Surface Structure of Bi(111) from Helium Atom Scattering Measurements. Inelastic Close-Coupling Formalism

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ABSTRACT: Elastic and inelastic close-coupling (CC) calculations have been used to extract information about the corrugation amplitude and the surface vibrational atomic displacement by fitting to several experimental diffraction patterns. To model the three-dimensional interaction between the He atom and the Bi(111) surface under investigation, a corrugated Morse potential has been assumed. Two different types of calculations are used to obtain theoretical diffraction intensities at three surface temperatures along the two symmetry directions. Type one consists of solving the elastic CC (eCC) and attenuating the corresponding diffraction intensities by a global Debye–Waller (DW) factor. The second one, within a unitary theory, is derived from merely solving the inelastic CC (iCC) equations, where no DW factor is necessary to include. While both methods arrive at similar predictions for the peak-to-peak corrugation value, the variance of the value obtained by the iCC method is much better. Furthermore, the more extensive calculation is better suited to model the temperature induced signal asymmetries and renders the inclusion for a second Debye temperature for the diatomic interaction potential.

INTRODUCTION

The electronic density structure of a surface determines its chemical behavior. While on surfaces like platinum, which is widely used as a catalyst, the effects of crystal face, surface steps, and kinks are well-known, more complicated electronic surface structures still lack a detailed treatment. Recently, the (111) surfaces of the semimetals bismuth (Bi) and antimony (Sb) have raised a lot of interest. Not only do they represent the two main ingredients of topological insulators,1,2 but they also both present a fairly strong electronic surface density corrugation despite exhibiting conducting surface states.3,4 The temperature dependence of these peculiar electronic structures may depend on the binding character of adsorbed species remarkably;3,4 thus, it is essential to determine a complete picture of an electronic surface structure before conducting adsorbate experiments on them. Helium atom scattering (HAS) experiments provide a low-energetic, completely nondestructive means of investigation to measure the pure surface properties of materials. The inert neutral helium atoms are already repelled from the electronic density corrugation above the surface, probing only surface effects. Close-coupling (CC) calculations5 provide a significant improvement compared to oversimple approximate methods. While the essential accurate knowledge of the interaction potential requires numerous measurements and a careful analysis, the effort may be worthwhile because the quantum mechanical treatment of the scattering procedure provides far better insight into the scattering processes.

Earlier CC investigations included the Debye–Waller (DW) factor to account for the thermal attenuation of scattering intensities. Heavy materials like bismuth, however, exhibit very low surface Debye temperatures, indicating an extremely fast decay of scattering intensities with the surface temperature. The inclusion of inelastic channels into the standard CC equations7 provides a natural extension within this theoretical framework, and as a result, the attenuation of the diffraction intensities arises automatically. When the number of diffraction channels (elastic and inelastic) is increased, the number of exiting fraction intensities. In this work, we are going to use the iCC equations to extract information about the interaction potential. In general, the number of fitting parameters for this type of scattering is quite high and settles around five in this specific case. For surface temperatures around 300 K, the number of total channels playing a role in...
this scattering is also quite high, typically more than 200. On the other hand, when working on a fixed geometry experimental setup, the whole experimental diffraction pattern is not fitted at once by solving a complete set of iCC equations (up to numerical convergence). Each experimental diffraction peak of the corresponding pattern has to be fitted by solving a complete set of those equations. As a result, the fitting procedure becomes rather cumbersome. To circumvent the expensive high-dimensional fitting procedure, previously fitted eCC potential parameters have been assumed as given and fixed.

**BISMUTH SURFACE STRUCTURE AND EXPERIMENTAL SETUP**

Bulk bismuth, like all of the heavier pnictogens, crystallizes in the rhombohedral A7 structure with two atoms per unit cell (space group R3m). A typical structural property of this crystal structure is the existence of puckered bilayers of atoms perpendicular to the [111] direction, as illustrated in Figure 1a.

The bonding of the atoms within these bilayers is of a strong covalent type, while the interbilayer bonding is closer to a van der Waals type. This is reflected in the relative distances between the layers, as labeled in Figure 1a. Because of this strong contrast in binding energies, bismuth crystals preferably cleave perpendicular to the [111] direction. The topmost layer has been determined to be of this prepared crystal reveals a 6-fold symmetry, as illustrated in Figure 1b. Despite the crystal’s 3-fold symmetry, the Bi(111) surface can be treated as being 6-fold symmetric in low energy HAS experiments. The lattice constant of this hexagonal-like surface structure has been determined to be \( a = 4.538 \text{ Å} \) by LEED and HAS measurements. This hexagonal surface structure leads to two distinguishable high symmetry directions of the crystal surface.

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**THEORETICAL BACKGROUND**

Inelastic Close-Coupling Equations. The CC formalism provides a method for calculating the diffraction intensities of scattering experiments exactly (up to numerical convergence) in the elastic as well as in the inelastic regime. The helium atom is considered to be a structureless and nonpenetrating particle, the one-phonon approximation is assumed, and the surface corrugation is described by a static as well as a dynamic time-dependent contribution. The time-dependent Schrödinger equation for a structureless particle is written as

\[
\frac{i\hbar}{\partial t} \Psi(r, t) = \left[ -\nabla^2 + V(r, t) \right] \Psi(r, t)
\]

where squared wave vector quantities are given in energy units with \( h^2/2m = 1 \), with \( m \) being the mass of the incident particle. The standard notation is also used here where capital letters are for vectors parallel to the surface (2D) and small letters are for vectors in 3D. The gas–surface interaction potential, \( V \), turns out to be dependent on time through the instantaneous position of the surface atoms, \( R + u(R, t) \), with \( u(R, t) \) being the deviation or displacement from the equilibrium position. If this displacement is considered to behave as a Gaussian function within the unit cell, it can be written along each surface degree of freedom as:

\[
u(x, t) = u_{x,0} \exp\left(-x^2/\sigma_x^2\right) \cos \omega t
\]

\[
u(y, t) = u_{y,0} \exp\left(-y^2/\sigma_y^2\right) \cos \omega t
\]

with \( u_{x,0} \) the initial amplitude, \( \omega \) the frequency of the active phonon mode, and \( \sigma_x \) the parameter describing the width of the Gaussian function. As long as the relative displacements \( u \) are small compared to the lattice constant, the interaction potential can be Taylor expanded up to first order (within the so-called single-phonon approximation) as:

\[
V(r, t) \approx V(r) + u(R, t) \cdot \nabla V(r)
\]

From the layer description of lattice dynamics, it is well-known that the \( u \) displacement can be, in general, written as

\[
\begin{align*}
\mathbf{u}(R, t) &= \sum_{Q\nu} A(Q, \nu, T) e^{iQ \cdot R} \cos(\omega \nu T) \\
&= \sum_{Q\nu} A(Q, \nu, T) e^{iQ \cdot R} \cos(\omega \nu T)
\end{align*}
\]
where the amplitude \( A \) includes the phonon polarization vector and the dependence on the surface temperature and \( \omega_0 (Q) \) is the frequency of the surface mode with quantum numbers \((Q, \nu)\). For most practical purposes, only displacements of atoms on the first layer significantly contribute to the interaction potential.

In the Taylor expansion given by eq 3, the zero order or static part of the interaction, \( V(r) \), is evaluated at zero displacements. Considering the periodicity of the lattice surface, this function can then be expanded into a Fourier series as

\[
V(r) = \sum_G V_G(z) e^{G \cdot R}
\]

with \( G \) being the 2D reciprocal lattice vector.

On the other hand, the wave function \( \Psi(r,t) \) has to take into account the double periodicity given by the Hamiltonian, in space and time. Thus, according to the Bloch theorem, \( \Psi(r,t) \) can be expanded as

\[
\Psi(r, t) = e^{-ikz/\hbar} \sum_{G, Q, \nu_0} \Psi_{G\nu_0+Q,\nu_0}(z) e^{i(K+G+Q) \cdot R} e^{i\nu_0 \nu_0(|Q|t)}
\]

where \( n_{Q\nu} \) stands for the number of phonons of the mode \((Q, \nu)\). In this work, we exclusively consider the inelastic effects on the elastic intensities. As commonly known, the Bragg law (for \( Q = 0 \)) is written as

\[
\Delta K = K_f - K_i = G
\]

Moreover, we also assume that only one mode is active in the scattering process and the coupling among phonons is neglected within the harmonic approximation. Thus, we can drop the subindex \((Q, \nu)\) in \( n_{Q\nu} \) for the number of phonons, writing only \( n \). Similarly, for the frequency of the active mode, we can simply write \( \omega \). After substituting eqs 3, 5, and 6 into eq 1, multiplying the resulting expression by \( e^{-i(K+G+Q) \cdot R} \) and then integrating over both time and the area of a single unit cell, one obtains the following set of coupled differential equations for the diffracted waves

\[
\frac{d^2}{dz^2} + k_{G,nz}^2 - V_G(z) \Psi_{G,n}(z)
\]

\[
= \sum_{G' \neq G} V_{G'-G}(z) \Psi_{G',n}(z) + A \sum_{G' \neq G} F_{G'-G}(z) \Psi_{G',n+1}(z) + A \sum_{G' \neq G} F_{G'-G}(z) \Psi_{G',n-1}(z)
\]

(8)

and

\[
\frac{d^2}{dz^2} + k_{G,nz}^2 - V_G(z) \Psi_{G,n+1}(z)
\]

\[
= \sum_{G' \neq G} V_{G'-G}(z) \Psi_{G',n+1}(z) + A \sum_{G' \neq G} F_{G'-G}(z) \Psi_{G',n+2}(z) + A \sum_{G' \neq G} F_{G'-G}(z) \Psi_{G',n}(z)
\]

(9)

where

\[
k_{G,nz}^2 = k^2 - (K_i + G)^2 - n\hbar\omega
\]

is the \( z \) component of the kinetic energy for the \((n, G)\)-diffracted wave and

\[
F_{G-G'}(z) \equiv [i(G - G')V_{G-G'}(z), V_{G-G'}(z)]
\]

is the contribution of the gradient of the interaction potential or vector force field \((V')\) represents the first derivative with respect to \( z \); the first term represents the \((x,y)\) components of the force, and the second one is its \( z \) component.

The iCC equations are solved numerically by imposing the standard boundary conditions given elsewhere. The theory is unitary; that is, the sum of diffraction probabilities (forming the diffraction pattern), for a given incident energy and angle, is equal to 1.

**Inelastic and Elastic Channels: Floquet Blocks.** Within this theoretical scheme, each diffraction channel is then represented by an effective potential formed by \( V_G(z) \) plus the asymptotic energy, given by

\[
(K_i + G)^2 + n\hbar\omega
\]

(12)

and is called an inelastic diffraction channel. Thus, any inelastic event, annihilation or creation, is represented by the transition from the entrance (or specular) channel to one of the channels with \((n - 1)\) or \((n + 1)\). Similarly, the wave functions associated with the discrete spectrum (bound states, labeled by \( \nu \)) of each channel are denoted by \( |K_i + G, n, \nu \rangle \) and those associated with the continuum one (diffracted beams) by \( |K_i + G, n, K_G, n, \nu \rangle \). In the literature, it is also said that the inelastic channels are dressed by the phonon field. The number of channels dressed by a given number of phonons form a block, called a Floquet block. Thus, if only single-phonon scattering is considered, at least three Floquet blocks must be included in the calculation: the blocks dressed by minus and plus one phonon of the active mode and the block dressed by zero phonons or pure elastic channels (those used for an eCC calculation). The number of diffraction channels within a given Floquet block is formed at least by those used to obtain numerical convergence in an elastic CC calculation. Multiphonon contributions of the same active mode are taken into account by including more Floquet blocks—those dressed by two, three, or more phonons by following the staircase structure of eqs 8 and 9 through \( n \pm 1 \).

**Intrablock and Interblock Couplings.** Furthermore, two coupling terms of very different nature are now present: \( V_{G-G'}(z) \) is responsible for the intrablock coupling, and the scalar function

\[
A(T) \cdot F_{G-G'}(z)
\]

(13)

for the interblock one. The latter is responsible for the thermal attenuation of the diffraction intensities (see the second term on the right-hand part of eqs 8 and 9) described many times from a phenomenological viewpoint by a DW factor. In previous publications on the phonon dispersion of the Bi(111) surface, the lowest lying, isolated Rayleigh mode was identified as the shear-vertical mode corresponding to the sole phonon dispersion line in the Debye model. According to the shear-vertical polarization of the suggested mode, the horizontal displacement of the lattice atoms can be neglected, simplifying the force term eq 11 to the vertical term

\[
F_{G-G'}(z) \approx V_{G-G'}(z)
\]

(14)

and consequently the inelastic coupling term to

\[
A(T) \cdot F_{G-G'}(z) \approx A_T \cdot V_{G-G'}(z)
\]

(15)

The average thermal displacement \( A_T(T) \) is related to the effective mean square displacement and has been estimated to be


\begin{equation}
A_x(T) \approx \frac{1}{aQ_0} \sqrt{\frac{384\hbar^2\pi T}{MK_0\Theta_D^2}}
\end{equation}

with \( T \) the actual surface temperature, \( \Theta_D \) the surface Debye temperature, \( M \) the mass of a surface particle, \( a \) the lattice constant, \( k_B \) the Boltzmann constant, and \( Q_0 \) is a fitting parameter for the Gaussian cutoff factor given by \( Q_0 = 2/\sigma \), with \( \sigma \) being the width parameter introduced in eq 2.

**Averaging over Phonon Frequencies.** On the other hand, when solving the iCC equations, frequency-dependent diffraction intensities are obtained, and these have to be averaged by assuming a density of phonons in order to compare with the experimental ones. The corresponding integration over phonon frequencies can be weighted by the Debye spectral density given by

\begin{equation}
\rho(\omega) = \frac{3\omega^2}{\omega_D^3}
\end{equation}

with \( \omega_D \) the Debye frequency. Thus, the final diffraction intensities are due to virtual phonon events only; no real phonon events are taken into account since the corresponding momenta are not involved in Bragg’s law. The term “virtual events” denotes that when the phonon is created in the dynamics it has to be annihilated in order to have a net energy balance equal to zero. The origin of the attenuation in the iCC formalism is precisely due to these virtual phonon events since they are responsible for the appearance of the new inelastic channels. Note that the quadratic dependence on phonon frequency is strictly speaking only valid for the bulk; the surface would be better represented by a linear dependence. However, the quadratic term was chosen since the Debye model that the simulation is compared to is built upon the bulk description of the material. A simulation comparing the intensities using a linear and a quadratic term for the Debye spectral density yielded no mentionable difference for the relative elastic diffraction intensities.

**Debye–Waller Attenuation Factor.** As previously mentioned, an alternative way to obtain diffraction intensities from the eCC equations that can be compared with the temperature-dependent experimental results and iCC calculations is by including a global attenuating factor, the DW factor. By doing this, the unitarity of the attenuated eCC equations is by including a global attenuating factor, the DW factor given by

\begin{equation}
\xi(x, y) = \xi_0 \left( \cos \left[ \frac{2\pi}{a} \left( x - \frac{y}{\sqrt{3}} \right) \right] + \cos \left[ \frac{2\pi}{a} \left( x + \frac{y}{\sqrt{3}} \right) \right] \right)
\end{equation}

with \( \xi_0 \) as the corrugation amplitude. The same corrugation function is, with a different lattice constant, assumed for the Bi(111) surface.

By assuming a corrugated Morse potential written as

\[ V(\mathbf{r}) = D (e^{-2k|z|} - e^{-k|z|}) \]

the intrablock coupling is given by

\[ V_{G-G}(z) = D \frac{\phi_{m,m}^{1/2}}{v_{0,0}^T} e^{-2k|z|} \]

assuming zero parallel momentum transfer to the surface and final angles near the specular angle. In this expression, \( \phi_{m}^{1/2} \) describes the average squared displacement of the atom perpendicular to the surface and \( \Delta k_x \) is the momentum transfer perpendicular to the surface during the scattering event.
\[ \nu_{\kappa,m} = \frac{\sqrt{3}}{2} \frac{a^2}{\pi} \sum_{k=-\infty}^{\infty} I_k(\alpha)(I_{k+n}(\alpha)I_{k-m}(\alpha)) + I_{k-n}(\alpha)I_{k+m}(\alpha) \]  
\hspace{1cm} (24)  

where \( \alpha = 2\kappa_0^2 \). Equation 24 is only exact for a corrugated Morse interaction potential. While modified versions of the interaction potential describe the long-range interaction more accurately, the sole change of \( V_0 \) in eqs 8 and 9 to a hybrid potential poses a certain inconsistency. As the inclusion of inelastic effects seems to eliminate the limitations of the Morse potential to model second-order diffraction intensities, \(^{4,25}\) the usage of the plain Morse potential avoids these inconsistencies while producing excellent results. A more in-depth analysis of a more complicated potential structure calculated numerically from ab initio simulations might further improve the results.

**RESULTS AND DISCUSSION**

**Inelastic TOF and Interaction Potential.** Previous investigations of the He–Bi(111) interaction potential \(^{27}\) revealed three well-defined bound state energies when a 9–3 interaction potential model was used. However, preceding close-coupling studies using various potential shapes on Sb(111) \(^{25}\) suggest that Morse- or Morse-like potential functions are much more suitable for representing the bound state energies of semimetallic surfaces.

To propose a more accurate Morse-like interaction potential, features resulting from inelastic resonance effects in time-of-flight (TOF) spectra were analyzed to identify an additional bound state level at smaller bound state energies. Figure 2 illustrates one of the spectra with an isolated feature originating from the fourth identified bound state as listed in Table 1.

![Figure 2. Time-of-flight spectrum of Bi(111) in ΓM direction at an incident angle of 54°9' and an incident energy of 17.5 meV. The suggested bound state energy level coincides with an observed increase in intensity around an energy transfer of +3 meV. L1 and RW indicate the suggested positions of the longitudinal resonance as well as the Rayleigh branch, while the features marked with \((n,m)\) label possible inelastic bound state resonance positions of the reciprocal vector \((n,m)\) with the bound state level \(l\).](image)

The last line of Table 1 lists the obtained bound state energy levels of the fitted first Fourier coefficient of the corrugated Morse potential

\[ V^{M}_{00}(x) = D[e^{-2xz} - 2e^{-xz}] \]  
\hspace{1cm} (25)  

with a potential depth \( D \) of \((7.898 \pm 0.126) \text{ meV} \) and a potential stiffness \( \kappa \) of \((0.884 \pm 0.024) \text{ Å}^{-1}\). With the highest identified bound state level much closer to the threshold, the attractive part of the fitted potential may be considered to describe the real interaction more accurately.

**eCC and iCC Analysis of Bi(111).** Previous investigations\(^3\) treated the electron density corrugation of the Bi(111) surface from the helium atom scattering (HAS) data using the GR method and the Eikonal approximation, including the Beeby correction. Thermal attenuation effects were included using the DW factor, with two different surface Debye temperatures to account for the two different attenuation features obtained from the measurements. Because the surface Debye temperature is an intrinsic surface property, given by the maximum energy of the phonons in the Debye model, it seems unsatisfactory to include a second temperature in order to account for the different attenuation of the scattering channels. Thus, all of the diffraction intensities issued from the eCC calculations plus the DW factor (eCC+DW) were achieved using only one surface Debye temperature \( \Theta_D = 85 \text{ K} \).

As mentioned previously, in order to reduce the number of fitting parameters in the CC calculations, only the surface corrugation amplitude was considered in the eCC calculations, while in the iCC calculations the parameter space was extended to include also the Gaussian cutoff value \( Q \). All six angular diffraction spectra (three temperatures at the two distinguishable high-symmetry directions \( \Gamma \overline{M} \) and \( \Gamma \overline{K} \)) were fitted separately using both methods. In all cases, the overall deviation of the measured diffraction intensities from the calculated intensities

\[ \sigma = \frac{1}{N} \sum_{n=1}^{N} (I_n^{\text{calc}} - I_n^{\text{exp}})^2 \]  
\hspace{1cm} (26)  

with \( N \) being the total number of scattering intensities considered per fit was minimized. The optimization algorithm is terminated after a relative accuracy of 0.1% in all of the considered parameters and conditions.

Figure 3 displays the experimental diffraction intensities as well as the best-fitting eCC + DW (red stars) and iCC results (blue downward triangles). To obtain comparable values, the experimental diffraction peak areas were normalized to their respective specular peak area for each spectrum separately. As can be seen in both directions, but especially at the high-temperature measurement in the \( \overline{\Gamma}K \) direction, the iCC method can almost perfectly account for the emerging asymmetry at varying temperatures, a feature that is vastly impossible for DW-attenuated features. In Table 2, for comparison, the corrugation amplitudes averaged over the three measured surface temperatures for each high symmetry direction given in percentage of the lattice length are listed for both applied calculation methods.

The corrugation amplitude values calculated by both methods are significantly lower than the ones obtained by approximate methods\(^3\) with the GR method assuming around
Angular scans in different surface temperatures. Upper panel: Angular scans in ΓM direction at three different surface temperatures. Lower panel: Angular scans in ΓK direction at three different surface temperatures.

Figure 3. Measured and calculated diffraction peak intensities in both distinguishable lattice directions at three surface temperatures and a beam energy of 17 meV. Black dots signify measured peak areas, red stars signify calculated peak intensities using elastic close-coupling with a DW attenuation, and blue downward triangles signify calculated peak intensities using the inelastic close-coupling approach. The “order” of the scattering peak refers to the number of reciprocal lattice vectors needed when fulfilling the Bragg condition (eq 7). Upper panel: Angular scans in ΓM direction at three different surface temperatures. Lower panel: Angular scans in ΓK direction at three different surface temperatures.

Figure 4. Natural logarithm of the calculated intensities divided by the elastic (unattenuated) specular intensity. Left panel: Attenuation of the specular contribution in both high-symmetry directions. The green line corresponds to a fit of a simple DW-like attenuation with a Debye temperature of ΘD = 85.9 K. Right panel: Attenuation of the calculated first-order diffraction peaks in both high-symmetry directions. The parallel but shifted behavior confirms a DW-like attenuation of the diffraction peaks with the same Debye temperature as for the specular.
as on the other side, enabling the iCC calculation with its higher adaptability due to the inclusion of inelastic contributions to also model some of the experimentally encountered peak asymmetries as for example in the 400 K surface temperature measurement in the direction depicted in Figure 3. Obviously, there are other experimental sources of asymmetry, as, for example, sample alignment or the changing visible surface area from the detector while rotating the sample. An extension of the coupling calculations, including a complete treatment of the overall force equation and the correct promoting of the iCC method into a remarkable tool for simulating effects of inelastic scattering contributions in temperature dependent measurements. A further, essential advancement will be the inclusion of fine phonon momentum in the iCC calculations, extending the Bragg condition to $K_n - K_f = G + Q$. A so-enhanced inelastic scattering code could predictably be used to model the experimental time-of-flight spectra and extract information about the mode-specific electron–phonon interaction on conducting surfaces. Using the inelastic close-coupling approach to simulate the scattering from surfaces with finite temperatures clearly renders the inclusion of an additional surface Debye temperature futile. By not being bound to an exponential attenuation characteristic, the method is more adaptive and thus better suited to describe the temperature-dependent scattering behavior.

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**Notes**

The authors declare no competing financial interest.

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