Ultrafast electron diffraction from a Bi(111) surface: Impulsive lattice excitation and Debye–Waller analysis at large momentum transfer

I. INTRODUCTION

Bismuth is a prototypical model system for studies of laser induced energy transfer from an excited electron system to the lattice system in the time domain. In its most common form, Bi exhibits the \( \alpha \)-arsenic or A7 structure and is a semimetal with the conduction band slightly lower in energy than the valence band. The charge carriers are holes at \( \Gamma \) point and electrons at \( \text{L} \) point in the Brillouin zone. The almost vanishing density of states at the Fermi energy results in a low number of free carriers of \( 10^{17} \)–\( 10^{19} \) cm\(^{-3}\). This makes this material very sensitive to optical excitations as changes in the electron occupation affects the potential energy surface and trigger atomic motion through displacive excitation. Bismuth is subject to a Peierls distortion which breaks the translational symmetry along the (111) direction. The crystal basis consists of two Bi atoms: atom 1 on an undistorted lattice site and atom 2 at a position slightly displaced from the center along the body diagonal of the unit cell. This equilibrium structure, in particular, the distance of the two atoms of the basis, can easily be perturbed by electronic excitation. When the distance is changed by an ultrafast displacive excitation, the Bi atoms perform a damped oscillation along the body diagonal. This mode of coherent atomic motion represents a symmetric \( \text{A}_{1g} \) optical phonon mode of the crystal.

Depending on the degree of fs (femtosecond)-laser optical irradiation, vastly different time constants for the excitation process of the Bi lattice were observed. Strong excitation with fluences of more than 6 mJ/cm\(^2\) generates so many electron hole pairs that this causes a rapid change in the potential energy surface resulting in nonthermal melting. For fluences of 18 mJ/cm\(^2\), the electronic acceleration of the atomic motion occurs as fast as 190 fs, resulting in ultrafast melting, destruction of the Bi-film, and a coherent \( \text{A}_{1g} \) phonon mode is not observed. For fluences lower than 6 mJ/cm\(^2\), the lattice response is reversible, the coherent \( \text{A}_{1g} \) optical phonon mode is excited, and the bond softening occurs which results in an inverse Peierls transition. Subsequently, the lattice is heated on slower time scales of 2–4 ps through energy transfer from the electron system to the lattice by electron phonon coupling and anharmonic coupling of the \( \text{A}_{1g} \) mode to acoustic phonons. The vibrational excitation of the surface atoms is even slower: thermal motion of the Bi surface atoms sets in on a timescale of 12 ps and has been attributed to the weak coupling between bulk and surface phonons.

Due to its high-atomic mass and weak bonds (the melting temperature is 271 °C), bismuth exhibits a low-Debye temperature of \( \Theta_D = 112 \text{ K} \) and thus a large vibrational amplitude of the thermal motion. These large displacements make Bi an ideal model system to
study lattice dynamics upon ultrashort optical excitation by means of diffraction techniques.

Here, we present a study of the lattice response of a Bi(111) surface upon fs-laser excitation. We analyze the lattice excitation of the surface atoms through time-resolved reflection high-energy electron diffraction (RHEED). Using the Debye–Waller effect, the onset of atomic motion was directly accessible in earlier studies through the transient intensity changes in the diffraction patterns. Electron diffraction allows for a large momentum transfer due to the possible large scattering angles which result in large intensity changes. Employing all detected diffraction spots of the RHEED pattern for the analysis provides the variation of the momentum transfer $\Delta k$ of diffraction, i.e., a wide range of parallel $k$ and vertical $k_z$ momentum transfers are available all at once. Such analysis is reported here.

The grazing incidence of the probing electrons ensures the necessary surface sensitivity and only the topmost bilayer of the Bi film contributes to the RHEED pattern. The excitation of the surface lattice is followed by means of the Debye–Waller effect $I/I_0 = \exp(-(u \cdot \Delta k)^2)$ with the vibrational amplitude $u$ of the atoms, the momentum transfer $\Delta k$, and the stationary sample.

If the intensity drop $\Delta I(t) = 1 - I(t)/I_0$ is not too large, i.e., $\Delta I(t) < 0.2$, then the intensity evolution $I(t)/I_0$ can linearly be converted with an error of less than 6% in the time constant to a transient change in vibrational amplitude $u(t)$ applying the linear expansion of the exponential function. This linear expansion, however, becomes inapplicable for intensity drops $\Delta I(t) > 0.2$ which easily occurs for systems with a low-Debye temperature, strong excitation, or diffraction at large momentum transfer $\Delta k$. Then, the intensity $I(t)$ decays with a time constant which becomes significantly shorter with the increase in the intensity drop $\Delta I(t)$.

Here, we used RHEED spots on three different Laue circles, i.e., with different $k_i$ and $k_f$, and various laser pump fluences for the excitation of the Bi(111) film in order to analyze the lattice dynamics of the Bi(111) surface. The nonlinearity of the exponential function causes the decrease in the time constant $\tau_{int}$ for the decay of RHEED spot intensity from 11 ps to 5 ps with the increase in the laser fluence $\Phi$ and the increase in the momentum transfer $\Delta k$. Irrespective of this large variation of $\tau_{int}$, we obtain a time constant of 12 ps for the heating of the bismuth surface which is independent of the level of excitation.

II. EXPERIMENTAL SETUP AND METHODS

A. Experimental setup

The time-resolved RHEED experiments are performed under ultrahigh vacuum conditions at a base pressure below $2 \times 10^{-10}$ mbar. A scheme of the experimental laser pump–electron probe setup is shown in Fig. 1. An amplified Ti:sapphire laser system delivers laser pulses with a central wavelength of 800 nm, a duration of 50 fs, and a pulse energy of 0.5 mJ at a repetition rate of 5 kHz. The third harmonic of the fundamental generates electron pulses via photo electron emission in a back-illuminated transparent gold plate, and the electron pulse is accelerated to a kinetic energy of 26 keV and is diffracted at the sample under grazing incidence. The diffraction pattern is detected by an MCP amplifier with a phosphor screen and recorded by a CCD camera. The 80%-part of the initial laser pulse is used to excite the sample under normal incidence. For compensation of the velocity mismatch and to ensure—over the entire sample—temporal and spatial overlap with zero time delay of probing electrons and pumping laser pulse, the pumping laser intensity pulse front is tilted by a grating in a 4f setup. The time delay between laser pump pulse and electron probe pulse is varied by an optomechanical delay line.

The grazing incidence of the electrons leads to a systematic change in the arrival times of the electrons across the sample. This so-called velocity mismatch of pumping laser pulse and probing electron pulse limits the temporal resolution to a few 10 ps. To compensate this effect and to ensure constant time delays across the sample, the pumping laser pulse intensity front is tilted by an angle of $7^\circ$ as described in detail in Ref. 31.

Two different sample systems were in-situ prepared and studied: few nm thick epitaxial Pb islands on Si(111) and a 8 nm thin epitaxial Bi(111) film grown on a clean Si(111)–(7 × 7) reconstructed...
with the Heaviside step function \( \Theta(t) \), the maximum intensity drop \( \Delta I_{\text{max}} \) and the decay time constant \( \tau_{\text{int}} \) for the intensity. The experimental decay time constant for the intensity of the (00)-spot of the Pb(111) islands on Si(111) is \( \tau_{\text{int}} = 3.0 \pm 0.4 \, \text{ps} \). The fit is shown as a solid line. Thus, the temporal resolution of the time resolved RHEED experiment at 26 keV is better than 3 ps.

C. Diffraction geometry

The Debye–Waller effect depends on the vector of momentum transfer \( \Delta k_{ij} \) of the specific diffraction spot \((k,l)\). Therefore, the precise knowledge of the diffraction geometry and the resulting momentum transfers \( \Delta k_{ij} \) of diffraction spots of order \((k,l)\) is indispensable. A scheme of the diffraction geometry in RHEED is shown in Fig. 3. The incident electrons with an initial momentum of \( k_0 \) define the radius of the Ewald sphere and the origin of the reciprocal lattice. The diffracted electrons have undergone a momentum transfer of \( \Delta k_{ij} = k_0 - k_i \), which can be separated into a component normal to the surface \( \Delta k_{ij,L} \) and components parallel to the surface \( \Delta k_{ij,S} \) and \( \Delta k_{ij,P} \).

For the 0th order Laue circle \((L_0)\), the momentum transfer in \( x \)-direction is zero and increases by one parallel reciprocal lattice distance from Laue circle to Laue circle. The second component parallel to the surface \( \Delta k_y \) is oriented normal to the plane spanned by the initial and specular beams.

Figure 4 shows the diffraction pattern of the Bi(111)-film grown on Si(111) taken at an electron energy of 26 keV, a grazing angle of incidence of 3.4°, and a static sample temperature of 90 K. The momentum transfer is determined for all diffraction spots from diffraction geometry and reciprocal lattice constants. The diffraction pattern is shown in units of \( \Delta k \) (left axis) and \( \Delta k \) (right axis). \( \Delta k_x \) increases with the order of Laue circles (dashed lines). Here, the (00)-rod is not in the center of the Laue circle because the incident electrons exhibit an azimuth angle \( \theta \) of 1° from the [112] direction. The values for \( \Delta k_x \) cover the range from 7 to 22 Å⁻¹. The momentum transfer \( |\Delta k_y| \) parallel to the surface is below 8 Å⁻¹ for all observed spots. Since \( \Delta k_x > |\Delta k_y| \), our experiment is mainly sensitive to a change in the vibrational amplitude perpendicular to the surface.

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**FIG. 2.** Impulsive heating of epitaxial lead islands on Si(111) at \( T_0 = 90 \, \text{K} \). The normalized intensity of the (00)-spot is plotted as function of the time delay between pump and probe pulse. The data are fitted with an exponential decay function (solid line). The time constant \( \tau_{\text{int}} \) was found to be 3.0 ps. The diffraction pattern was taken at an electron energy of 26 keV with a grazing angle of incidence of 3.4°.

**FIG. 3.** Scheme of momentum transfer in RHEED adopted from Ref. 53. The incident electrons have a momentum \( k_0 \) and are diffracted at the surface of the sample. The origin of reciprocal space is marked by (000). The position of the diffraction spots on the screen is determined by the projection of the intersection of the lattice rods with the Ewald sphere. \( L_0 \) indicates the different orders of Laue circles.
III. RESULTS AND DISCUSSION

Time-resolved RHEED measurements were performed on an 8 nm thin Bi-film on Si(111). The base temperature of the sample was \( T_0 = 90 \) K and the incident pump laser fluence \( \Phi \simeq 1.4 \, \text{ml/cm}^2 \). The intensity of all diffraction spots is analyzed as a function of time delay. In Fig. 5(a), the intensity evolution is exemplarily shown for diffraction spots on the three Laue circles: the (00)-spot, the (10)-spot, and the (20)-spot. All diffraction spots show an intensity drop that can be described by an exponential decay function. The intensity drop is caused by the Debye–Waller effect. The minimum intensity is reached after \( \sim 40 \) ps. Cooling of the thin film occurs via thermal transport to the Si substrate on a timescale of 500–1000 ps \([2,28]\) and therefore cannot be observed on the timescale of 50 ps after excitation. The intensity decay \( I(t)/I_{0} \) of the three diffraction spots in Fig. 5(a) scales with the squared momentum transfer that rises from 86.5 \( \AA^{-2} \) for the (00)-spot to 472 \( \AA^{-2} \) for the (20)-spot. The time constant obtained from the exponential fit decreases from 11.5 ps for the (00)-spot to 5.4 ps for the (20)-spot. To clearly illustrate the difference of the time constants, the normalized intensity drop \( \Delta I(t) \) is plotted in Fig. 5(b).

In earlier works, the transient intensity of ultrathin hetero films was directly converted into a temperature curve employing a stationary calibration measurement.\([22,26]\) Here, we analyze the transient spot intensity without such conversion. For simplicity, we apply the Debye model in the high-temperature regime \((T \gg \Theta_{\text{surf}})\) and assume an isotropic MSD \((\langle x'^2 \rangle)\) proportional to the temperature

\[
\langle x'^2 \rangle = \frac{3h^2T}{MkB_{\text{surf}}^2},
\]

where \( \Theta_{\text{surf}} \) is the effective surface Debye temperature in the framework of individual harmonic oscillators \([\Theta_{\text{surf}} = 47 \, \text{K for the Bi(111) surface}] \) and \( M \) is the atomic mass of Bi. We also assume an exponential increase in MSD, i.e., an exponential rise in temperature \( T(t) \) to a maximum temperature \( T_0 + \Delta T_{\text{max}} \), with a time constant \( \tau_T \),

\[
T(t) = T_0 + \Delta T_{\text{max}} \cdot \Theta(t)(1 - \exp(-t/\tau_T)).
\]

The intensity is

\[
I(t)/I_{0} = \exp \left[ -z\Delta T_{\text{max}} \cdot \Theta(t)(1 - \exp(-t/\tau_T)) \right],
\]

with \( z = h^2/\hbar k_{\text{surf}} \). For small values of \( z\Delta T_{\text{max}} \), we can safely use a linear approximation of the exponential because the higher order terms in the expansion are negligibly small,

\[
I(t)/I_{0} \approx 1 - z\Delta T_{\text{max}} \cdot \Theta(t)(1 - \exp(-t/\tau_T)).
\]

With this approximation, the maximum intensity drop is \( \Delta I_{\text{max}} = z\Delta T_{\text{max}} \) and the time constant \( \tau_{\text{int}} \)—as experimentally determined from the transient intensity decay—is almost the same as \( \tau_T \) from the temperature curve. The question arises up to what arguments \( z\Delta T_{\text{max}} \) we can use the linear approximation?

We modeled the intensity to obtain the time constant \( \tau_{\text{int}} \) in dependence of the intensity drop \( \Delta I_{\text{max}} \). An exponential temperature rise with a time constant of \( \tau_T = 12 \) ps [see Fig. 6(a) and observed in Ref. 16] is converted into the corresponding intensity \( I(t) \) using Eq. (6). \( I(t) \) is plotted in Fig. 6(b) as a function of the time delay for 5 different values of \( z\Delta T_{\text{max}} \) (solid lines) and fitted with an exponential decay function as given by Eq. (3) (dashed lines). For small values \( z\Delta T_{\text{max}} = 0.2 \), the calculated intensity \( I(t) \) exhibits almost the same behavior like \( T(t) \) and is well described by the fit function [Eq. (3)].

The intensity drop \( \Delta I_{\text{max}} \) is \( \leq 18\% \) and the time constant obtained from the exponential fit (dashed line) \( \tau_{\text{int}} = 11.3 \) ps deviates only by 6% from \( \tau_T \).

With the increase in the values for \( z\Delta T_{\text{max}} \), however, the time constant obtained from the exponential fit \( \tau_{\text{int}} \) (dashed lines in Fig. 6) decreases. In the right panel of Fig. 6, the fitted time constant \( \tau_{\text{int}} \) is plotted as a function of the intensity drop \( \Delta I_{\text{max}} \). For \( \Delta I_{\text{max}} \)}
approaching unity, i.e., drop to intensity to almost zero, the time constant $t_{\text{int}}$ decreases to 3 ps and less. We therefore have to expect strongly varying experimental time constants $t_{\text{int}}$ depending on the degree of excitation ($\Delta T_{\text{max}}$) or momentum transfer ($\sigma$). The varying time constants of 5.4–11.5 ps obtained for the different orders of Laue circles shown in Fig. 5 are thus explained by the correlation of $\Delta T_{\text{max}}$ and $t_{\text{int}}$ as shown in Fig. 6(c). The correct time constant of the temperature rise $T_{\text{r}}$ can only be found by extrapolation to $\Delta T_{\text{max}} = 0$. Therefore, under our diffraction conditions at large momentum transfer $\Delta k$ and large intensity drop $I_{\text{int}}$, the time constants $t_{\text{int}}$ can be much shorter than $T_{\text{r}}$. In the following, we perform a thorough Debye–Waller analysis in order to prove that the preconditions for such analysis are still valid.

From the change in the spot intensity, we obtain information about the change in the MSD,

$$\ln(I(T)/I_{0}) = 1/3\Delta k^2 \left( \langle u^2(T) \rangle - \langle u^2_{0} \rangle \right). \quad (8)$$

From the kinematic diffraction theory,36,37 we expect a linear dependence of the negative logarithm of the intensity $\ln(I(T)/I_{0})$ as a function of $\Delta k^2$ with a y-axis intercept equal to zero [Eq. (8)]. The slope $-d[\ln(I(T)/I_{0})]/d(\Delta k^2)$ is equal to one third of the change in the MSD $\Delta \langle u^2(T) \rangle = \langle u^2(T) \rangle - \langle u^2_{0} \rangle$ or, if the effective surface Debye temperature $\Theta_{\text{surf}}$ is known [here $\Theta_{\text{surf}} = 47 K$], proportional to the temperature rise $\Delta T_{\text{max}}$, respectively. Figure 7 depicts $-\ln(I_{\text{int}}/I_{0})$ for all diffraction spots plotted as a function of the squared momentum transfer $\Delta k^2$. The value $I_{\text{int}}$ is the minimum intensity obtained from the fit for the maximum transient temperature. The expected behavior for kinematic diffraction theory and isotropic vibrational motion is plotted as the dashed line. The data are, however, better described by a linear fit with a y-axis intercept $> 0$. Such positive intercept was also observed in transmission electron diffraction experiments40–42 and is caused by multiple scattering effects. The offset observed in transmission electron diffraction was found to be proportional to the temperature change as well and is explained by dynamical two beam diffraction theory.

The scatter of the data in Fig. 7 and the large variation of the intensity of the diffraction spots in Fig. 4 are attributed to multiple scattering effects. Through the fitting of the Debye–Waller drop for all the 14 analyzed diffraction spots, many of these dynamic scattering effects are averaged out and we can apply a kinematic analysis of the
Debye–Waller effect. We also did not find any systematic deviations as a function of parallel $\Delta k_1$ or vertical $\Delta k_L$ momentum transfer. This justifies the pre-assumption of an isotropic thermal motion. The present data do not provide insight into any potential non-equipartition in parallel or vertical vibrational amplitude. Finally, we obtain a change in the MSD at $t = 38$ ps that is $\Delta(\langle u^2 \rangle) = 8.8 \times 10^{-3}$ Å$^2$.

To obtain information about the change in MSD $\Delta(\langle u^2 \rangle)$ as a function of time, we performed a Debye–Waller analysis same as in Fig. 7 for every time delay step during a measurement. In Fig. 8, $\Delta(\langle u^2 \rangle)$ and the intercept (inset) are plotted as function of the time delay. The change in MSD $\Delta(\langle u^2 \rangle)$ is a measure for the transient temperature $T(t)$ and is fitted by an exponential function with a time constant of $(12.7 \pm 1.3)$ ps. Due to the noise and large error bars the intercept as a function of time was fitted with this fixed time constant of $12.7$ ps (inset of Fig. 8). With the surface Debye temperature $\Theta_{D,\text{surf}} = 47$ K, the maximum change in MSD for $t \to \infty$ is converted to an asymptotic temperature change in $\Delta T_{\text{max}} = 54$ K.

A. Variation of pump fluence

The intensity drop $\Delta I_{\text{max}}$ depends on the absorbed energy that was changed by varying the pump fluence. In Fig. 9, the intensity as a function of the time delay is plotted for three diffraction spots (same as in Fig. 5) and four different pump fluences $\Phi$ between 0.4 and 2 mJ/cm$^2$. The intensity drop $\Delta I_{\text{max}}$ becomes larger with the increase in the pump fluence for all diffraction spots. The (00)-spot ($\Delta k^2 = 86.5$ Å$^{-2}$) shows only a weak variation of $\tau_{\text{int}}$ from 11.7 to 10.7 ps upon increasing pump power. The intensity decay is still in the regime of the linear approximation and the maximum error of the time constant is <10%. For the (10)-spot ($\Delta k^2 = 295$ Å$^{-2}$), a significant reduction of the time constant $\tau_{\text{int}}$ to 9.1 ps can already be observed. The (20)-spot ($\Delta k^2 = 472$ Å$^{-2}$) exhibits intensity drops $\Delta I_{\text{max}}$ up to 90% and $\tau_{\text{int}}$ becomes shorter by a factor of more than 2 for the highest pump fluence of 2 mJ/cm$^2$: a time constant of $\tau_{\text{int}} = 5.3$ ps is observed.

For each pump fluence, a Debye–Waller analysis same as in Fig. 7 was performed for the minimum intensity $I(T_{\text{max}})$ obtained from the exponential fit. The slope of the Debye–Waller analysis averaged over all spots is plotted as a function of pump fluence in Fig. 10. The slope rises linear with the pump power. Thus, the change in the mean square displacement $\langle u^2 \rangle$ as well as the change in temperature rises linear with the fluence.

FIG. 9. Time resolved measurements were performed with different incident pump fluences between 0.4 and 2 mJ/cm$^2$. The intensity is plotted as a function of the time delay for three diffraction spots. The momentum transfer increases from (a) to (c). Data are fitted with an exponential decay function (solid lines).

FIG. 10. For each pump power, the slope $\Delta T_{\text{max}} = -\ln(I(T_{\text{max}})/I_0)$ over $\Delta k^2$ was determined same as in Fig. 7. The slope rises linear with the pump power. Thus, the change in the mean square displacement $\langle u^2 \rangle$ as well as the change in temperature rises linear with the fluence.
was employed to follow the onset of vibrational motion under conditions comparable to our incident laser fluences.\(^{16}\) The Debye–Waller effect is sensitive to \(\Delta T\) and thus less sensitive to optical phonons.\(^{52}\) Because optical phonons at the same energy density exhibit a smaller vibrational amplitude than low-frequency acoustic phonons, we would also expect a delayed drop of intensity as the Debye–Waller effect is sensitive to \(\Delta u^2\) and thus less sensitive to optical phonons.\(^{53}\) Variations of the strength of anharmonic coupling by changes in the sample temperature or manipulation of the electronic surface state are promising routes for future clarification of the mechanism of lattice excitation.\(^{54}\)

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