3. For the off-diagonal polarization configuration (b) the four peaks all appear, while for the diagonal case (a) the low-frequency peak (46 cm\(^{-1}\)) is missing. This polarization dependence is explained in accordance with the symmetry of the mode patterns, which will be discussed in the next section.

An additional confirmation that the observed peaks originate from the reconstructed clean Ge(001) surface, was the observation that they are completely quenched by the deposition of Au on this surface, which induces a \((c(8 \times 2)\) reconstruction.

### 4.3.2. Surface vibration mode patterns

The observed surface peak frequencies in Fig. 18 correspond very well to calculated eigenfrequencies for the Ge(001) \((2 \times 1)\) reconstruction from Tüttüncü et al. [173] and Stigler et al. [165,172], derived by means of the adiabatic bond-charge model and density-functional perturbation theory, respectively. The individual assignment of each observed surface Raman peak to a specific elongation pattern according to the calculations from Ref. [173] was performed in consideration of two criteria: (i) close eigenfrequency match; (ii) confinement to those calculated surface eigenmodes with the lowest predicted damping by bulk coupling.

Because for each eigenmode the calculated bulk coupling depends individually on its wave vector \(q\), the \(\bar{q}\)-values are labeled here as follows: wave vectors on the \(\bar{\Gamma}-\bar{\Gamma}\) direction of the \(\bar{BZ}\) point along the dimer rows, i.e. in direction [110], while \(\bar{\Gamma}-\bar{J}\) represents the row-to-row direction [110], and \(\bar{\Gamma}-\bar{K}\) the intermediate high-

| 300 K | 40 K | AA | RA | SRS | MD-LDF | HAS | type |
|-------|------|----|----|------|--------|-----|------|
| 60.2  | 61.6 | 62 | 62 | 64   | RW     |     |      |
| 64.4  | 64.9 |
| 65.7  | 69.9 | 76 | 74 | 78   |
| 74.5  | 77.3 |
| 88.2  | 83.6 |
| 119.7 | 121.7| 122| 120| 120  | O      |     |      |
| 131.7 | 132.1|    |    |      |
| 135.6 | 135.4| 135|    |      |
| 159.4 | 161.3| 152| 159| O    |
| 171.5 |
| 181.7 | 182.4|
| 187.9 | 185.7|
| 211.9 |
| 219.3 | 221.5|
| 224.8 | 227.6|
| 239.5 | 244.1|
| 257.1 | 260.2|
| 272.3 | 274.8|
| 282.9 | 285.7|
symmetry direction.

The resulting allocated displacement patterns are listed in Fig. 19. The 46 cm\(^{-1}\) peak \(S_1(J)\) is attributed to the \(J\)-point of a transverse acoustic mode. Its non-zero frequency is purely induced by its finite wave vector in row-to-row direction. The subsequent 62 cm\(^{-1}\) peak \(S_2(K)\) is assigned to a vibration of the first-layer atoms with components in both the surface normal and dimer bond directions, while the second-layer atoms move in the dimer row direction. The \(S_3(R)\) \(\vec{q}\) peak at 122 cm\(^{-1}\) represents a dimer rocking with \(\vec{q}\) vectors in the range between \(\vec{I}\) and \(\vec{R}\). The displacement pattern in the figure applies for the latter \(\vec{q}\) vector. Finally, the pattern of the \(S_4(K)\)-mode at 227 cm\(^{-1}\) consists of a dimer stretch and backbond twist.

According to Stigler et al. [172], the symmetry properties of these elongation patterns allow the observation of the transverse acoustic mode only in off-diagonal polarization configuration due to its shear-horizontal character, while the other modes should be observable in both polarization configurations. This agrees very well with the experimental results in Fig. 18.

**4.3.3. Phonon wavevector consideration**

The occurrence of surface vibration modes with \(\vec{q}_j\) wave vectors in the edge range of the BZ of the Ge(001) \((2 \times 1)\) reconstruction was traced back to the antiferromagnetic in-row order of the Ge dimer buckling and the dynamical flip-flop behavior of the Ge dimers. The AF buckling order together with the flip-flops implies on short time scale a doubling of the surface unit cell to \((2 \times 2)\), which implies a reduced BZ, in which the former zone-edge point \(\vec{J}\) is converted to the BZ center, and thus regularly accessible for Raman scattering. The relevance of the short-time \((2 \times 2)\) periodicity for SRS relies on the instantaneous character of the light scattering process. Furthermore, the row-to-row coherence of the buckled dimers is disturbed on short time scale by the flipping, which, according to STM results, occurs collectively in groups of about 30 in-row dimers [167]. This breaking of the translation symmetry allows also scattering from \(\vec{J}\) and \(\vec{R}\).

These considerations are supported by the Raman results for the well-ordered low-temperature static \((4 \times 2)\) reconstruction. Here, the enhanced surface unit cell leads to an additional reduction of the BZ size and, moreover, because of the higher order, a stronger confinement of the relevant \(\vec{q}\)-range to the BZ center is expected. Furthermore, the vibration eigenfrequencies themselves should be rather invariant, because they are essentially determined by the next-neighbor interactions, as shown by the results of the local-coupling transfer calculations by Stigler et al. [172].

Raman spectra at 40 K show quite sharp peaks at 68, 127, and 227 cm\(^{-1}\), which are very close to the 300 K values of the peaks \(S_2\) to \(S_4\), while peak \(S_1\) is missing [174]. These observations have been explained consistently by considering that the \(\vec{R}\)-point of the \((2 \times 1)\), which at 300 K was relevant for \(S_2\) to \(S_4\), is backfolded to the center of the \((4 \times 2)\) BZ. In contrast, the \(\vec{J}\)-point, which gave rise to \(S_1\), has no high-symmetry equivalent in the low-temperature phase.

Thus, by considering the interplay of Ge-dimer flip-flop dynamics, local disorder, and the instantaneous character of the light scattering process, a consistent interpretation was obtained of the results from the surface vibration modes of the disordered dynamical \((2 \times 1)\) as well as the ordered static \((4 \times 2)\) reconstruction of the Ge(001) surface.

---

**Fig. 18.** Raman spectra of Ge(001) at 300 K for \(A_1\) (upper panels) and for \(A_2\) (lower panels) symmetry at excitation energy 2.33 eV. The red spectra originate from oxidized Ge, the black ones from the p(2 \times 1)c(4 \times 2) reconstruction. In the lower part of each panel: intensity difference \(\Delta I\), representing the reconstruction-induced surface contribution: three surface phonon modes are detected for the parallel polarization configuration \(z(x)x(z)\), and four surface phonon modes for the configuration \(z(x)y(z)\) (from Ref. [174]). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Fig. 19.** Top view (left side) and side view (right side) of the displacement patterns, calculated in Ref. [173], for the surface phonon modes of Ge(001), which are observed as Raman peaks. The \(S_2(J)\) is a transverse acoustic mode, while the \(S_1(R)\), the \(S_4(R)\) dimer rocking mode, and the \(S_3(K)\) dimer-stretch and backbond-twist mode are optical modes (from Ref. [174]).
5. Two-dimensional adsorbate systems

The (111)-oriented semiconductor surfaces with their threefold symmetry are suitable templates for two-dimensional self-organized metal adsorbate arrangements. Depending on the metal element, the adsorbed atoms may be bonded individually to the substrate surface, as it is the case, e.g., for 1/3 ML of the group-IV elements Sn and Pb on Si(111) or Ge(111), or, e.g., as trimers for 1 ML of the noble metals Au and Ag.

Generally, in two-dimensional adsorbate systems, electron localization is strengthened due to the enhanced impact of electronic correlations by Coulomb repulsion, which may result in a Mott–Hubbard insulating ground state. Besides, for spin systems the magnetic order is strongly affected when atoms with antiferromagnetic coupling are arranged in a triangular two-dimensional lattice, as it applies for the (111)-oriented semiconductor surfaces. In this case, spin frustration occurs, which hampers long-range magnetic ordering. The interplay of the electron spin and electronic correlations results in competing ground states as, e.g., a spiral spin density wave antiferromagnet and a gapless quantum spin liquid [175,176]. In this context, the (√3 × √3) reconstruction two-dimensional electron system, generated by 1/3 ML of Sn adatoms on Si(111), acts as a model system [177–179], for which row-wise collinear antiferromagnetic alignment has been reported [180].

For several adsorbate materials various structural ordering patterns may be achieved by choice of the metal coverage and the subsequent annealing temperature. Detailed considerations of the atomic positions and stability criteria for the two-dimensional adsorbates have resulted in a variety of structure models, whose atomic positions are often closely related. In spite of this geometric similarity, characteristic differences in the vibration mode behavior may be expected due to the strong impact of the individual orbital bond strengths and orientations on the various eigenmode frequencies.

The first section of this chapter, Section 5.1 focuses on the (√3 × √3) reconstruction of Pb on a Si(111) substrate, which is known for its quite weak adsorbate-substrate interaction. Subsequently, Section 5.2 deals with the Sn-induced (√3 × √3) reconstruction on the Si(111) surface, and finally in Section 5.3 the closely related system Sn/Ge(111) is treated. For the latter a temperature-induced transition between the (√3 × √3) and the (3 × 3) reconstruction has been reported, in contrast to Sn/Si(111), that retains its (√3 × √3) reconstruction also at cryogenic temperatures.

5.1. Pb- (√3 × √3)/Si(111)

The Pb/Si(111) system has found great research interest over the last two decades, because of its atomically sharp interface due to the immiscibility of both elements [181]. A recent theoretical study has predicted that the Pb layer thickness also affects the phonon band structure and the electron-phonon coupling strength [182]. Two-dimensional quantum films [183] can be prepared, and also various two-dimensional and quasi-two-dimensional electron gases at the interface, which allow the tuning of the chemical potentials [184]. The electronic decoupling of the Pb from the Si substrate enables the formation of one-dimensional transport along two-dimensional ribbons whose lateral extension is determined by the terrace width [185]. This has resulted in studies of growth modes triggered by quantum well states [183], proximity effects of superconducting states of Pb islands [186], and Rashba-splitting due to spin-orbit coupling [187,188]. A further hint for the particular relevance of the electron-phonon coupling is the observation of superconductivity in the so-called striped incommensurate Pb ML phase, [189,190]. From the thickness dependence of the superconducting behavior, Pb–Si-interface phonons were considered to dominate the electron-phonon interaction [190].

In the monolayer coverage regime, a great variety of Pb superstructures occurs, from chain-like linear phases to hexagonal phases, which appear within the so called devil’s staircase regime between 1.20 and 1.33 ML [184,191–193]. These superstructures are based on two structural patterns: the (√3 × √3) unit cell and the (√3 × √3) unit cell, which correspond to coverages of 6/5 ML and 4/3 ML, respectively [184,191]. For quite some time, a large effort was spent to clarify the atomic structure of the unit cells [192,194–196]. For the (√3 × √3) reconstruction a detailed study of the vibration modes by Raman as well as first-principle calculations has been reported [197], that aimed at the question of whether the vibration modes allow the distinction between two proposed local structures: H3 and T4 (Fig. 20).

Both reconstructions comprise four Pb atoms per (√3 × √3) surface unit cell. As a common feature, three of them are located quite close to T1 positions on top of the first-layer Si atoms. The difference between the two models originates from the remaining fourth Pb atom, which may be located either above a hollow site (H3) or above a second layer Si atom (T4). Because of the calculated slight energy difference between both structures [less than 0.01 eV per (1 × 1) unit cell [193,198]], superstructures with different coexisting local structures may be formed, e.g. the striped incommensurate (SIC) phase, which is supposed to be composed of H3 and T4 domains [184].

5.1.1. First-principles calculations

In Ref. [197], DFT-based slab calculations were performed for both models H3 and T4 to derive the eigenfrequencies, displacement patterns, and the Raman response of the relevant surface localized eigenmodes, and subsequently compared with experimental Raman spectra. Thereby, slabs of 7 Si-bilayers were used to model the system. The calculations were performed in the generalized gradient approximation (GGA) [199] within the projector augmented-wave
method (PAW) [200], as implemented in the software package VASP [201]. The Si and Pb pseudopotentials which were employed include 3s3p and 5d6s6p electrons as valence electrons, and the wavefunctions were expanded in a plane-wave basis set up to an energy cutoff of 400 eV. The spin degree of freedom was not considered, and also the effect of spin-orbit coupling at the Pb atoms was disregarded.

The vibration frequencies and eigenvectors at the H3 structure were obtained by employing density functional theory [139]. The Raman features were calculated via the electronic polarizability tensor after the determination of the dielectric response. It was noted that this theoretical approach to calculate Raman lines delivers a limited accuracy with respect to the intensities of experimental lines due to the neglect of electronic resonance effects [30,202].

The calculation results gave access to the correlation between the eigenfrequencies and eigenvectors, and besides allowed the classification of the vibration modes. As a general trend, the modes involving essentially displacements of the heavy Pb atoms appear at considerably lower frequencies than those which are based on displacements of the much lighter Si atoms. Furthermore, a classification of the modes in four groups can be performed according to the following scheme:

(i) in-plane sliding vibrations of the Pb adlayer as a whole with frequencies below 15 cm⁻¹;
(ii) out-of-plane vibrations with perpendicular displacements of the Pb adatoms in the range 15 − 45 cm⁻¹;
(iii) in-plane modes with combined displacements of both Si and Pb atoms in the range 45 − 95 cm⁻¹;
(iv) Si substrate related vibrations at higher frequencies, i.e. above 95 cm⁻¹.

5.1.2. Calculated and experimental Raman spectra

The calculated Raman spectra are shown in Fig. 21, together with experimental surface Raman intensities for the symmetries A' and A". Obviously, the calculated eigenmodes of the H3- and T4 structural models are quite similar. This finding is plausible in view of the rather weak coupling between the Pb layer atoms and the Si substrate, which results in rather decoupled vibrations of the Pb layer and a minor relevance of the exact Pb atom positions with respect to the substrate atoms. The low-frequency in-plane sliding modes in region (i) are not considered, because they are not experimentally accessible. In region (ii), calculated out-of-plane Pb vibration modes appear for T4 (H3) at 21.5 cm⁻¹ (22.1 cm⁻¹) and 37.9 cm⁻¹ (37.3 cm⁻¹). They agree very well with the experimental values of 18.2/19.6 cm⁻¹ and 32.8/33.2 cm⁻¹ for A' and A" respectively. Good agreement is also obtained for the combined Pb/Si displacement modes in region (iii). Here, calculated surface modes at 49.6 and 60.3 cm⁻¹ for T4 and 49.8 and 60.5 cm⁻¹ for H3 closely match A'/A" Raman lines at 45.1/45.5 cm⁻¹ and 64.0/65.4 cm⁻¹. Finally, the calculations yield surface modes at 81.5 and 92.8 cm⁻¹ for T4 and at 81.6 and 92.2 cm⁻¹ for H3. In this spectral range a very broad band appears in the experimental Raman spectra which indicates surface modes but does not allow for a particular mode assignment. The Si-dominated modes beyond 95 cm⁻¹ are not considered in detail, because their enhanced depth range does not allow a reliable description by the applied slab modelling.

In summary, the calculated surface modes for the H3- and T4 structure of the (√3 × √3) reconstructions of Pb/Si(111) allow a very detailed assignment of the experimentally observed surface Raman modes. Furthermore, they reveal that the vibration dynamics does not allow the distinction between both structures. Instead, they confirm the decoupled character of the Pb-dominated vibration eigenmodes as a result of the weak bonding of the adsorbate to the substrate.

5.2. Sn-(√3 × √3)/Si(111)

Upon adsorption of isoelectronic Sn atoms on the Si(111)-(7 × 7) surface, after annealing to ≈970 K a two-dimensional self-organized structure is formed with a Sn coverage of 1/3 ML. From STM, a (√3 × √3) reconstruction has been reported, which not only applies for RT, but also was shown to persist at low temperatures down to 6 K [203]. The two-dimensional self-ordered Sn arrangement consists of single Sn atoms on T4 positions [204], in contrast to the Au triangles of the Au-(√3 × √3)/Si(111) surface reconstruction with a 1-ML Au coverage (see Section 6.1). As for the electronic properties, a Mott transition from metallic behavior to an insulating ground state was observed below 60 K [177,178]. Furthermore, in a combined theoretical and experimental study a row-wise antiferromagnetic spin alignment of the Sn atoms in the triangular lattice of Sn-(√3 × √3)/Si(111) was reported [180]. Detailed studies of the exact positions of the adsorbed Sn atoms have resulted in new insights and revealed quite interesting aspects considering the size of the superstructure unit cell. While a prerequisite for the (√3 × √3) reconstruction is the equivalence of all Sn atoms, structural analysis by X-ray standing wave experiments has shown that the adsorbed Sn atoms are not located on equal heights: every third Sn atom along the [11̄2] direction shows a slight protrusion (“up” position), which consequently implies an enlarged (√3 × √3) surface unit cell that also comprises two Sn atoms in “down” positions (one up, two down: 1U2D) [204]. The vertical position difference between the upper Sn atom and the two lower ones is in the range of Δh = 0.26 Å [204]. The seemingly contradicting appearance of a (√3 × √3) superstructure in conventional scanning tunneling microscopy (STM) and LEED is explained by a fluctuating periodic...
vertical position exchange between the “up” atom and the “down” atoms, which makes them appear equivalent for time-averaging experiments. From time-resolved STM at about 200 K a ms time scale was reported for the fluctuations [205]. The Sn-atom fluctuations have been modeled in detail within the dynamical fluctuation (DF) model [204–207]. In literature, the assigned fluctuation mode has been denoted as DF mode. In contrast to various other self-organized adsorbate systems, for Sn/Si(111) no experimental data from HAS on vibration modes are available. Recently, a Raman study of the surface vibrations at different temperatures has been published [159], which will be discussed in the next sections.

5.2.1. Surface Raman spectra of Sn-(√3×√3)/Si(111)

The surface Raman spectra of Sn/Si(111) for RT and T ≈ 40 K are shown for both polarization configurations z(∥xx∥)z (red) and z(∥xy∥)z (green) at excitation energy 2.54 eV. Vibrational modes with frequencies below 130 cm⁻¹ are shown and discussed in more detail below. (from Ref. [159]) (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3

| Symmetry and eigenfrequencies (in cm⁻¹) of the surface vibration eigenmodes of Sn-(√3×√3)/Si(111) above ≈ 130 cm⁻¹, measured by Surface Raman Spectroscopy in z(∥xx∥) polarization configuration at RT and LT ≈ 40 K, and the corresponding results of ab initio calculations within DFT-LDA (from Ref. [159]). |
|---|---|---|---|---|
| Sym. | RT | LT | Sym. | LDA |
| A | 164.6 | 169.4 | A | 146.1 |
| E | 183.4 | 185.5 | E | 174.9 |
| E | 227.8 | 230.3 | A | 219.3 |
| A | 308.6 | 309.8 | A | 322.7 |
| A | A | A | A | 311.2 |
| A | 329.5 | 331.9 | A | 329.5 |
| E | 350.0 | 350.4 | E | 347.3 |
| A | 356.7 | 358.2 | A | 352.7 |
| A | 383.0 | 385.5 | A | 380.9 |
| A | 413.7 | 416.5 | A | 421.3 |
| E | 447.1 | 450.5 | E | 437.0 |
| E | 482.9 | 487.5 | E | 474.9 |
| A | A | A | A | 505.0 |

Fig. 22. Surface Raman spectra of the Sn/Si(111) surface at RT and LT ≈ 40 K for both polarization configurations z(∥xx∥)z (red) and z(∥xy∥)z (green) at excitation energy 2.54 eV. Vibrational modes with frequencies below 130 cm⁻¹ are shown and discussed in more detail below. (from Ref. [159]).

5.2.2. Calculated structure and vibration modes

As a base for the determination of the surface vibration modes of the Sn-(√3×√3)/Si(111) system, its atomic structure has been modeled by DFT-LDA and DFT-GGA calculations [159]. This calculation has confirmed the above-mentioned T₃₃ positions of the Sn atoms and predicts a length of approximately 2.7–2.8 Å for the bond to the closest substrate atoms. Comparative calculations for Sn-(√3×√3)/Ge(111) give the same result. The electronic charge density distribution of this bond is shown in Fig. 23 for both systems, and indicates a rather covalent bond character. The stability of this configuration is underscored by the calculation outcome that the (√3×√3) reconstruction is established even if a priori a larger (3 × 3) periodicity with non-equivalent Sn atoms is allowed.

Based on this structure, the surface vibration mode symmetry, their elongation patterns, and the corresponding eigenfrequencies have been determined by frozen phonon calculations. The results in the spectral range between 130 cm⁻¹ and about 500 cm⁻¹ are listed in Table 3 together with the experimental Raman results from Fig. 22. An excellent agreement between experiment and theory was achieved. The calculated eigenmodes represent all the experimentally observed Raman peaks and the calculated eigenfrequencies match the measured values with an average deviation of only 7.2 cm⁻¹ (low-temperature values).

Exemplarily, the elongation patterns of two selected surface vibration eigenmodes with prominent Raman peaks are plotted in Fig. 24. The experimental peak at 185.5 cm⁻¹ (low-temperature value) is attributed to a tilting vibration of the Si trimer, bound to
the Sn atom, as shown in Fig. 24(a) with a calculated frequency of 174.9 cm$^{-1}$. Fig. 24(b) schematically shows the pattern of a symmetric breathing movement of the Si trimer below the Sn atom along the Sn–Si bond direction. Its calculated vibration frequency is 329.5 cm$^{-1}$ and it is attributed to the Raman peak at 331.9 cm$^{-1}$. The Raman peak which appears for both polarization configurations at 230.3 cm$^{-1}$ is explained in terms of an E-symmetry mode with a calculated eigenfrequency of 219.3 cm$^{-1}$. Its displacement pattern is rather complex. One of the three Si atoms bound to Sn moves towards the Sn atom in the bond direction, causing in turn the distortion of the neighboring Si trimer. More details can be found in Ref. [159]. Overall, the data in Table 3 confirm an excellent agreement at 230.3 cm$^{-1}$.

The vibrational eigenmodes of Sn/Ge(111) will be analyzed in detail below. As for Sn/Si(111), several structural phase transitions were reported at temperatures $T \approx 40$ K [206,215,222,223]. Within the DF model, the transition is proposed to be mediated by a soft phonon mode [206], i.e., a freezing of the DF vibration mode elongation pattern. To reveal beside the DF mode also the other surface vibration eigenmodes of Sn/Ge(111) in detail, MD-DFT calculations were performed, partly in combination with HAS experiments [206,216,224]. In the following sections the vibration dynamics of Sn/Ge(111) and the impact of the SPT are discussed on the basis of a recent combined study by SRS together with ab initio calculations [159].

5.3.1. Surface Raman spectra of Sn/Ge(111)

In contrast to time-averaging experimental methods, like conventional LEED and STM, the Raman process gives a snapshot-like analysis of the vibrational dynamics of the surface [17]. Therefore, it may be expected that the Raman spectra of the $(\sqrt{3} \times \sqrt{3})$ reconstruction above $T_{\text{SPT}}$ and the $(3 \times 3)$ periodicity below the phase transition have a high similarity. An analogous situation has been reported for the electronic structure of both Sn/Ge(111) reconstructions measured by photoelectron spectroscopy [224].

The expectation is confirmed by the comparison of the Sn/Ge(111) surface Raman spectra, which are shown in Fig. 25 at RT (both polarization configurations) and at $T \approx 40$ K for Sn/Ge(111). Obviously, the $(2 \times 8)$-reconstruction-induced Ge(111) surface vibration peaks from Fig. 17 are replaced by novel ones due to the adsorbate-induced reconstruction. A prominent and narrow peak is observed in both polarization configurations, located at 104.9 cm$^{-1}$ for $T \approx 40$ K. On the low-frequency side as well as on the high-frequency side of this peak groups of three peaks occur: low-frequency side: 82.3, 89.7, and 96.8 cm$^{-1}$; high-frequency side: 113.5, 121.4, and 135.2 cm$^{-1}$.

Moreover, above the bulk 2 TA(X) phonon frequency (163 cm$^{-1}$) three double groups of peaks appear at 188.8, 194.7, 220.1, 224.2, 241.8, and 246.6 cm$^{-1}$. Finally, similar to the clean Ge(111)-(c(2 × 8) surface, additional peaks are located on the low-frequency ramp of the bulk LTO Ge phonon (256.8, 276.5, and 285.4 cm$^{-1}$). They probably have the same origin of the corresponding signatures of the clean surface. A comparison of the RT and 40 K spectra reveals a very close similarity, with only the expected slight anharmonicity-induced shifts of the peak frequency and T-dependent peak widths. Thus, here no impact of the reported temperature-induced SPT is observed. This is not surprising, because this transition just implies a freeze of the DF mode without a reordering of the atomic positions. Therefore the surface vibration dynamics should essentially remain unaffected.

5.3.2. Calculated structure and vibration modes

The DFT calculations of the structure and vibration modes of Sn/Ge(111) in Ref. [159] have been performed along the same scheme as for Sn/Si(111). Qualitatively, for Sn-$(\sqrt{3} \times \sqrt{3})$/Ge(111) the same result was obtained as for Sn-$(\sqrt{3} \times \sqrt{3})$/Si(111), with the Sn atoms on the $T_4$ positions. The resulting bond charge density contours for both material systems are compared in Fig. 23. In both cases a covalent bonding with some charge accumulation between Sn and the topmost atoms of the substrate was obtained. Table 4 shows the calculated bond lengths, derived from DFT-LDA as well as from DFT-GGA. Each method predicts for both systems bond lengths of ca. 2.7–2.8 Å, with the expected tendency of LDA to underestimate the bond distance. The resulting distances slightly exceed the sum of the atoms covalent radii, which amounts to 2.52 Å for Sn–Si and 2.63 Å for Sn–Ge [225]. Bond distances and charge distributions suggest that the covalent Sn–Si or Sn–Ge bond is somewhat weaker than...
the homatomic Si–Si or Ge–Ge bond in the bulk materials. Interestingly, the structural optimization calculations yield for the Sn atoms on Ge(111) different heights if a $3 \times 3$ periodicity is allowed, thus confirming this enlarged surface unit mesh, while for Sn/Si(111) also for these conditions a ($\sqrt{3} \times \sqrt{3}$) reconstruction results. This trend is in line with the abovementioned observation of different phases for both systems at low temperature. The height difference of the Sn atoms for Sn–Si(Ge)(111)–($\sqrt{3} \times \sqrt{3}$) is estimated in about 0.3 Å both in DFT-LDA and DFT-GGA.

The resulting symmetries and eigenfrequencies of the calculated vibration modes are listed in Table 5 together with the experimental values from Fig. 25. Because of the higher atomic mass of Ge with respect to Si, there is a general trend to lower eigenfrequencies. This effect is further supported by the somewhat weaker bonds in the Sn/Ge(111) system (see Fig. 23). Exemplarily, the prominent Raman peak measured at 105.0 cm$^{-1}$ (LT) corresponds to the Sn/Si(111) peak measured at 183.4 cm$^{-1}$. It originates from the Ge trimer tilt mode (cf. Fig. 24(a)) and its frequency is calculated for Sn/Ge(111) at 97.0 cm$^{-1}$. Furthermore, a one-to-one correspondence between the surface vibration spectra of Sn/Si(111) and Sn/Ge(111) may be hampered by a different degree of surface localization of some displacement patterns, which may be the reason for the observation of an enhanced number of surface vibration peaks for Sn/Ge(111). The peaks below 100 cm$^{-1}$ all correspond to distinct vertical displacements of the Ge dimers at the $T_4$ positions, in phase or antiphase and with and without participation of the Sn atom. Overall, all peaks which were observed in SRS could be assigned to calculated eigenmodes and a very good agreement between the experimental and calculated frequencies occurred with a mean deviation of 5.3 and 5.8 cm$^{-1}$ at RT and T $\approx$ 40 K, respectively. The disagreement between the calculated and the experimentally observed symmetry of some modes has been ascribed to spurious polarization components in the SRS experiment.

Similar to the Sn/Si(111) spectra above 130 cm$^{-1}$, also for the Sn/Ge(111) spectra above 80 cm$^{-1}$ the only differences between RT and 40 K are slight peak shifts and different peak widths. Thus, the SPT of Sn/Ge(111) between the ($\sqrt{3} \times \sqrt{3}$) reconstruction and the $3 \times 3$ one has no impact for the surface vibration dynamics in this spectral range. The vibrational signatures of the phase transition in the low-frequency region will be the subject of the next section.
5.3.3. Temperature-induced structural phase transition

After the previous observation that the cooling-induced freeze-out of the Sn atom fluctuations of Sn/Ge(111), i.e., the SPT from the ($\sqrt{3} \times \sqrt{3}$) reconstruction to (3 × 3), does not noticeably influence the surface vibration modes above 80 cm$^{-1}$, in this section the possible impact on the low-frequency modes is analyzed. The temperature-dependent low-frequency Raman spectra of Sn/Ge(111) below 80 cm$^{-1}$ are compared with the corresponding ones of Sn/Si(111), where the ($\sqrt{3} \times \sqrt{3}$) reconstruction persists at low temperatures. Furthermore, for both material systems these experimental results are compared with ab initio calculations.

The low-frequency Raman spectra for Sn/Ge(111) at RT and 40 K in both polarization configurations are shown in Fig. 26. Their main peak occurs at 55.6 cm$^{-1}$ for RT and is only slightly shifted to 55.8 cm$^{-1}$ for 40 K. In literature, this eigenfrequency was also reported from HAS experiments and has been assigned to the DF mode, in which the displacement vectors of all Sn atoms are pointing vertically in phase, and which has only small admixtures of other modes [216,226].

However, in the Raman spectra this peak occurs with equal strength for $z(xx)z$ and $z(xy)z$ polarization, indicating E symmetry, in contrast with the A symmetry of the vertical Sn displacements in the DF mode. Moreover, the ab initio calculations predict a closely matching E-type surface vibration eigenmode at 55.3 cm$^{-1}$, representing a lateral displacement of the Sn atom, with corresponding tilting of the subjacent Ge trimer, as illustrated in Fig. 27.

The frequency of the DF mode has been predicted to reduce with decreasing temperature for Sn/Ge(111) at the $K$ point of the surface BZ, and vanish with the SPT [206]. In principle this softening cannot be observed in SRS, which only covers the center of the BZ. However, the temperature-dependent Raman spectra in Fig. 26 directly reveal a distinct signature of the phase transition. Upon cooling below T$_{SPT}$ a shoulder appears at the low-frequency edge of the main peak, centered at 49.6 cm$^{-1}$. It has been interpreted as a backfolding of a RW from the $K$ point of the BZ, whose frequency at this zone edge was determined to $\approx50$ cm$^{-1}$ by HAS [227]. This transformation of the $K$ point to the new $\Gamma$ point is a direct consequence of the transition from the ($\sqrt{3} \times \sqrt{3}$) to the (3 × 3) reconstruction. Therefore, a quantitative analysis of the backfolded RW may yield further information about this SPT.

The inset of Fig. 26 shows the intensity development of the backfolded-RW peak versus temperature in the range below 225 K, which corresponds to T$_{SPT}$ [210,211]. A strong increase of the RW intensity is observed with decreasing temperature, while it vanishes near T$_{SPT}$. This development is interpreted in terms of random fluctuations of all Sn atoms on a short time scale above T$_{SPT}$, followed by the start of a freeze-out upon cooling to T$_{SPT}$, initially in small patches without coherence. Further cooling results in larger (3 × 3) reconstructed patches. The increased coherence length leads to the increase of the Raman intensity of the backfolded RW. This behavior indicates a phase transition of the order-disorder type, in agreement with literature [211,216,228], even though a transition of the displaceable type is common for systems with soft phonons.

For comparison, the low-frequency Raman spectra for Sn/Si(111) are shown for both polarization configurations in Fig. 28. The peak at 88.3 cm$^{-1}$ corresponds to the main peak of Sn/Ge(111) in Fig. 27 (calculated frequency for Sn/Si(111): 83.5 cm$^{-1}$). In contrast to Sn/Ge(111), no indication of new features occurs upon cooling. Furthermore, the main peak is shifted with temperature by 2.4 cm$^{-1}$, in contrast to the case of Sn/Ge(111). This clear distinction is a possible hint to their different LT behavior, and could be a starting point to evaluate the phase transition regarding the absence of anharmonic terms for Sn/Ge(111) to electronic correlations. Apart from the main peak, an additional structure appears at 118.0 cm$^{-1}$ (arrow in Fig. 28) in parallel polarization configuration and decreasing at LT. It may originate from a second-order process involving the $K$ and $M$ points of the surface BZ, which have an elevated density of states because of the flat phonon dispersion [206]. The weak feature just below 60 cm$^{-1}$ at LT was attributed to a calculated mode at 58.7 cm$^{-1}$, whose eigenvector is a vertical breathing mode of the whole surface.

In summary, all observed SRS peaks of Sn/Ge(111) as well as Sn/Si(111) have been assigned to vibration eigenmodes from first principles calculations, and a very close frequency match was achieved. Moreover, the comparison of both material systems has confirmed that the SPT between the ($\sqrt{3} \times \sqrt{3}$) and the (3 × 3) reconstruction of Sn/Ge(111) at T$_{SPT}$ $\approx225$ K is characterized in the Raman spectrum by the backfolded RW peak below T$_{SPT}$, and the temperature dependent development of the RW peak intensity indicates an order-disorder phase transition.

6. Tuning from two-dimensional to quasi-one-dimensional adsorbate systems

A prominent objective within the playground of adsorbate/semiconductor material systems is the controlled dimensional tuning from two-dimensional structures to the one-dimensional case of self-assembled atomic chains. This aim can be achieved by the appropriate choice of deposition parameters, such as coverage, temperature, and especially the orientation of vicinal substrate surfaces, e.g., Si(553). At the end of this range of dimensional tuning,
the one-dimensional systems give rise to a substantial enhancement of the electron-electron and electron-phonon interactions because of the strongly reduced screening efficiency. This can induce complex quantum phenomena, such as conductance quantization, spin chains, electronic correlation-induced spin-charge separation excitations, as well as charge and spin density waves [229,230]. Furthermore, triplet superconductivity and Tomonaga-Luttinger liquid behavior have been reported [231–233].

Detailed structural examinations of such chains have revealed that they generally cannot be considered as straight rows of single metal atoms, but rather contain, e.g., dimerized double chains, zigzag chains, honeycomb chains or combinations of these elements in parallel. Therefore it seems plausible that for many of these material systems the exact atomic structure is still disputed, and the study of eigenvibration modes may contribute to clarify this question by comparing experimental results with those of calculations for different structural arrangements.

A viable material system for dimensional tuning is Au on Si. This chapter starts with the two-dimensional Au-(√3 × √3)/Si(111) reconstruction in Section 6.1, followed by Au chains on terraced vicinal Si(hnk) (Section 6.2), where the choice of the vicinal surface orientation ((553), (557), or (775)) allows the tuning of the (111)-terrace widths, and consequently the variation of the detailed face orientation ((553), (557), or (775)) allows the tuning of the one-dimensional systems the exact atomic structure is still disputed, and the study of eigenvibration modes may contribute to clarify this question by comparing experimental results with those of calculations for different structural arrangements.

The surface space group of the CHCT structure is p31m (corresponding to the three-dimensional point group C3v) [243], while p3 (corresponding to C3v) applies for the TT model. Both groups show an equivalent behavior regarding RS. They feature Raman-active modes of A1 and E symmetry [244]. As outlined in Section 2.5, the observation of the A1 modes is allowed only in parallel polarization configuration (z(XX)/z(YY)), while the E modes may be observed also in orthogonal polarization configurations, e.g., z(xy) [27].

6.1. Au-(√3 × √3)/Si(111)

Upon deposition of Au atoms in the monolayer range on the Si(111) surface, various reconstructions or a mixture of these may result, depending on the temperature treatment and coverage θAu [234]. The different reconstructions are induced by the appropriate choice of the annealing temperature Tann after Au deposition, and remain stable during the subsequent cooling to room temperature. A two-dimensional Au pattern on a Si(111) surface can be prepared for coverages θAu ≈ 1 ML and beyond, by annealing to Tann = 900 K. A (√3 × √3)R30° superstructure results, which is rotated in-plane by 30° with respect to the bulk unit cell. Therefore, this reconstruction is also referred to as Au-(√3 × √3)R30°/Si(111).

Extensive experimental and theoretical studies of the structural and electronic properties of the Au-(√3 × √3)/Si(111) surface have been reported, e.g., in Refs. [235–241]. A metallic behavior was detected due to a half-filled surface band [242].

The most widely accepted structural base unit of the Au-(√3 × √3)/Si(111) reconstruction comprises one Au trimer per surface unit cell, which corresponds to a coverage of 1 ML Au. For the detailed atomic structure various models have been proposed, some of them with only very slight differences. Among the most relevant ones are the twisted-trimer (TT) model and the conjugate honeycomb-chained (CHCT) model, which are compared in Fig. 29.

Twisted-trimer (TT) model (Fig. 29(a)) was proposed by Chester et al. [235,236] after medium-energy ion scattering and Monte Carlo simulations. The conjugate honeycomb-chained-trimer (CHCT) model, presented in Fig. 29(b) originates from DFT calculations within the local density approximation by Ding et al. [237]. Further candidates are the honeycomb-chained-trimer (HCT) model by Zhang et al. [238], which was proposed after angle-resolved photoelectron measurements, and the H3-missing-top-layer (H3-MTL) model by Kadohira et al. [239] as a result of first-principles calculations within the local density approximation.

The first three models (TT, CHCT, and HCT), which feature a coverage of 1.0 ML of Au, are all characterized by a trimer of Au atoms close to the H3 position. Furthermore, the Si atoms of the topmost layer are also arranged as trimers. The three models only slightly differ in size of the Au and Si trimers and their relative orientation, which furthermore determines the surface symmetry. The mirror symmetry plane of the CHCT and HCT models is absent for the TT model. In all proposed models, the Au atoms form a flat layer atop the Si surface and show no corrugation. A direct comparison of the thermodynamical stability of the one-ML structures by DFT-LDA and DFT-GGA calculations revealed the CHCT model as the most stable one, followed by the TT model, while the HCT model turned out to be unstable [208]. Therefore, the following considerations will focus on the CHCT and TT models.

The surface space group of the CHCT structure is p31m (corresponding to the three-dimensional point group C3v) [243], while p3 (corresponding to C3v) applies for the TT model. Both groups show an equivalent behavior regarding RS. They feature Raman-active modes of A1 and E symmetry [244]. As outlined in Section 2.5, the observation of the A1 modes is allowed only in parallel polarization configuration (z(XX)/z(YY)), while the E modes may be observed also in orthogonal polarization configurations, e.g., z(xy) [27].

6.1.1. Surface Raman spectra of Au-(√3 × √3)/Si(111)

Because of the high mass of the Au atoms (mass number A = 197), the Au-derived vibration modes are expected at rather low frequencies. Actually, besides two Raman features around 220 cm−1 and two around 400 cm−1, a series of peaks is observed between 50 and 200 cm−1 [208]. The polarization-dependent surface-vibration intensity in this frequency range at T = 20 K is shown in Fig. 30. The spectra result from the usual procedure as the Raman-intensity difference between the freshly prepared surface and the aged one. The parameters of the individual peaks were obtained from fits with Voigt profiles. Note especially the sharp peak at 75 cm−1 and the strong one at 183 cm−1. Interestingly, the latter was not observed at RT. Furthermore, almost all peaks occur for both polarization configurations, indicating their E-symmetry character.

6.1.2. First-principles calculations of Au-(√3 × √3)/Si(111)

The eigenfrequencies, symmetry characters, and elongation patterns of the surface-vibration eigenmodes of the 2D reconstruction Au-(√3 × √3)/Si(111) were calculated as described in detail in Chapter 3 within the DFT, as implemented in the VASP package [201,245]. For the Au-Si(111) system, they encompass (i) a total...
energy determination of periodic Au-covered Si(111) slabs (6 bilayers) within LDA and GGA, and (ii) a two-stage vibration-mode analysis. This analysis first determines the vibration frequencies and eigenvectors according to the frozen-phonon method, and subsequently the differential Raman scattering efficiency through the vibration-induced modulation of the dielectric susceptibility $\chi(\omega)$, yielding the Raman-susceptibility tensor. The DFT-inherent underestimation of the electronic band gap was accounted for by the choice of the excitation wavelength.

The underlying structural models were TT and CHCT, which were preselected for reason of their thermodynamical stability. A large number of surface-localized modes was obtained, and subsequently for those with strong surface localization the Raman scattering efficiency was derived for the relevant laser frequency. The resulting calculated Raman spectra for $z(\text{xx})z$ polarization ($A'$-modes) for both atomic structure models are shown in Fig. 31. Comparison with the experimental result in Fig. 30(a) shows large deviations for the spectrum calculated for the TT model. On the contrary, the spectrum calculated for the CHCT model is in satisfactory agreement, especially when considering the approximations in the theoretical approach. Therefore, the CHCT-based results are employed for the interpretation of the experimental data.

Because of the strong similarity between the CHCT and TT structural model, the frozen-phonon calculations for both models show roughly corresponding eigenvectors, as the structural elements such as Au and Si trimers are common to the two models. In contrast, the eigenfrequencies are clearly model-dependent, because the specific orientations of the Au and Si trimers result in bonds of different strength at the two surfaces. An illustrative example is, e.g., a symmetric expansion (breathing mode) of the Au trimers. As shown in Fig. 32, within the CHCT model the Au movement is limited by the presence of Si atoms, which are located exactly in the direction of the Au displacement. Within the TT model instead, this is not the case due to the rotation of the Si trimers, and this expansion is not constrained by the presence of other atoms anymore. Therefore, the frequency of this mode is calculated to be 127 cm$^{-1}$ within the CHCT model, and only about 85 cm$^{-1}$ in the TT structure. Further exemplary eigenvibrations are an in-plane translation of the Au trimers with an additional substrate contribution and a rotation mode of the Au trimers, whose calculated frequencies within the CHCT model are 55 and 45 cm$^{-1}$, respectively. They are correlated to experimental peaks at 66 and 54 cm$^{-1}$.

Besides these Au-induced vibrations in the low-frequency region, the CHCT-based calculations also yield Si-atom vibration modes at 400 and 417 cm$^{-1}$, which correspond to experimentally observed peaks at 401 and 419 cm$^{-1}$, respectively.

Altogether, for the CHCT model by far the best agreement with the experimental results is obtained, and an assignment of the spectral features is achieved. Remaining discrepancies may be due to approximations in the calculations and/or non-ideal surface conditions, such as domain borders.

6.2. Au chains on Si(hhk)

Vicinal Si(hhk) substrates with appropriately chosen angular mis-cut with respect to the (111) orientation (e.g., distinct values in the
The adsorption of Au monolayers on these stepped Si substrates leads to the formation of highly ordered atomic wire arrays by self-assembly [1]. Their structural and consequently also their electronic properties can be controlled by changing the vicinal angle (thus the terrace width and step morphology) [1], as well as through doping by Au [2]. Along with the Au chains a so-called Si honeycomb structure can be formed which exhibits new properties based on the redistribution of surface charge between the step edge and the Au chain [3]. These systems offer a prototype for studying quantum phenomena in quasi-one-dimensional systems, such as long-range spin order [4], two-dimensional spin interactions [246], metal-insulator transitions [247], Rashba splitting [248], and spin chain dimerization [249]. The variability offered by chains formed on different high-index Si surfaces allows the investigation of the interplay between charge, spin and lattice in a family of related surfaces [250].

6.2.1. Au chains on Si(553)

The Si(553) surface can be described as equally spaced (111) terraces, separated by single atomic steps with a height of 3.14 Å and a step-to-step distance of 14.8 Å. Au deposition with a coverage of 0.48 ML leads to the formation of double chains on the terraces, as reported by Ghose et al. [251]. In the structural model of Krawiec [252], the Au double chain exhibits a dimerization, which induces a doubling of the unit cell along the chain direction. The currently accepted structural DFT-calculated model of Au/Si(553) from Braun et al. [253] consists of an atomic geometry similar to the Krawiec model [252], but introduces a strong buckling of the Si step edge where every third Si step edge atom is displaced by 0.8 Å in the way depicted in Fig. 33. In contrast to the model of Erwin [254], which introduces the buckling of the step edge by considering the electronic spin of Si atoms, the rehybridized structure in Braun et al. [253] is diamagnetic. The rehybridized model is energetically favorable with respect to the models from Krawiec and Erwin.

The formation of this rehybridized structure is accompanied by a surface charge transfer of about 1.6 electrons per (1 × 6) unit cell from the step edge to the Au chains, in contrast to the charge transfer of one electron per unit cell deduced by Hogan et al. [253]. By the additional charge at the Au chains its dimerization is enhanced from 5% to 14%. Indeed, the relationship between the magnitude of the Au dimerization and the filling of the Au bands has been pointed out by different authors [255,256]. A reversible structural phase transition in Au/Si(553) can be induced by electron doping with a STM tip [257,258] or by cooling down to 40 K [259].

Raman spectra of the diatomic-Au chain decorated Si(553) surface (see Fig. 34(a)) reveal a rich structure as expected from a surface with such a complex geometry. The vibrational modes can be classified according to their frequency range as marked in the upper panel of Fig. 34(a). The spectral range up to 100 cm⁻¹ contains mainly Au-dominated low-frequency vibration modes due to higher mass of Au atoms. At higher frequencies, vibration modes should involve the rather light Si atoms. The broad feature around 150 cm⁻¹ is considered an activation of acoustic modes of the Si substrate and resembles roughly the 2 TA band at 300 cm⁻¹ (not shown here) at half frequency. A detailed assignment of measured vibrational modes by comparison with DFT-based calculations of frequencies and vibrational patterns can be found in Ref. [260]. A few selected modes, relevant for further discussion, are presented in Fig. 34 in panels (b) and (c). More specifically, as indicated by the calculated phonon dispersion patterns, the two phonon modes at 392 and 414 cm⁻¹ are assigned vibrations of the Si step edge (Fig. 34(c)), while modes at 60 and 87 cm⁻¹ (Fig. 34(b)) are associated to vibrations within the Au chain.

The comparison of the room- and low-temperature spectra reveals distinct changes in the appearance of the vibrational modes in Fig. 34. Besides some less pronounced changes, one of the step-edge-related modes (414 cm⁻¹) disappears at low temperature. Additionally, a new mode appears at 87 cm⁻¹, while the 60 cm⁻¹ mode remains unaffected. It seems appropriate that for the interpretation of this behavior we have to consider not only static but also dynamic aspects of the temperature-induced structural changes. Since the buckling in the step edge is linked with a charge transfer and dimerization of the Au diatomic chains [255], the thermally excited fluctuation of the step edge atoms, known in Au-stabilized vicinal Si(111) surfaces [205], could be a key element for the interpretation. Step edge fluctuations have a strong influence on the electronic band structure via buckling in the step edge geometry, similar to the charge injection discussed in Refs. [255,256]. Hence, the temperature-induced fluctuation seems to influence not only the step-edge-related modes in the spectral range around 400 cm⁻¹, but also the low-frequency Au-chain-associated vibrations by the change in the chain dimerization. The latter is strongly connected to the charge transfer from the step edge to the Au chains.

It seems plausible that an intended and controllable modification of the charge distribution in the surface is required for a detailed investigation of the phase transition. For the Au/Si(553) system, it has been shown that selective hydrogen adsorption at the step edge changes the electronic charge distribution and can be used to tune the system between metallic and insulating phases [255]. Moreover, the low atomic mass of hydrogen does not introduce dramatic structural changes in the atomic geometry, having only a low impact on vibrational frequencies and hence conserves the comparability of the vibrational spectra of hydrogenized and clean surfaces. The step-edge hydrogenation is accompanied by the introduction of additional charge into the surface, opening a new possibility to manipulate the phase transition for a detailed investigation of its underlying mechanism. At RT, the Raman spectrum of the step-edge H-passivated Au/Si(553) surface appears very similar to the spectrum of the clean surface, as shown in Fig. 35. This occurs because selective hydrogen adsorption at the step edge changes the electronic charge distribution within the surface rather than inducing structural changes.

The sharp phonon mode at 87 cm⁻¹, visible in the low-temperature spectrum of the clean surface in Fig. 35, is shifted or not visible at all in the other spectra. This supports the idea that
of the vibrational modes, while the characteristic modes are marked by vertical lines. Spectral ranges are marked in the spectra by double arrows according to the origin of the vibrational modes, while the characteristic modes are marked by vertical lines (from Ref. [261]).

this mode is directly associated to the dimerization of Au chains. The dimerization is affected by hydrogen and by thermally induced step edge fluctuations, explaining the vanishing of the associated phonon at 87 cm\(^{-1}\) in the other spectra. In contrast, the spectrum from the cooled hydrogenated surface shows a third mode in the high-wavenumber region, at 378 cm\(^{-1}\), which is does not occur in the other spectra. The phonon displacement pattern which matches exactly this frequency is associated to a vibration mode along the Au chain. Hereby not only the atomic geometry of the step edge results in a charge injection, resembling the effects of the opening of the step edge atoms, e.g., the 414 cm\(^{-1}\) mode, associated with the calculated 406 cm\(^{-1}\) mode. On the other hand the phase-transition-induced slight change in the Au-chain dimerization activates a planar vibration of the chain, measured at 87 cm\(^{-1}\), respectively the 86 cm\(^{-1}\) calculated mode. The hydrogenation of the step edge results in a charge injection, resembling the effects of the step edge fluctuations without hydrogenation and therefore stabilizing the RT phase at low temperature. Consequently the phase transition is governed by thermally excited step edge fluctuations, giving rise to an oscillating charge transfer from the step edge to the Au chain. Hereby not only the atomic geometry of the step edge (masking the threefold periodicity at higher temperatures), but also that of the Au chains (origin of the twofold periodicity) is altered. This conclusion supports the order disorder scenario for the phase transition in the clean Au-(5 \(\times\) 2)/Si(553) without H. H passivation of the step edge has an analogue effect to thermal disorder, locking the charge redistribution, as depicted in Fig. 33 and stabilizing the RT phase by charge injection.

6.2.2. Au chains on Si(557) and Si(775)

One of the advantages of the SRS is its sensitivity to the surface structure. Hence, the comparison of Raman spectra from similar structures can help to assign related spectral features to common structural motifs on the surface. Here we discuss a comparison between vibrational spectra of surfaces with similar and opposite vicinality. The general assignment of vibrational modes to three different ranges, i.e., the high-frequency range for Si–Si surface vibrations, surface- and boundary-condition induced (Au sub-ML, much heavier than Si) activation of acoustical bulk modes, and Au–Si in the low-frequency range (mass/bond stiffness related) is maintained. Additionally, a dependence on local structural elements like Au single/double chains and buckled vs. non-buckled step edges is evident. Moreover, the larger width of the terraces in the (557) surface is compensated by Si ad- and rest atoms, providing an entirely new structural element.

![Fig. 34. Surface Raman spectra of the Au-(5 \(\times\) 2)/Si(553) reconstruction at 300 and 30 K (a), calculated vibrational patterns of selected characteristic modes of the room temperature phase for Au-chain related (b), and Si-step-edge vibrations (c). The spectra where taken in zxx polarization configuration with excitation energy 1.91 eV. Spectral ranges are marked in the spectra by double arrows according to the origin of the vibrational modes, while the characteristic modes are marked by vertical lines (from Ref. [261]).](image1)

![Fig. 35. Surface Raman spectra of Au-(5 \(\times\) 2)/Si(553) above (RT, red lines) and below the phase transition temperature (blue lines) without (a) and with (b) step edge hydrogenation. The spectra were taken in zxx polarization configuration with excitation energy 1.91 eV. (from Ref. [261])](image2)
In Fig. 36, SRS spectra from (553), (775), and (557) are compared. Unfortunately, no calculations of vibrational modes of the (775) and (557) surfaces are available. Hence, the interpretation of similarities and differences between the spectra can be performed only on the phenomenological level. The high similarity between the spectra from (553) and (775) suggests a high similarity of these surfaces despite of the slightly different vicinalities and terrace widths. This may be explained by a step-edge bunching and the formation of larger compensation steps due to higher stability of the (553) system.

As expected, the higher complexity of the unit cell in the case of the double Au chains ([553] and [775]) delivers a larger variety of vibrational modes with participation of Au atoms in the lower spectral range. Au single chains, in the case of (557), produce simpler spectra with only few lines. The range around 150 cm$^{-1}$, with activated acoustic bulk phonons, differs significantly for the opposite vicinalities, suggesting a strong dependence of the activation mechanism on projection angle of the bulk phonon dispersion onto the surface.

Also the step-edge/honeycomb-related modes reveal large differences for the opposite vicinalities, while the two step-edge modes in (553) and (775) are hardly distinguishable. Only one, strongly shifted, step-edge/honeycomb-related mode appears for the (557) surface. The sensitivity of the 415 cm$^{-1}$ mode to the buckling of the step edge (in the [553] case), discussed in the previous section, proves to be relevant also in this case. The strong buckling in the (557) case seems to suppress the appearance of the step-edge-related mode.

6.3. Au-(5×2)/Si(111)

In contrast to the previously discussed two-dimensional Au-(√3×√3)/Si(111) superstructure (see Section 6.1), also Au chains can be formed on the Si(111) surface. Upon annealing to $T_{\text{anneal}}=1050$ K, a pure Au-(5×2)/Si(111) reconstruction is obtained with a Au coverage in the range of $\theta_{\text{Au}}\approx0.6–0.7$ ML.

The strongly anisotropic Au-(5×2)/Si(111) reconstruction consists of quasi-one-dimensional Au chains. The prefix “quasi” indicates that the chains do not obey a strict one-dimensional confinement, since they experience some coupling, e.g., via the substrate [262]. Due to the quasi-one-dimensional confinement, within each chain the interactions between the electrons strongly gain relevance, resulting in the emergence of correlation-related phenomena.

The Au-(5×2)/Si(111) reconstruction has been extensively investigated with respect to its structural and electronic properties in experimental, theoretical, as well as in joint studies [140,143,263–269]. Many of these reports treat the question of electronic correlations and related effects. Recently, new results of the impact of additional Si atoms on the Au chains were reported [270]. Metallic behavior of the Au chains was observed from RT down to 20 K by IR spectroscopy [268], in line with DFT calculations, which predict a half-filled electron band.

The detailed atomic structure of the Au chains in the (5×2) reconstruction has been debated since many years, despite numerous experimental and theoretical investigations. This discussion was recently enriched by new proposals [140], suggesting several modified models. A model for a Au coverage of 0.6 ML was suggested by Erwin, Barke, and Himpel (hereafter called EBH model) [264]. It results from a first-principles study and its predictions are in accordance with results from STM and photoemission spectroscopy. For the same Au coverage, an alternative model was proposed by Abukawa and Nishigaya, based on RHEED and STM observations [265]. It features Y-shaped Au structures and Si adatoms. However, due to energetic instability in DFT simulations, together with incongruity with results of Reflectance Anisotropy Spectroscopy (RAS), it was rejected by Hogan et al. [145]. Furthermore, Seino and Bechtold also rejected this model because of its instability in ab initio calculations [266]. Kwon and Kang later proposed another structure, modeling a Au coverage of 0.7 ML, which improves the agreement with STM images [140]. This so-called KK model is energetically more favorable than the EBH model, giving an energy gain of 0.92 eV per (5×2) surface unit cell. The KK model was later supported by a surface X-ray diffraction study [267], as well as by DFT calculations [271], and results of RAS [269]. Therefore, the following analysis of the SRS spectra of the Au-(5×2)/Si(111) reconstruction is confined to the EBH and the KK model. Employing first-principles calculations, the experimental vibrational eigenmodes are compared to the predictions of both models to verify the compatibility with experimental data.

In the EBH model, shown in Fig. 37(a), the Au atoms are assembled in two parallel chains in [110] direction. One of these chains consists of a row of single Au atoms, while the other is formed by a double row of dimerized Au atoms. Alongside of these chains, a Si honeycomb chain is located. The periodicity of this basic structure is only (5×1). The experimentally observed (5×2) periodicity, e.g., in LEED [272], is obtained by considering additional Si adatoms between both Au chains, which induce a slight inversely-phased tilt of adjacent Au dimers. This slight tilt is omitted in Fig. 37(a), as it is not considered in the surface-vibration mode calculations which are presented here for comparison with the Raman results.

The KK model strongly resembles the EBH model, apart from one additional Au atom per (5×2) surface unit cell, which results in a slightly enhanced coverage of 0.7 ML. It is depicted in Fig. 37(b). Due to these additional Au atoms in the double row, which are shifted slightly towards the single one, the Au rows are appropriately described collectively as a Au triple chain, while the Si honeycomb chain persists as in the previous model. In contrast to the EBH model, the KK model yields an intrinsic (5×2) periodicity. Furthermore, as discussed in Ref. [140], additional Si adatoms on the surface are believed to be present in small amounts (coverage of ≈ 0.025 ML) even at well prepared surfaces [2,269,270,273]. It was observed that locally no Si adatoms are present on the surface, while other areas show a coverage of ≈ 0.05 ML.

Because of its pronounced anisotropy, the Au-(5×2)/Si(111) surface reconstruction has only a single symmetry operation, a glide plane, and belongs to the 2D space group p1g1, which corresponds to the 3D point group C$_1$. This group has two non-degenerate
irreducible representations $A'$ and $A''$, which give rise to two Raman tensors $R_{A'}$ and $R_{A''}$ [31] (see Eqs. (10) and (11)). Thus, vibration modes with $A'$ symmetry should be observable in parallel polarization configuration, e.g., $z(\overline{xx} \overline{z})$, while those with $A''$ symmetry should appear in crossed configuration $z(xy)\overline{z}$.

6.3.1. Surface Raman spectra of Au-(5 × 2)/Si(111)

Fig. 38 shows the SERS intensity of the Au-(5 × 2)/Si(111) surface reconstruction, obtained as the difference between the Raman intensity immediately after the flash-annealing preparation of this reconstruction and the spectrum after aging. Fig. 38(a)–(d) cover the intensity immediately after the flash-annealing preparation of this face reconstruction, obtained as the difference between the Raman vibration modes of clean Si(111)-(7×7) and the spectrum of the reference to color in this figure legend, the reader is referred to the Web version of this article.)

Thus, the evaluation of the spectra in the various polarization configurations allows not only the determination of the vibration eigenfrequencies, but also gives access for each individual vibration mode to the diagonal $A'$ Raman-tensor element $R_{yy}$ perpendicular to the x-directed Au-chains, and to the off-diagonal $A''$ elements $R_{xy}$ and $R_{yx}$. In this way, these modes can be correlated with the results of first-principles model calculations, as described in the following.

6.3.2. First-principles calculations of Au-(5 × 2)/Si(111)

For the assignment of the experimentally observed SERS features to adsorbate-induced vibration eigenmodes, first-principles calculations were employed. The eigenfrequencies, symmetry, and elongation patterns of the surface-vibration eigenmodes of the one-dimensional reconstruction Au-(5 × 2)/Si(111) were calculated within the procedure described above for the two-dimensional reconstruction Au-(â√3×√3)/Si(111). In Fig. 39, the calculated polarized Raman spectra for Au-(5 × 2)/Si(111) according to the KK- and EBH-model are shown in the second and third row, respectively. The experimental results from Fig. 38 are shown in the upper row for comparison. Obviously, the spectral positions as well as the relative intensities of the experimentally observed peaks in z(zy) polarization between 50 and 80 cm$^{-1}$ ($A'$ modes) are well reproduced within the KK model. The calculated frequencies of 56, 63, 71, and 78 cm$^{-1}$ are assigned to the experimental peaks at 51, 61, and 69 cm$^{-1}$.

The displacement patterns of these dominant calculated eigenvibration modes are depicted in Fig. 40. They are all localized primarily at the gold atoms. Two of them show displacement patterns primarily perpendicular to the chain direction [110], while the other two show no clearly distinguishable orientation. The absence of vibration features in the experimental $A'$ Raman spectrum with z(zy) polarization, i.e., parallel to the chains, is reproduced much better within the KK model than by the prediction of strong peaks according to EBH.
 Altogether, the KK-based calculations show a considerably stronger agreement with the experimental observations than those for the EBH model. The remaining discrepancies for the $A''$ modes in $z(xy)$ polarization, which apply for both models, may be partially related to limitations of the computational approach, such as the disregard of the well-established domains and the omission of the associated Si adatoms and Si adsorbate atoms, which have been detected on the surface by several research groups [2,264,273]. Furthermore, the preference for the KK model agrees with results from surface X-ray diffraction [267], RAS [269], and IR spectroscopy [270].

### 6.4. One-dimensional In chains on Si(111)

The $(4 \times 1)/(8 \times 2)$ surface structure induced by In deposition on Si(111) surfaces represents a prototype example of a one-dimensional metallic conductor at RT, which undergoes a Peierls-like transition into an insulating state at low temperature [274]. It is a prominent example of the atomic-scale one-dimensional metallic nanowires which was intensively investigated experimentally, among other methods, by SRS and theoretically by DFT-based calculations of the surface vibrational modes and their role in the phase transition.

A ML of In on Si(111) allocates chains of In atoms on the Si surface extending along the $[1 \bar{1} 0]$ direction. The commonly accepted
structural model, which has been established by experiment and theory for the RT phase of the In nanowire structure, is a \((4 \times 1)\) surface reconstruction, shown in Fig. 41(a). It consists of rows, each comprising two In zigzag chains, and are separated by a Si zigzag chain in between, resembling the \(\pi\)-bonded chains of the clean Si(111)\(\{2 \times 1\}\) surface. When the system is cooled to about 120 K, the In/Si(111) surface undergoes a phase transition into an \((8 \times 2)\) structure Fig. 41(b). Upon this phase transition, the In atoms within the double row of zigzag chains rearrange into a hexagon-like pattern and the structure becomes insulating \([274,275]\). This transition from the one-dimensional metallic \((4 \times 1)\)- to the insulating \((8 \times 2)\) structure has been associated with a first-order Peierls transition. This is a displacive transition between two distinct geometrical surface structures, which is associated with the formation of a CDW \([77,276]\).

By SRS surface vibration modes are observed in the range from 20 cm\(^{-1}\) up to 500 cm\(^{-1}\) for the \((4 \times 1)\)- and \((8 \times 2)\) surface structure (see Fig. 42) \([28,202,277,278]\). Due to the large atomic mass difference of In (\(A = 115\)) and Si (\(A = 28\)) surface-localized modes involving In (Si) displacements should appear at lower (higher) frequencies \([202]\). Thus the surface Raman spectrum may be divided into two frequency domains: In the low-frequency range below 90 cm\(^{-1}\), the surface vibrational modes involve mainly displacements of the In atoms of the upper atomic layer, in the high frequency range above 90 cm\(^{-1}\), vibrational modes involve mainly displacements of the Si atoms in the subsurface layers. In correspondence to the Raman spectra, DFT-based frozen-phonon calculations \([77,279]\) for the \((4 \times 1)\)- and \((8 \times 2)\) structures reveal a rich surface-mode structure with high-energy phonons between about 90 and 480 cm\(^{-1}\). In the surface Raman spectra of Fig. 42, the phase transition from the \((4 \times 1)\)- to the \((8 \times 2)\) structure is immediately evident from the enhanced number of the surface vibration modes and the mode-frequency shifts. Accordingly, the phase transition can be monitored by recording Raman spectra for different temperatures around the phase transition temperature as will be shown in Fig. 47(a).

In particular for the low-frequency surface vibration modes, which are strongly correlated to the surface structure, a detailed microscopic picture has been developed both for the \((4 \times 1)\)- and the \((8 \times 2)\) reconstruction by recent frozen-phonon calculations \([28]\). Tables 6 and 7 give an overview on experimentally determined frequencies of Raman modes and associated mode frequencies from frozen-phonon calculations localized in the top In-layer, including the symmetry properties for the respective modes \([28,77]\). The displacement patterns of the associated modes are shown in Figs. 43 and 44 for the \((4 \times 1)\)- and \((8 \times 2)\) structures, respectively. Due to the doubling of the surface unit cell along the two main surface directions, i.e., [11̅2] perpendicular and [1̅10] parallel to the chain direction, the surface unit mesh contains in the low-temperature structure four times as many atoms as in the RT structure. Correspondingly, the number of surface optical modes at \(\Gamma\) should scale with \(3n - 2\) (with \(n\) denoting the number of atoms in the surface unit cell in a two-dimensional lattice). Neglecting the structural rearrangement within the In chains, the additional phonon modes of the low-temperature \((8 \times 2)\) structure would arise from backfolding of the respective \((4 \times 1)\) surface modes at the \(\Gamma\), \(X\), \(Y\), and \(M\) points of the surface BZ of the \((3 \times 1)\) structure \([28]\).

However, the \((8 \times 2)\) eigenmodes do not refer simply to the \((4 \times 1)\) backfolded modes, but depend also on the structural modification within the unit mesh, i.e., the transition from the In chain structure to the In hexagon structure. Thus the surface phonon modes depend both on translational symmetry changes, i.e., backfolding according to the change of the surface unit mesh size, and local bonding configuration according to the change from chain-like to hexagon-like surface structure \([28]\).

In order to understand the Raman selection rules in the \((4 \times 1)\)- and \((8 \times 2)\) phase, shown in Fig. 45, it is important to consider the symmetries in the corresponding surface structures. Symmetry elements of the \((4 \times 1)\) In zigzag chain structure are a twofold rotation, a mirror and a glide plane according to a \(p m g\) 2D space group. The \((8 \times 2)\) hexagon structure has only a glide reflection plane according to a \(p g\) 2D space group (Fig. 41). The associated 3D space groups for the \((4 \times 1)\) and \((8 \times 2)\) reconstructions are the orthorhombic \(C_{2v}\), and the monoclinic \(C_{2h}\).

The corresponding normal vibration modes, which are shown in Figs. 43 and 44, separate according to their displacement patterns into \(A'\) and \(A''\) surface modes, conserving and breaking the sym-

---

**Table 7**

Measured low-temperature phonon mode frequencies (cm\(^{-1}\)) of In/(8 \(\times 2\))/Si(111) and assigned calculated modes in the range from 10 to 90 cm\(^{-1}\). Extracted from fits in Ref. [28]. The errors are given for the 90% confidence interval.

| Exp. (cm\(^{-1}\)) | FWHM | Symm. | Theory \((8 \times 2)\) |
|-----------------|--------|-------|-----------------------|
| 19.6 ± 0.1      | 4.0 ± 0.6 | \(A'\) | 20.0 \((8 \times 2\)) |
| 23.4 ± 0.1      | 2.4 ± 0.2 | \(A'\) | 22.2 \((8 \times 2\)) |
| 27.1 ± 0.5      | 3.7 ± 1.3 | \(A'\) | 26.8 \((8 \times 2\)) |
| 28.3 ± 0.1      | 2.9 ± 0.4 | \(A'\) | 27.4 \((8 \times 2\)) |
| 35.0 ± 0.4      | 9.5 ± 3.6 | \(A''\) | 32.3 \((4 \times 1)\) |
| 37.7 ± 0.1      | 1.0 ± 0.5 | \(A'\) | \(\phantom{0}\) |
| 41.4 ± 0.1      | 2.9 ± 0.1 | \(A', A''\) | 53.8 \((8 \times 2\)) |
| 48.1 ± 0.2      | 2.8 ± 0.8 | \(A', A''\) | 59.0 \((8 \times 2\)) |
| 55.5 ± 0.2      | 4.0 ± 0.2 | \(A'\) | 69.6 \((8 \times 2\)) |
| 57.8 ± 0.1      | 1.4 ± 1.0 | \(A'\) | \(\phantom{0}\) |
| 60.0 ± 0.1      | 4.1 ± 1.1 | \(A'\) | \(\phantom{0}\) |
| 63.5 ± 0.5      | 10.4 ± 5.0 | \(A', A''\) | \(\phantom{0}\) |
| 69.0 ± 0.0      | 1.4 ± 0.2 | \(A'\) | 87.2 \((8 \times 2\)) |
| 80.6 ± 0.3      | 11.4 ± 6.0 | \(A'\) | \(\phantom{0}\) |
| 85.4 ± 0.3      | 6.7 ± 0.7 | \(A', A''\) | \(\phantom{0}\) |

Fig. 42. Raman spectra of In/Si(111) at excitation energy 1.91 eV in a broad spectral range up to 500 cm\(^{-1}\) for the \((4 \times 1)\) structure at RT and the \((8 \times 2)\) structure at low temperature (30 K). Spectra are taken at \(z(x)z, z(y)z, z(x)z(A')\) and \(z(y)z, z(x)z(A'')\) polarization configurations. The direction of the Indium chains refers to \(y\) (from Ref. [202]).
Raman tensor components couple strongly to the electronic structure of the surface and is involved in the Peierls transition in the regime above $T_c$ (see Section 6.5 and Ref. [28]).

The analysis of the surface electronic anisotropy [275] shows that In–Si bonds lead to surface electronic states within the first atomic layers, which show a pronounced optical absorption for light polarized along the $[1\bar{1}0]$ direction. This has a strong impact on the surface electronic band structure and related surface optical transitions, which are important for the Raman scattering process, as discussed above. The analysis of the surface electronic anisotropy [275] shows that In–Si bonds lead to surface electronic states within the first atomic layers, which show a pronounced optical absorption for light polarized along the $[1\bar{1}2]$ direction in the visible range (around 1.5 eV). This optical anisotropy of the surface structure is reflected in the $a$ and $b$ components of the Raman tensor: in parallel configuration a strong Raman signal of the $A'$ modes shows up in $(xx)$ polarization, while in $(yy)$ polarization, a weak $A''$ Raman signal occurs [28,202]. The Raman experiments were recorded with 1.91 eV laser photon energy, resulting in the $A'$ scattering mainly exciting surface electronic transitions with $x$ polarization. The $A''$-scattering depends on crossed $(xy)$ and $(yx)$ polarization configuration involving both $x$ and $y$ polarizations and thus is equivalent for $(xy)$ and $(yx)$.

Experimentally it has been demonstrated that the In–Si surface modes indeed show pronounced surface resonances, by choosing various different laser excitation lines in the visible spectral range [202]. The resonance enhancement and spectral dependence of the resonance enhancement differ for the individual surface modes, showing that the deformation potential of the individual modes is distinct and in particular will affect different electronic states of the surface electronic band structure, depending on the displacement pattern of the surface mode. RRS from the Si bulk phonon modes occurs at the $E_1$ gap of Si around 3.4 eV. This is spectrally well separated from the surface resonances, and thus by surface resonant excitation, the surface modes are selectively enhanced.

It should be noted that all these findings are very similar to the descriptions in the introduction and the results for the Sb/III-V(110) model system in Section 2.6. Surface and bulk optical properties differ significantly: The surface shows a pronounced optical anisotropy related to the surface electronic band structure. The surface RRS utilizes these surface optical transitions, which lead to a selective enhancement of the surface phonon scattering. The Raman tensor elements reflect the structural anisotropy and depend significantly on the chosen polarization directions of incident and scattered light, i.e., in the $A'$ configuration very different scattering efficiencies result for $(xx)$ and $(yy)$ polarization configuration.

6.5. Electron-phonon coupling in atomic metallic chains

RRS is a widely applied method to investigate electronic properties in bulk and low dimensional solids. In contrast to single-particle methods (electron/ion based spectroscopies), the main contributions of electronic properties to Raman spectra manifest themselves
mainly in inelastic scattering of light, involving combined electron-phonon quasiparticles. Phase transitions which are based on changes in electronic properties offer a possibility to follow the development of electronic parameters, e.g., upon composition, pressure or temperature variations [280]. Those phase transitions which are accompanied by structural changes exhibit for each phase a specific set of phonon modes, which can be detected by RS, while electronic phase transitions (e.g., Mott insulator – metal transition) can show phonon modes only of the metallic phase with intensities dependent on the free carrier concentration [281]. In contrast, in phase transitions driven by structural changes the electron-phonon coupling affects the main phonon line parameters such as eigen-frequency and phonon lifetime by energy exchange.

The coupling between the electronic system and vibrational excitations in one-dimensional bulk materials was investigated and explored for selected materials as representatives of broad material classes such as Bechgaard salts [282] and blue bronze [283]. Similar extensive studies have been reported for one-dimensional polymers, such as polyacetylene (see e.g. Ref. [284]).

For the surface-bound structures in the two-dimensional case only few experimental investigations with helium scattering are present in literature [227,285,286]. The presently discussed quasi-one-dimensional metallic chains on Si surfaces were investigated by SRS and will be discussed below on two examples of In chains on a flat Si[111] substrate and Au chains on the terraces of the Si[553] substrate.

6.5.1. Electron-phonon coupling in In-(4 × 1)-(8 × 2)/Si[111]

The In-(4 × 1)-(8 × 2)/Si[111] phase transition is an example of a Peierls transition, i.e., a metal-insulator transition accompanied by a change in lattice periodicity. An important aspect of the surface vibrational properties of the In/Si[111] system is their role in the phase transition and in particular their interaction with the electronic structure. The Peierls transition leads to a correlated electron-phonon state by the formation of CDWs below the phase transition temperature $T_c$ which is accompanied with a lattice distortion. Due to interaction between electron density and lattice distortion below $T_c$, Peierls theory predicts the existence of collective electron-density-lattice-excitations, i.e. amplitude modes which are Raman active and phase modes which are IR active [282,287–289], while only above $T_c$ in the uncorrelated phase, electronic and phononic single particle excitations exist. Collective modes like phonons are not only intrinsically interconnected with the structure and electronic periodicity of the given phase, but also their characteristic temperature dependent behavior near the phase transition can indicate the coupling strength with the electronic system. This is especially the case in CDW systems [282]. The energy exchange between phonons and electrons results in the softening of the phonon frequency in the so-called Kohn anomaly [290].

In Fig. 46 the general behavior of the Kohn anomaly above, and the amplitude mode below the phase transition temperature is shown. Below $T_c$, a stationary softened G mode ($q \approx 0$) is expected, while above $T_c$ a propagating mode at the border of the Brillouin zone ($2q_F$) occurs. These modes have similar vibrational patterns, as shown in the upper part of Fig. 46, while their different momenta are generated by the “umklapp” process in the phonon dispersion due to doubling in periodicity in the Peierls transition. Depending on the degree of interaction between the phononic and electronic system, the frequency softening can reach a complete relaxation of the vibrational mode at the transition temperature in the strong coupling regime (frequency equals zero at $T_c$), or it results in a partial softening for the near resonant coupling case as indicated in Fig. 46 by the dashed and full lines, respectively [292,293].

Fig. 45. Polarized Raman scattering from the low-temperature (8 × 2) and the room-temperature (4 × 1) phase of In/Si[111]. The spectra were taken with excitation energy 1.91 eV. The scattering geometries were z(xy)z and z(yz)z (blue lines), as well as z(zy)z and z(pσ) (red lines). The polarization vector of the exciting laser radiation is either perpendicular or parallel to the direction of the Indium chains (y). (from Ref. [29]) (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 46. Temperature dependence of amplitude, phason and Kohn anomaly in a Peierls material. In the correlated phase the amplitude (black line) is Raman active, while the phason (blue line) is IR active. In the uncorrelated phase (T > Tc) the Kohn anomaly occurs at a phonon with Peierls vector ~ q, associated with the electronic nesting condition and is therefore not visible in RS (q > 0). Strong phonon-electron interaction results in a transfer of vibrational energy to the charge fluctuations, leading to complete phonon energy relaxation (dashed lines) while the near-resonant case (full lines) provides a distribution of energy with only partial relaxation at $T_c$. Below $T_c$, the structure refers to an (8 × 2) reconstruction, while above to a (4 × 1). The respective unit cells are indicated as rectangles. (adapted from Ref. [291]) (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
Also the amplitudon excitations in the correlated phase have a pronounced temperature dependence when heating the correlated phase to \( T_c \) as given by \( \omega^2(T) \propto \left((T - T_c)\right) \) \cite{282,289}. The Peierls amplitudon modes in In/Si(111) are essentially the shear and rotary modes coupled to the charge density modulation (see Fig. 44). They should appear in the Raman spectrum at the \( \Gamma \) point below \( T_c \) and show a significant softening close to the first-order phase transition.

SRS spectra of In/Si(111) for various temperatures above and below the phase transition between \( (4 \times 1) \) and \( (8 \times 2) \) are presented in Fig. 47(a). The resonances observed experimentally were assigned to specific vibrational modes by comparison to first-principles computations as discussed above \cite{28,202,277,278}. Here we discuss the low-frequency modes at 20, 28, 42 cm\(^{-1}\) in the \( (8 \times 2) \) phase and the 55 cm\(^{-1}\) mode observed for both phases, which all involve displacements of In atoms (see Fig. 44). In Fig. 47(b), the temperature dependence of the normalized frequencies of these modes is plotted. The modes at 20 and 28 cm\(^{-1}\) (as measured at 44 K), which are assigned to the shear and rotary modes, exhibit a partial phonon softening when approaching the phase transition temperature and vanish above it. The mode at 42 cm\(^{-1}\), in contrast, shows a constant frequency with decreasing temperature, while the mode at 55 cm\(^{-1}\) exhibits only moderate temperature shift.

These observations agree very well with our analysis of a first-order Peierls transition \cite{294,295}. The rotary and shear modes are strongly coupled to the electronic system, i.e., the CDWs in the correlated state, by the lateral displacements of the In atoms. This is shown in Fig. 48 from according DFT calculations: the alternating red and blue lobes reveal how the rotary mode leads to a modulation of charge density in the outer rows of the In zig-zag chains, the shear mode in the inner rows. These two modes show the softening which is expected for Peierls amplitudon modes; however, this softening remains only partial because the transition is discontinuous. The 42 and 55 cm\(^{-1}\) modes, in contrast, are related to vertical displacements of In atoms. Hence they are only weakly coupled to the in-plane CDW and display a behavior related to the lattice expansion with temperature increase. Remarkably, the 42 cm\(^{-1}\) mode shows no frequency shift at all, i.e., the lattice expansion is compensated for by a stiffening of the involved In bonds. The 55 cm\(^{-1}\) mode displays a side-effect drop in eigenfrequency at the phase transition due to the structural changes upon the phase transition. Interestingly, the form of the frequency drop of vibrational modes directly involved in the electronic phase transition, is proportional to \( \sqrt{T - T_c} \). This strongly indicates a partial phonon softening as expected from Peierls/CDW theory suggesting a coupling between these specific surface vibrational states and the electronic structure. Indeed, as indicated by the anomalous temperature dependence of the shear and rotary modes (see Fig. 47), they cause distinct changes in the electronic band structure, resulting in the metal-insulator phase transition. We would like to note that the Kohn anomaly of the associated phonon modes in the uncorrelated \( (4 \times 1) \) state cannot be observed with SRS, because zone-edge phonons are involved. Only after backfolding into the \( (8 \times 2) \) structure, the respective modes refer to zone-center modes and show up as the amplitudon modes as discussed above.

Fig. 47. Phase transition in vibrational spectra of In/Si[111]. (a) Raman spectra of the phase transition at excitation energy 1.91 eV and polarization z\(\times\)x. (b) Frequency of selected modes. The corresponding vibrational patterns are shown in the insets. While modes with vertical displacements are hardly affected by the phase transition, the shear and rotary modes at 20 cm\(^{-1}\) and 28 cm\(^{-1}\) are considerably softened near the phase transition (from Ref. [276]).

6.5.2. Electron-phonon coupling in Au-(5 \( \times \) 2)/Si(553)

In contrast to the phase transition in the In-(4 \( \times \) 1)-(8 \( \times \) 2)/Si(111) system, for Au-(5 \( \times \) 2)/Si(553) the effects of the structural and electronic transition are not very pronounced. As discussed in Section 6.2.1, the x2 streaks in LEED remain visible in the complete temperature range. Nevertheless, the appearance of additional x 3 streaks in the LEED patterns at temperatures below 120 K indicates a faint structural change. Also the metallicity of the surface remains. Moreover an order-disorder character of the phase transition seems to be supported by the gradual appearing of the step-edge-related vibration mode in temperature dependent Raman spectra in Fig. 49(a). Nonetheless, the phase-transition-induced step-edge geometry change, accompanied by the charge transfer, causes a filling of the Au chain related electronic bands. The resulting
re-dimerization of the Au chain not only alters the geometry of the chain but also modifies the filled states [255,256]. As was shown in Ref. [3], changes in the step edge geometry of a Au-chain-stabilized vicinal Si surface can alter the electronic band structure and charge redistribution in the surface. Following this interpretation, the role of the step edge oscillations in the order-disorder phase transition can be understood in terms of the coupling of step edge atomic geometry and Au-chain induced electronic properties. Upon the reduction of temperature and, successively, the occupation number of phononic states, the ground state of the system becomes predominant.

A close inspection of frequencies of vibrational modes involving directly the Au-chain atoms at low wavenumbers, and therefore directly dependent on the dimerization of the Au chains, reveals important details about the coupling between the electronic system and phononic states. In Fig. 49(b), normalized temperature-dependent frequency shifts of characteristic lines from the surface Raman spectra are shown. The normalization is required in order to distinguish potential deviations from thermally induced shifts, e.g., exhibited in the 2 TA bulk mode. In contrast to the other lines, including the bulk 2 TA mode, the 87 and 42 cm$^{-1}$ modes, assigned to the Au-chain located modes with transversal in plane and, respectively, longitudinal displacement pattern, show strong temperature shifts. Interestingly, the shift for the mode with longitudinal displacement pattern is more pronounced than the one from the transversal in-plane mode, indicating a cross link between the re-dimerization (in-plane change of atomic Au coordinates) and longitudinal in-plane vibrations. At the same time the 61 cm$^{-1}$ mode, having a displacement pattern with components only perpendicular to the surface, shows no temperature dependence, while the transverse vibration at 87 cm$^{-1}$ exhibits only a moderate frequency shift. Noticeably, the observed frequency shifts by far exceed the usual (temperature caused) lattice-constant-expansion induced frequency shifts, which are expected to be below one percent for this temperature range. The results in Fig. 49(b) suggest that a partial softening of the longitudinal and, to a lesser extent, in-plane transversal Au-chain-related modes is observed, similar as in the In/Si(111) system discussed above.

Although no theoretical calculations exist for a possible effect of electron-phonon coupling in Au-(5 × 2)/Si(553) on phonon frequencies, the analogy to the well investigated In-(4 × 1)-(8 × 2)/Si(111) system suggests that a resonant coupling is also important in the former case. While the In-(4 × 1)-(8 × 2)/Si(111) system shows a Peierls transition from a conductive into an insulating state, accompanied by a change of the reconstruction (from In chains to In hexagons), the Au-(5 × 2)/Si(553) system undergoes an order-disorder transition with a charge transfer between fluctuating step edges and Au chains, accompanied by changes in atomic geometry of both surface structure elements. In these examples phonon anomalies are visible in Raman spectra, pointing towards a particularly pronounced electron-phonon coupling.

7. Summary

In this article, the application of Raman spectroscopy for surface analysis has been reviewed, with special reference to metal-induced one-dimensional and two-dimensional atomic structures on Si and Ge surfaces. These systems have gained much interest in recent years because of the potential realization of novel electronic effects due to their low dimensionality (e.g., Peierls transition, spin and charge density waves, Tomonaga-Luttinger liquid), which are strongly connected with the atomic structure. Moreover, in many of these systems, the surface structures are rather complex and may undergo phase transitions depending on temperature. The determination of the surface structure with standard surface analytical methods has turned out to be a difficult task.

As shown in this review, surface Raman spectroscopy from adsorbate-induced vibration modes can be applied for surface analytics and can deliver very valuable information on surface structures by the analysis of surface vibration mode eigenfrequencies and symmetry properties. When exploiting resonant enhancement by choosing surface RRS conditions, in many examples a surprisingly large scattering efficiency is achieved from the surface modes. Vibrational RS, in particular, in combination with ab initio calculations of the surface vibration mode eigenfrequencies, symmetries, elongation patterns, and Raman scattering spectra, is very powerful in addressing surface structures and monitoring structural phase transitions. This is due to the fact that surface localized modes are strongly dependent on atomic masses, chemical bonding and structural arrangement within the uppermost few atomic layers and thus a very sensitive indicator of structural changes.

After the introduction, in the following two chapters an outline has been presented of the basics of RS, on the one hand from the experimental point of view with reference to, e.g., resonance, symmetry aspects, and the equipment requirements for achieving sufficient sensitivity. On the other hand, the current status in theory has been summarized, which by now allows, besides the ab initio calculation of surface and adsorbate structures and their vibration modes, also the prediction of Raman scattering efficiencies, thus enabling the quantitative simulation of surface Raman spectra. As an illustration of this close interplay between experiment and theory, SRS results from (sub-)ML Sb structures on InP(110) and GaAs(110) as “model
systems” have been reviewed. The Sb monolayer structures illustrate the role of symmetry selection rules and underscore the potential of exploiting the selective resonance to surface states. Moreover, for Sb/GaAs(110) the concept of the disentanglement of surface features and bulk phonons by considering difference spectra has been developed. The latter is particularly useful in the case of non- or weakly surface-resonant Raman, as used in the following chapters, e.g., on clean Si and Ge surfaces.

In the main part of the article, a variety of material systems have been discussed, based on Ge(111), Ge(001), and particularly Si substrates with (111) and vicinal (hhk) orientations. As (sub)monolayer adsorbate metals, Au, Sn, Pb, and In were employed. For the two- and quasi-one-dimensional structures which were obtained for different substrate orientations and deposition conditions, many well-defined surface vibration peaks were observed in the Raman spectra, which were consistently assigned to eigenmodes with characteristic symmetry and elongation patterns in correlation with ab initio calculations.

For the clean Si(111) surface with a (7 × 7) reconstruction a series of six surface Raman peaks has been detected in the range between 62.5 and 420.0 cm\(^{-1}\). Based on the DAS structure model, they were assigned, e.g., to adatom vibrations and in-plane wagging modes and the backfolded Rayleigh mode, in good agreement with molecular dynamics calculations. Likewise, the clean Ge(111)-(2×8) surface gave rise to a series of modes between 60.2 and 285.7 cm\(^{-1}\). The reported results of molecular dynamics calculations and HAS have been confirmed, and moreover, the Raman spectra have shown to date unobserved surface vibration modes with excellent frequency resolution. For the (001)-oriented Ge surface, the selection-rule analysis of the observed surface Raman peaks from the dynamic (2 × 1) reconstruction at 300 K has shown that RS, due to the instantaneous character of the scattering process, sees the transient (2 × 2) reconstruction, in contrast to time-averaging methods like LEED and STM, which see the (2 × 1) mean geometry.

For the two-dimensional adsorbate system Pb-(\(\sqrt{3} \times \sqrt{3}\))Si(111) in the striped incommensurate phase the combination of SRS with ab initio vibration calculations for the proposed H\(_3\) and T\(_4\) geometry enabled the identification of six vibration modes between 18.2 and 107.0 cm\(^{-1}\) and their classification as out-of-plane vibrations of Pb, combined Pb–Si modes and Si-related ones. However, a discrimination between both models, which differ mainly with regard to the registry of the Pb monolayer to the Si substrate was impossible, because their calculated surface vibration mode frequencies are almost identical. This indicates a very weak coupling of the Pb layer to the Si substrate.

Two-dimensionally reconstructed Sn-adsorbate structures were investigated on Si(111) and Ge(111) with temperature-dependent SRS and DFT, aiming at (i) the assignment and comparison of the surface modes of these closely related systems, and (ii) the possible impact of the temperature-driven phase transition between (\(\sqrt{3} \times \sqrt{3}\)) and (3 × 3), which occurs for SnGe(111) at T ≈ 220 K, but is absent for Sn/Si(111). For both systems a large series of surface vibration modes has been identified, for Sn/Si(111) between 164 and 488 cm\(^{-1}\), and for SnGe(111) between 80 and 285 cm\(^{-1}\). All observed peaks were reproduced by the DFT simulations with a mean frequency deviation below 5.8 cm\(^{-1}\) for SnGe(111). As a fingerprint of the phase transition to (3 × 3) for SnGe(111) a backfolded Rayleigh wave appeared, whose intensity increase with decreasing temperature below ≈ 220 K confirmed the order-disorder character of the transition.

The two-dimensional Au-(\(\sqrt{3} \times \sqrt{3}\))Si(111) system, which comprises Au trimers as basic structural elements, was investigated with a view to to distinguish between four closely related models, which, e.g., predict slightly different trimer orientation angles. From a comparison of the calculated stability of these models together with the compatibility of their vibration mode frequencies and symmetry properties with the experimental Raman results, the conjugate honeycomb-chained-trimer model (CHCT) turned out to be the most favorable one.

On stepped vicinal Si(hhk) surfaces with orientations (553), (557), and (775), which give rise to (111)-oriented terraces of different widths, the surface vibration modes were investigated after decoration with Au nanowires. A rich variety of modes was observed, which can be classified according to their origin from different structural elements of these surfaces: the dimerized Au atom rows, the Si honeycomb structure, and the step edge structure. Local vibrational modes associated with the Au dimer rows occur below ≈ 100 cm\(^{-1}\), while vibrational modes from the Si honeycomb and step structure arise at higher frequencies, around 400 cm\(^{-1}\). The Au-derived spectral features have shown a high similarity on Si(553)- and Si(775) substrates, which both give rise to double Au chains, in contrast to the simpler surface structure of single Au chains on Si(557), which exhibit a distinctly different vibration spectrum. For Si(553), Raman spectra together with DFT calculations have revealed that the spectral changes at low temperature reflect a transition from fluctuating step edges to an ordered low-temperature phase. This transition is accompanied with a transfer of electronic charge between surface states at the steps and those of the Au dimer chains, which affects the dimerization of the Au chains. The charge transfer is reflected by a change in eigenfrequencies of the vibrational modes of the Au chains, while the ordering at the step edges is reflected by the associated step-edge modes. The frequency shifts of the surface modes are in agreement with an order-disorder transition, which can be suppressed by hydrogen passivation of the dangling bonds at the step edges.

Also for the quasi-one-dimensional Au chains of the system Au-(5 × 2)/Si(111) several structure models have been presented in literature, the most promising ones by Erwin et al. (EHB model, coverage 0.6 ML) and by Kwon and Kang (KK model, coverage 0.7 ML). With DFT a series of Au-induced vibration modes was calculated for both models in the range between ≈ 40 and 150 cm\(^{-1}\). As expected for this strongly anisotropic system, a strong dependence of the Raman scattering efficiency on the light polarization configuration was predicted: while EHB yields by far the strongest efficiency when the incoming and the scattered light are both parallel to the Au chains, for KK this occurs when both polarizations are perpendicular to the chains. The latter result is in accordance with the experimental Raman spectra. Moreover, the main Raman peak frequencies agree quite well with the values calculated within KK. Therefore, the results strongly favor the KK model. However, as an obvious discrepancy it should be mentioned that for crossed polarization of the incoming and scattered light peaks with a considerable intensity occur in the experiment, while both models predict a very low scattering efficiency.

The Raman investigations on the In/Si(111) system, together with DFT-based frozen-phonon calculations, allowed the assignment of the Raman lines to surface vibrational modes with respect to their frequency, symmetry, and displacement pattern. This gave a clear confirmation of the atomic structures related to the conductive (4 × 1)-In-chain structure at RT and those which belong to the isolating (8 × 2) phase at low temperature, as well as a deeper insight into the mechanism of the associated first-order Peierls transition. The vibration fingerprint of the phase transition at about 120 K does not only show the expected enhanced number of modes in the enlarged unit cell, but also reveals a significant structural modification from an In-chain structure to a hexagon cluster pattern. This modification is substantially initiated by two low-frequency modes, i.e., an in-plane shear mode at 20 cm\(^{-1}\) and a rotary mode at 28 cm\(^{-1}\), located in the In-chains. The temperature dependence of the eigenfrequencies of these phonon modes shows a phonon softening which is indicative of the strong electron-phonon coupling governing the phase tran-
sition. Due to this coupling the LT structure is characterized by the formation of a CDW, associated with the structural rearrangement of the surface atoms.

In one-dimensional metallic chain systems (In and Au-(5 × 2) on flat and vicinal Si(111) surfaces, respectively), with the precise understanding of relevant vibrational modes and their displacement patterns, it was possible to draw conclusions on the coupling between the phononic and electronic states. A partial phonon softening was observed by following the corresponding phase transitions accompanied by the formation of CDW or charge displacement between different surface structural motifs. This partial softening of phonons in metallic chains indicates a resonant electron-phonon coupling, in which the energy gained by the reconstruction of the surface upon the phase transition is in the order of the phonon energy.

In conclusion, this review article demonstrates that the combination of experimental and theoretical SRS is a very useful and novel approach to study surface structural properties, yielding the vibration eigenfrequencies, symmetry properties, and elongation patterns. Moreover, the working principles of surface RRS are discussed. Thus, the traditionally very wide-spread applications of RS for the structural analysis of organic and inorganic materials and structures are extended to surface studies by recording surface localized vibrational modes. This opens many new possibilities for future applications, since the surface RRS just depends on the electronic and atomic/molecular structure of any regularly structured surface or interface and should be applicable in many cases.

Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft in the research units FOR 1162 (project Ge 1855/10-2), FOR 1700 (projects Es 127/12-1, SA 1948/2-1), and TRR 142 (project number 231447078). The Senatsverwaltung für Wirtschaft, Technologie und Forschung des Landes Berlin, the Ministerium für Innovation, Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and the Bundesministerium für Bildung und Forschung and funding within ERFRE 1.8/07 are also acknowledged. The Höchstleistungsrechenzentrum Stuttgart (HLRS) is gratefully acknowledged for grants of high-performance computer time. We acknowledge computational resources provided by the HPC Core Facility and the HRZ of the Justus-Liebig-Universität Gießen and by the Paderborn Center for Parallel Computing (PC²). Moreover, we thank U. Bass, M. Liebhaer, R. Hölldobler, K.M. Wolf, J. Plaickner, S. Chandola, J. Räthel, and M. Vastag for experimental and technical support. S. Wippermann and S. Neufeld are acknowledged for their contribution to the theoretical models.

List of acronyms

| BSE    | Bethe-Salpeter equation |
| BZ     | Brillouin zone          |
| CCD    | charge coupled device   |
| CDW    | charge density wave     |
| CHCT   | conjugate honeycomb chained trimer |
| DAS    | dimer adatom stacking fault |
| DF     | dynamical fluctuation   |
| DFT    | density functional theory |
| DP     | density functional perturbation theory |
| DE     | deformation potential   |
| EBH    | Erwin Barke Himpel      |
| ECLS   | epitaxially continued layer structure |
| EFIRS  | electric-field-induced Raman scattering |
| FWHM   | full width at half maximum |
| GGA    | GGA generalized gradient approximation |
| HAS    | Helium atom scattering  |
| HCT    | honeycomb chained trimer |
| HREELS | high-resolution electron energy loss spectroscopy |
| KK     | Kwon Kang               |
| LDA    | local density approximation |
| LDF    | local density functional |
| LEED   | low-energy electron diffraction |
| LO     | longitudinal optical    |
| LTO    | longitudinal and transverse optical |
| MD     | molecular dynamics      |
| ML     | monolayer               |
| MD-DFT | molecular dynamics density functional theory |
| NIR    | near infrared           |
| PAW    | projector augmented-wave |
| RAS    | reflectance anisotropy spectroscopy |
| RHEED  | reflectance high-energy electron diffraction |
| RS     | Raman spectroscopy      |
| RRS    | resonant Raman scattering |
| RT     | room temperature        |
| RV     | Rayleigh wave           |
| SEF    | surface excess function |
| SERS   | surface enhanced Raman scattering |
| SIC    | striped incommensurate  |
| SRS    | surface Raman spectroscopy |
| SPT    | structural phase transition |
| STM    | scanning tunneling microscopy |
| TA     | transverse acoustic     |
| TERS   | tip enhanced Raman scattering |
| TO     | transverse optical      |
| TT     | twisted trigem           |
| UHV    | ultrahigh vacuum         |
| UV     | ultraviolet             |
| VIS    | visible                 |

References

[1] J.N. Crain, J.L. McChesney, F. Zheng, M.C. Gallacher, P.C. Snijders, M. Bissen, C. Gundelach, S.C. Erwin, F.J. Himpsel, Chains of gold atoms with tailored electronic states, Phys. Rev. B 69 (2004) 125401, https://doi.org/10.1103/PhysRevB.69.125401.
[2] J. Barke, S. Polci, V.O. Eneyhausen, K.-H. Meiwes-Broer, Confined doping on an amorphous H structure, Phys. Lett. 109 (2012) 066801, https://doi.org/10.1016/j.physleta.2012.04.003.
[3] S. Rübenkönig, D. Vongehr, Surface roughness dependence of resonant softening, Phys. Rev. B 85 (2012) 041408(R), https://doi.org/10.1103/PhysRevB.85.041408.
[4] G. Benedek, J. Toennies, Helium atom scattering spectroscopy of surface structures in the Si(557)-Au reconstruction from first principles, Phys. Rev. B 76 (2007) 035410, https://doi.org/10.1103/PhysRevB.76.035410.
[5] J. Aiubach, J. Schäfer, S.C. Erwin, S. Meyer, C. Lobo, J. Settelein, R. Claessen, Evidence for long-range spin order instead of a Peierls transition in Si(553)-Au chains, Phys. Rev. Lett. 111 (2013) 137203, https://doi.org/10.1103/PhysRevLett.111.137203.
[6] S. Riikonen, D. Cvetko, V. DeRenzi, L. Floreano, A. Morgante, M. Peloi, SERS surface enhanced Raman scattering, Surf. Sci., ISSN: 0039-6028 299 (1994) L565–L570, https://doi.org/10.1016/0039-6028(94)00234-X.
[7] J. Albrecht, J. Schäfer, S. Mietke, S. Meyer, Atomically controlled quantum chains hosting a Tomonaga-Luttinger liquid, Nat. Phys. 7 (2011) 776, https://doi.org/10.1038/nphys2051.
[8] K. Rossnagel, On the origin of charge-density waves in select layered transition-metal dichalcogenides, J. Phys. Condens. Matter 23 (21) (2011) 213001, https://doi.org/10.1088/0953-8984/23/21/213001.
[9] H. Ibach, D.L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations, Academic Press, 1982, ISBN: 9781483259451.
[10] H. Nicolai, H. Hofmann, Surface phonons in InP(110), Surf. Sci., ISSN: 0039-6028 328 (3) (1995) 1561–1565, https://doi.org/10.1016/0039-6028(95)00234-0.
[11] H. Nicolai, Phonons in 110 surfaces of InP and InAs, Phys. Rev. B 56 (1997) 13194–13201, https://doi.org/10.1103/PhysRevB.56.13194.
[12] G. Benedek, J. Toennies, Helium atom scattering spectroscopy of surface phonons: genesis and achievements, Surf. Sci., ISSN: 0039-6028 299 (1994) 587–611, https://doi.org/10.1016/0039-6028(94)90068-1.
[13] M. Nusser, T. Prost, F. Tommasini, Low-energy vibrations at the InSb(110) surface, Phys. Rev. B 52 (1995) 16720–16726, https://doi.org/10.1103/PhysRevB.52.16720.
[14] D.E. Aspnes, A.A. Studna, Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV, Phys. Rev. B 27 (1983) 985–1009, https://doi.org/10.1103/PhysRevB.27.985.
E. Speiser et al. / Surface Science Reports 75 (2020) 100480
L. Liu, C.S. Jayanthi, S.-Y. Wu, Complex dynamics of the Si(111)-7×7 reconstructed surface from high-resolution helium atom scattering, EPL (Europhysics Letters) 41 (6) (1998) 647–650, https://doi.org/10.1209/epl/i1998-00535-1.

Y. Sugimoto, J.-O. Christensen, T. Hama, M. Yoshida, Y. Fudou, S. Ando, N. Fujii, K. Miyauchi, P. Andraschko, E. Poblenz, A. Siegel, A.-J. Song, Y. Zhang, X. Cheng, X. Wei, J. Fritsch, P. Pavone, U. Schröder, Ab initio calculation of surface phonons in Si(111)-(7×7) semimetal surface, Phys. Rev. B 89 (2014) 165430, https://doi.org/10.1103/PhysRevB.89.165430.

D.J. Chadi, C. Chiang, New c – 2 × 8 unit cell for the Ge(111) surface, Phys. Rev. B 23 (1981) 1843–1846, https://doi.org/10.1103/PhysRevB.23.1843.

R.S. Becker, J.A. Golovchenko, B.S. Swartzentruber, Tunneling images of germanium surface reconstructions and phase boundaries, Phys. Rev. Lett. 54 (1985) 2678–2680, https://doi.org/10.1103/PhysRevLett.54.2678.

R.S. Becker, B.S. Swartzentruber, J.S. Vickers, T. Klitsner, Dimer–adatom–stacking-fault (DAS) and non-DAS (111) semiconductor surfaces: a comparison of the Ge(111)-(2×8) to Si(111)-(2×2), -(5×5), -(7×7), and -(9×9) with scanning tunneling microscopy, Phys. Rev. B 39 (1989) 1633–1647, https://doi.org/10.1103/PhysRevB.39.1633.

T. Takeuchi, A. Selloni, E. Tosatti, Atomic dynamics and structure of the Ge(111)-(2×8) surface, Phys. Rev. B 51 (1995) 10844–10850, https://doi.org/10.1103/PhysRevB.51.10844.

P. Molnář-Mata, J. Zegenhagen, The lost symmetry of Ge(111)-(2×8), Solid State Commun. 103 (4) (1994) 393–396, https://doi.org/10.1016/S0038-1098(94)85044-9.

N. Takeuchi, A. Selloni, E. Tosatti, Do we know the true structure of Ge(111)-(2×8)? Phys. Rev. Lett. 69 (1992) 648–651, https://doi.org/10.1103/PhysRevLett.69.648.

J. Lobo, D. Farías, E. Hulpke, J.P. Toennies, E.G. Michel, Phonon dispersion curves of the Ge(111)-(2×8) surface determined by He atom scattering, Phys. Rev. B 74 (2006) 035303, https://doi.org/10.1103/PhysRevB.74.035303.

B. Beela, J. Räthel, E. Speiser, N. Esser, J. Schäfer, J. Geurts, Vibrational modes of Ge(111) (2×8) reconstruction in Sn(111), Phys. Rev. B 100 (2019) 035437, https://doi.org/10.1103/PhysRevB.100.035437.

L. Dobrozhsny, D. Mills, Vibrational properties of a adsorbed surface layer on a simple model crystal, J. Phys. Chem. Solids, ISSN: 0022-3697 30 (5) (1969) 1043–1058, https://doi.org/10.1016/0022-3697(69)90359-X.

L. Dobrozhsny, D.L. Mills, Theory of surface optical phonons on reconstructed surfaces, Phys. Rev. B 7 (1973) 1322–1330, https://doi.org/10.1103/PhysRevB.7.1322.

H.J.W. Zandvliet, The Ge(001) surface, Phys. Rep., ISSN: 0370-1573 388 (1) (2003) 1–40, https://doi.org/10.1016/S0370-1573(03)00032-2.

J. Kramers, P. Platzmann, J. Kuk, Atomic structure and vibrational signatures of the structural phase transition of Sn(111) compared to Sn(111), Phys. Rev. B 57 (1998) 4649–4655, https://doi.org/10.1103/PhysRevB.57.4649.

C. Varga, B. Poelsema, H. van Swol, B.S. Swartzentruber, J. Fritsch, H. Zandvliet, Identification of the Au coverage and structure of the Au(111)–(5 × 2) surface, Phys. Rev. Lett. 113 (2014) 086101, https://doi.org/10.1103/PhysRevLett.113.086101.

M. Tabatabaei, M.R. Pederson, Infra-red intensities and Raman-scattering activities within density-functional theory, Phys. Rev. B 54 (1996) 7830–7836, https://doi.org/10.1103/PhysRevB.54.7830.

A.C. Albrect, On the theory of Raman intensities, J. Chem. Phys. 34 (5) (1961) 1467–1484, https://doi.org/10.1063/1.1701032.

M. Walter, M. Moseler, Ab-initio wave-length dependent Raman spectra: Placeck approximation and beyond, J. Chem. Theory Comput. 16 (2020) 576–586, https://doi.org/10.1021/acs.jctc.9b00584.

D. Rappoport, Berechnung von Raman-Intensitaten mit zeitabhängiger Dichte-funktionaltheorie, Ph.D. thesis, Karlsruher Institut für Technologie, 2007.

G. Hajdu, K. Hummer, G. Kresse, J. Furthmüller, F. Bechstedt, Linear optical properties in the projector-augmented wave methodology, Phys. Rev. B 73 (2006) 045112, https://doi.org/10.1103/PhysRevB.73.045112.

J.L. Luo, H. Kong, Identification of the Au coverage and structure of the Au(111)–(5 × 2) surface, Phys. Rev. Lett. 113 (2014) 086101, https://doi.org/10.1103/PhysRevLett.113.086101.

M. Liewehr, B. Hallig, U. Bass, J. Geurts, S. Neufeld, S. Sanna, W.G. Schmidt, E. Speiser, N. Takeuchi, J. Räthel, E. Speiser, N. Esser, J. Schäfer, J. Geurts, Vibrational modes of Ge(111)-(2×8) to Si(111)-(2×2), -(5×5), -(7×7), and -(9×9) with scanning tunneling microscopy, Surf. Sci., ISSN: 0039-6028 167 (1) (1986) 235–247, https://doi.org/10.1016/S0039-6028(86)80414-9.

W. Schmidt, J. Bernholc, Step-induced optical anisotropy of Si(111)H surfaces, Phys. Rev. B 61 (2000) 7604–7608, https://doi.org/10.1103/PhysRevB.61.76040.

C. Hogan, E. Ferraro, N. McAlinden, J.F. McGilp, Optical fingerprints of Si honeycomb chains and atomic gold wires on the Si(111)-(5×2)-Au surface, Phys. Rev. Lett. 111 (2013) 087401, https://doi.org/10.1103/PhysRevLett.111.087401.

W. Mönch, Semiconductor Surfaces and Interfaces, Vol. 26 of Springer Series in Surface Science, 3 edn., Springer, 2001, https://doi.org/10.1007/978-3-642-05003-3.

J. Kim, M.-L. Yeh, F.S. Khan, J.W. Wilkins, Surface phonons of the Si(111)-7×7 reconstructed surface, Phys. Rev. B 52 (1995) 14705, https://doi.org/10.1103/PhysRevB.52.14705.

I. Stich, K. Terakura, B.E. Larson, First-principles finite-temperature characterization of dynamics of the Si(111)-7×7, Phys. Rev. Lett. 74 (1995) 4491, https://doi.org/10.1103/PhysRevLett.74.4491.

I. Stich, J. Kohanoff, K. Terakura, Low-temperature atomic dynamics of the Si(111)-7×7, Phys. Rev. B 54 (1996) 2642, https://doi.org/10.1103/PhysRevB.54.2642.

L. Su, J. Summerlin, Y.-Y. Wu, Complex dynamics of the Si(111)-7×7 surface: total-energy calculations, Phys. Rev. B 68 (2003), https://doi.org/10.1103/PhysRevB.68.201303.R.
G. Santoro, S. Scandolo, E. Tosatti, Charge-density waves and surface Mot insulators for adlayer structures on semiconductors: extended Hubbard modeling, Phys. Rev. B 59 (1999) 1891–1901, https://doi.org/10.1103/PhysRevB.59.1891.

G. Profeta, E. Tosatti, Triangular moitt-hubbard insulator phases of Sn(3\times 3) and SnGe(3\times 3) surfaces, Phys. Rev. Lett. 98 (2007) 086401, https://doi.org/10.1103/PhysRevLett.98.086401.

S. Modesti, L. Patacca, G. Ceballos, I. Vobornik, G. Panaccione, G. Rossi, L. Ottaviano, R. Larciprete, S. Lizzit, A. Goldoni, Insulating ground state of Sn(3\times 3) surface, Phys. Rev. B 83 (2011) 035410, https://doi.org/10.1103/PhysRevB.83.035410.

G. Li, P. Høfner, J. Schäfer, C. Blumenstein, S. Meyer, A. Bostwick, E. Rotenberg, M. Svec, V. Chab, M. C. Tringides, Resolving the coverage puzzle of the Pb/Si(111) interface, Phys. Rev. Lett. 99 (2007) 166103, https://doi.org/10.1103/PhysRevLett.99.166103.

H. Morikawa, I. Matsuda, S. Hasegawa, STM observation of Sn(3\times 3) \sqrt{3}\times \sqrt{3}R30\degree surface, Phys. Rev. B 76 (2007) 205406, https://doi.org/10.1103/PhysRevB.76.205406.

A. E. Escudero, D. M. Goodner, J. S. Okasinski, M. J. Bedzyk, X-ray standing wave analysis of the Sn(3\times 3) \sqrt{3}\times \sqrt{3}R30\degree surface, Phys. Rev. B 70 (2004) 235416, https://doi.org/10.1103/PhysRevB.70.235416.

F. Ronci, S. Colonna, A. Cricenti, G. Le Lay, Evidence of Sn adatoms quantum tunneling at the Sn–Sn(3\times 3) surface, Phys. Rev. Lett. 99 (2007) 166103, https://doi.org/10.1103/PhysRevLett.99.166103.

R. Pérez, J. Ortega, F. Flores, Surface soft phonon and the \sqrt{3}\times \sqrt{3} \times 3 phase transition in Sn(111) and Sn(3\times 3) surfaces, Phys. Rev. Lett. 86 (2001) 237005, https://doi.org/10.1103/PhysRevLett.86.237005.

J. Ortega, R. Pérez, F. Flores, Dynamical fluctuations and the \sqrt{3}\times \sqrt{3} \times 3 transition in Sn(111) and Sn(3\times 3), J. Phys. Condens. Matter 14 (2002) 5979, https://doi.org/10.1088/0953-8984/14/24/307.

B. R. Keesling, M. L. Tegenkamp, D. Lükermann, H. Pfnür, B. Slomski, G. Landolt, J. H. Dil, Fermi surface of Pb/Si(111) and Sn/Si(111) surfaces, Phys. Rev. Lett. 98 (2007) 086401, https://doi.org/10.1103/PhysRevLett.98.086401.

P. E. Blöchl, Projected augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979, https://doi.org/10.1103/PhysRevB.50.17953.

G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186, https://doi.org/10.1103/PhysRevB.54.11169.

K. Fehske, J. Schäfer, N. Esser, W. Richter, J. F. McClure, Surface phonons of the Si(111): in–(4 \times 1) and (8 \times 2) phases, Phys. Rev. B 76 (2007) 205406, https://doi.org/10.1103/PhysRevB.76.205406.

H. Morikawa, I. Matsuda, S. Hasegawa, STM observation of Sn(3\times 3) \sqrt{3}\times \sqrt{3}R30\degree surface at low temperature, Phys. Rev. B 65 (2002) 201308, https://doi.org/10.1103/PhysRevB.65.201308.

A. E. Escudero, D. M. Goodner, J. S. Okasinski, M. J. Bedzyk, X-ray standing wave analysis of the Sn(3\times 3) \sqrt{3}\times \sqrt{3}R30\degree surface, Phys. Rev. B 70 (2004) 235416, https://doi.org/10.1103/PhysRevB.70.235416.

F. Ronci, S. Colonna, A. Cricenti, G. Le Lay, Evidence of Sn adatoms quantum tunneling at the Sn–Sn(3\times 3) surface, Phys. Rev. Lett. 99 (2007) 166103, https://doi.org/10.1103/PhysRevLett.99.166103.

M. E. Dávila, J. Avila, M. C. Asensio, G. Le Lay, J. Ortega, R. Pérez, F. Flores, Phonon dynamics of the Sn(3\times 3) \sqrt{3}\times \sqrt{3} surface, Appl. Surf. Sci. 210 (2001) 3–14, https://doi.org/10.1016/S0169-4332(99)00540-6.

F. Ronci, S. Colonna, A. Cricenti, G. Le Lay, Evidence of Sn adatoms quantum tunneling at the Sn–Sn(3\times 3) surface, Phys. Rev. Lett. 99 (2007) 166103, https://doi.org/10.1103/PhysRevLett.99.166103.

R. Pérez, J. Ortega, F. Flores, Surface soft phonon and the \sqrt{3}\times \sqrt{3} \times 3 phase transition in Sn(111) and Sn(3\times 3), Phys. Rev. Lett. 86 (2001) 237005, https://doi.org/10.1103/PhysRevLett.86.237005.

J. Ortega, R. Pérez, F. Flores, Dynamical fluctuations and the \sqrt{3}\times \sqrt{3} \times 3 transition in Sn(111) and Sn(3\times 3), J. Phys. Condens. Matter 14 (2002) 5979, https://doi.org/10.1088/0953-8984/14/24/307.

B. R. Keesling, M. L. Tegenkamp, D. Lükermann, H. Pfnür, B. Slomski, G. Landolt, J. H. Dil, Fermi surface of Pb/Si(111) and Sn/Si(111) surfaces, Phys. Rev. Lett. 98 (2007) 086401, https://doi.org/10.1103/PhysRevLett.98.086401.

P. E. Blöchl, Projected augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979, https://doi.org/10.1103/PhysRevB.50.17953.

G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186, https://doi.org/10.1103/PhysRevB.54.11169.
E. Speiser et al. / Surface Science Reports 75 (2020) 100480
[280] T.P. Devereaux, R. Hackl, Inelastic light scattering from correlated electrons, Rev. Mod. Phys. 79 (2007) 175–233, https://doi.org/10.1103/RevModPhys.79.175.

[281] H.-T. Kim, B.-G. Chae, D.-H. Youn, S.-L. Maeng, G. Kim, K.-Y. Kang, Y.-S. Lim, Mechanism and observation of Mott transition in VO₂-based two- and three-terminal devices, New Journ. Phys 6 (2004) 52, https://doi.org/10.1088/1367-2630/6/1/052.

[282] G. Grüner, Density Waves in Solids, Frontiers in Physics, Perseus Publishing, Cambridge, 2000.

[283] G. Travaglini, I. Mörke, P. Wachter, CDW evidence in one-dimensional K₀.₃MoO₃ by means of Raman scattering, Solid State Commun., ISSN: 0038-1098 45 (3) (1983) 289–292, https://doi.org/10.1016/0038-1098(83)90483-0.

[284] L. Yu, Solitons and Polaron in Conducting Polymers, World Scientific Publishing, Singapore, 1988, ISBN: 9971-50-053-1, https://www.worldscientific.com/doi/pdf/10.1142/9789814503136_fmatter.

[285] E. Hulpke, J. Lüdecke, The giant surface phonon anomaly on hydrogen saturated W(110) and Mo(110), Surf. Sci., ISSN: 0039-6028 287288 (1993) 837–841, https://doi.org/10.1016/0039-6028(93)91083-2 proceedings of the 8th International Conference on Solid Surfaces.

[286] E. Hulpke, J. Lüdecke, Hydrogen-induced phonon anomaly on the W(110) surface, Phys. Rev. Lett. 68 (1992) 2846–2849, https://doi.org/10.1103/PhysRevLett.68.2846.

[287] H.J. Schulz, Lattice dynamics and electrical properties of commensurate one-dimensional charge-density-wave systems, Phys. Rev. B 18 (1978) 5756–5767, https://doi.org/10.1103/PhysRevB.18.5756.

[288] B. Horovitz, H. Gutfreund, M. Weger, Infrared and Raman activities of organic linear conductors, Phys. Rev. B 17 (1978) 2796–2799, https://doi.org/10.1103/PhysRevB.17.2796.

[289] E. Turi, S. Barriś, Dynamic structure factor of a one-dimensional Peierls system, Phys. Rev. B 43 (1991) 8431–8436, https://doi.org/10.1103/PhysRevB.43.8431.

[290] W. Kohn, Image of the fermi surface in the vibration spectrum of a metal, Phys. Rev. Lett. 2 (1959) 393–394, https://doi.org/10.1103/PhysRevLett.2.393.

[291] H. Schafer, Entkopplung von elektronischer und struktureller Ordnung im stark korrelierten System K₆Mo₉O₃₀, Ph.D. thesis, Universität Konstanz, 2010.

[292] J.P. Pouget, B. Hensson, C. Escribe-Filippini, M. Sato, Neutron-scattering investigations of the Kohn anomaly and of the phase and amplitude charge-density-wave excitations of the blue bronze K₀.₃MoO₃, Phys. Rev. B 43 (1991) 8421–8430, https://doi.org/10.1103/PhysRevB.43.8421.

[293] H. Schäfer, V.V. Kabanov, M. Beyer, K. Biljakovic, J. Demsr, Disentanglement of the electronic and lattice parts of the order parameter in a 1D charge density wave system probed by femtosecond spectroscopy, Phys. Rev. Lett. 105 (2010) 066402, https://doi.org/10.1103/PhysRevLett.105.066402.

[294] C. González, F. Flores, J. Ortega, Soft phonon, dynamical fluctuations, and a reversible phase transition: Indium chains on silicon, Phys. Rev. Lett. 96 (2006) 136101, https://doi.org/10.1103/PhysRevLett.96.136101.

[295] C. González, J. Guo, J. Ortega, F. Flores, H.H. Weitering, Mechanism of the band gap opening across the order-disorder transition of Si(111)(4 × 1)-in, Phys. Rev. Lett. 102 (2009) 115501, https://doi.org/10.1103/PhysRevLett.102.115501.