Ordinary and supernumerary resonant scattering of low energy electrons from the BiCu$_2$(111) surface alloy

To cite this article: Bene Poelsema et al 2017 New J. Phys. 19 013024

View the article online for updates and enhancements.

Related content
- Atomic beam diffraction from solid surfaces
  Daniel Farias and Karl-Heinz Rieder
- Quantum well structures in thin metal films: simple model physics in reality?
  M Milun, P Pervan and D P Woodruff
- LEED and DLEED as modern tools for quantitative surface structure determination
  K Heinz
Ordinary and supernumerary resonant scattering of low energy electrons from the BiCu$_2$(111) surface alloy

Bene Poelsema$^{1,2}$, Michael S Altman$^3$, Raoul van Gastel$^1$, Harold J W Zandvliet$^1$ and Arie van Houselt$^1$

1 Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
2 Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People’s Republic of China
3 Author to whom any correspondence should be addressed.

E-mail: b.poelsema@utwente.nl

Keywords: resonant scattering, LEEM, VLEED

Abstract
Electron intensity versus energy curves from the ordered substitutional BiCu$_2$(111)-surface alloy, obtained with low energy electron microscopy (LEEM), show distinct unexpected intensity dips under normal incidence conditions. The dips above 10 eV are found to be characteristic of ordinary resonant scattering of electrons. Their positions represent resonant scattering into image potential states, involving scattering along $\mathbf{G}_{10}$ and $\mathbf{G}_{11}$ reciprocal lattice vectors. A detailed analysis of additional specular intensity dips at energies below 10 eV demonstrates that these originate from supernumerary resonant scattering, now also along lower symmetry directions, that should be forbidden in this energy range for the perfect crystal. LEEM is highly sensitive to detect these often neglected features which, if not properly disentangled or discarded, hamper its potential to extract the rich information about atomic positions and unoccupied electronic states encoded in very low energy electron scattering.

Introduction
Electron diffraction intensities at very low energies in low energy electron microscopy (LEEM) contain rich local information on the atomic positions and unoccupied electronic states [1–3]. In order to quantitatively decode this information it is crucial to disentangle these intensities from possibly interfering effects. One such effect, obvious but often overlooked, is resonant scattering, which is well documented in He atom scattering but less well understood in electron scattering. Four decades after the discovery of the quantum nature of electrons [4] and He atoms [5], it became clear that the same quantum nature enables a detailed probing of the attractive parts of the potentials that govern the interaction of these particles with surfaces of single crystals. For thermal energy He atom scattering (TEAS) an early theoretical study by Cabrera et al [6] predicted that resonant scattering, in TEAS often referred to as bound state resonances [7], should exist. Minima (sometimes even maxima) could be observed in intensity versus scattering angle at a fixed angle of incidence, specular intensity versus angle of incidence, or intensity versus energy traces. Resonant scattering can be observed when the following conditions are fulfilled:

$$E_{fi} = E_i + \varepsilon_n \quad \text{and} \quad k_f - k_i = \mathbf{G}_{i-f},$$

where $i$ and $f$ refer to initial and final states of the diffracting particles with their energy and wave vectors given by $E$ and $k$, respectively. The wave vectors $k_i$ and $k_f$ are connected by an arbitrary vector of the sample’s reciprocal lattice $\mathbf{G}_{i-f}$. $\varepsilon_n$ is the binding energy of the nth state relative to the vacuum level in the attractive potential well of the diffracting particles in front of the surface. In the case of He, this potential is defined by Van der Waals type interactions and its depth is of the order of several meV. For the case of thermal atoms, it is added that bound state resonances are typically observed for surfaces with high corrugation, such as alkali-halides. Probably the best documented experimental results were published for He diffraction from graphite [7] and from LiF(001) surfaces [8, 9].

© 2017 IOP Publishing Ltd and Deutsche Physikalische Gesellschaft
Several years after Cabrera, Celli, and Manson’s seminal work for TEAS [6], Echenique and Pendry predicted that it should be possible to observe bound state resonances in low energy electron diffraction (LEED) as well [10]. Shortly thereafter, McRae [11] demonstrated that indeed bound state resonances can be detected in electron diffraction. We emphasize that a lot of confusion has arisen about the nature of bound state resonances in LEED. They should not be confused with the so-called surface states, which occur on (111) faces of, e.g., Cu, Ag, Au and Ni where a parabolic energy band exists in the gap of the surface projected density of states. Here we consider image states, i.e. energy levels inside the potential well of an electron above a metal surface due to image forces. These states reside typically less than one eV below the vacuum level, thus far above the Fermi level, and, hence, they are unoccupied. They also must not be confused with Gundlach states [12, 13] reported in scanning tunneling spectroscopy. Gundlach states are electron standing waves, which become available when the STM-tip, operated in the field emission regime, gets very close to a metal surface. In contrast, the pure image states are a property of the macroscopic surface and are sometimes called Rydberg states for obvious reasons.

Image potential states that underlie resonances in electron diffraction attract lately renewed attention in two-photon photo-emission studies. Here the first photon promotes an electron from the conduction band into one of the image potential states below the vacuum level. After a selected delay time, a second photon is sent to eject the excited electron into vacuum with a well-defined kinetic energy. Note that the individual photons have insufficient energy to eject electrons directly from the conduction band into vacuum [e.g., 14, 15]. From a variation of the delay time, the lifetime of the electrons in their excited states can be determined and these are typically several tens to over hundred fs [16].

Clear evidence for the resonant electron scattering via image potential states has been derived from high resolution electron loss spectra [17, 18]. Owing to the high resolution capability in these experiments, sharp features which fulfill the conditions set by equation (1) were detected.

**Experimental**

In our experiments we use a mechanically polished Cu single crystal, aligned to the (111) crystallographic direction with an accuracy of approximately 0.1° [19], manufactured by Surface Preparation Laboratories. Further preparation steps included repeated cycles of Ar⁺ ion bombardment and annealing. After this process LEEM images reveal large defect-free terraces. Bismuth on Cu(111) forms a variety of sometimes coexisting phases, which have been studied in great detail by means of diffraction techniques [20]. For an accurate temperature measurement we follow the process described in [21], which exploits the rich phase diagram of Bi/Cu(111) [21–23]. For this study we prepare the ordered (√3 × √3)R30° substitutional BiCu₂ alloy (in the following referred to as √3-BiCu₂ structure), maximal at an ideal coverage of 1/3. Bismuth was vapor phase deposited from a Knudsen cell onto the Cu(111) surface, kept at 630 K. The ideal coverage was established by interrupting the deposition exactly at the maximum intensity of the √3 diffraction peaks of the √3-BiCu₂-phase. In this situation, all Bi atoms ideally occupy only one of the three equivalent sub-lattices of the hard hexagon model while the other two are unoccupied [24–26]. The resulting sharp diffraction peaks suggest a high degree of ordering. In fact the diffraction pattern is quite mundane since it only shows the √3 peaks without any evidence for broadening, etc. The optimum Bi coverage for the √3-BiCu₂ coincides exactly with a sudden strong increase of the specular intensity (see figure 2 of [22]). This is easy to track in LEEM during the deposition of Bi and in practice we interrupt the deposition immediately when a significant increase of the specular intensity is detected. We estimated the accuracy of the Bi coverage at ±0.003 monolayer.

Figure 1 shows a representative bright field LEEM image obtained with 3.0 eV electrons and a field of view of 6 μm. The image shows wide terraces separated by step-bunches) and the specular intensity is taken from the integral brightness. The results are dominated by contributions from the wide terraces and thus characteristic of a surface without atomic defects. The step density is still low after the alloying process, which means that expelled Cu atoms were sufficiently mobile to reach pre-existent steps and the overall surface remains extremely flat.

**Results and discussion**

Let us consider a low energy electron approaching a metal surface with parallel periodicity Λ at normal incidence. Upon approaching the surface the electron loses potential energy and thus gains kinetic energy. When its correspondingly decreasing wavelength λ equals Λ, the condition given by equation (1) is fulfilled. This opens a new diffraction channel in which the electron resides in an eigenstate \( \psi \) of the image potential with an energy given by equation (1) depending on the energy \( E = -0.85/(n + 0.21)^2 \) [10], see figure 2. (For completeness we mention that the experimental locations of the image states on Cu(111) are at slightly lower energies [27]. No experimental values are known for the √3-BiCu₂ structure considered here. The precise locations do not modify the general principle embodied in equation (1). Once captured (and traveling parallel to
the surface in the eigenstate (resonant state), the electron often undergoes a reverse diffraction process to join the specular beam. An assumed free electron with initial energy 14 eV would travel at a velocity of about \(2 \times 10^6\) m s\(^{-1}\). With an assumed realistic lifetime of about 20–24 fs for clean Cu(111)\[^{[27]}\], such an electron can travel a distance of about 40–50 nm parallel to the surface. The actual lifetime may depend on the Bi adlayer. For epitaxial Bi(111), a lifetime of 161 fs has been reported for the \(n = 1\) state of the image potential\[^{[28]}\]. Unfortunately, we could not find any number for the current BiCu\(_2\)(111) case. During its journey the electron may scatter from a defect, e.g. a domain boundary, or undergo one or more inelastic processes. Such an electron is lost from the specular beam, and, if applicable, also from other beams that emerge from the surface, which gives rise to dips in the intensity versus energy \((I, E)\)-curves.

In order to obtain experimental access to the resonant states, LEEM \((I, E)\) curves were measured in the temperature range 515–695 K, i.e. below the order–disorder phase transition for Bi/Cu(111)\[^{[20]}\]. Figure 3 shows characteristic LEEM \((I, E)\) curves in the energy window from about 10 to 50 eV. This energy window features three peaks, located around 29 eV, 21–23 eV and about 16 eV, respectively. We first try to rationalize the origin of these three peaks. As discussed below it is quite straightforward to do so for the two peaks at 29 and 21–23 eV. We found no such trivial explanation for the third one at 16 eV. We argue that this peak is an artifact and rather is the natural result of a strong intensity dip at 13.5 eV, which we attribute to resonant scattering (see below), superimposed on a sloping intensity background between 10 and 19 eV.

The position of the peak measured at 29 eV shows no temperature dependence and is attributed to Bragg scattering from the Cu(111) layers. The Cu(111) interlayer spacing amounts to 2.08 Å, which for free electrons

---

**Figure 1.** LEEM image of the \(\sqrt{3}\)-BiCu\(_2\) surface, after preparation at 630 K. The electron energy is 3.0 eV and the field of view is 6 \(\mu\text{m}\). The curved dark lines are atomic steps and step bunches. Micrometer wide terraces dominate the image. The irregularly shaped dark area at the bottom is a defected area in the used channel plate.

**Figure 2.** Image potential (dotted line) of an electron in front of a metal surface. The eigenstate binding energies \(\varepsilon_n\) (solid lines) were calculated with an analytical model\[^{[10]}\].
would produce a Bragg peak at 34.7 eV. Together this leads to an inner potential of about 5 eV experienced by
the probing electrons, which fits nicely in the realm of values found in LEED IV structure determinations [29].

The temperature dependence of the Bragg peak intensity $I$ (obtained by subtracting the intensity at 49.5 eV in
figure 3 from the value at 29 eV) is plotted in figure 4. A convincing logarithmic dependence of the Bragg peak
intensity as a function of temperature is obtained. The Debye-Waller Factor, DWF, for the temperature-
dependent diffraction intensity is usually written as:

$$DWF = \exp \left[ -\langle u \cdot \Delta k \rangle^2 \right] \approx \exp \left[ -u_{\perp}^2 \Delta k_{\perp}^2 \right]$$

with $\Delta k_{\perp}$ and $u_{\perp}$ denoting the perpendicular components of the wave vector change and the thermal
displacement of the atoms, respectively. In the Einstein approximation used here, the mean-square displacement
of the atoms is given by:

$$u_{\perp}^2 = \frac{3h^2 T}{m k_B \Theta_D}$$

where $h$ and $k_B$ have their usual meaning, $m$ is the mass of the vibrating atoms and $\Theta_D$ is the Debye temperature.

From the slope of the curve in figure 4 we obtain $\Theta_D = 255 \text{ K}$. This result is lower than the literature result
for bulk copper (310 at 300 K). This is no surprise since the surface Debye temperature is typically lower than its
bulk value (e.g. [30]). Rough scaling with the coordination number is obtained (compare [30]). That would in
this case lead to $310 \times 9/12 = 233 \text{ K}$. A slight enhancement may be expected due to the presence of the $\sqrt{3}$ Bi-
layer. The overall resulting value for \( \Theta_D \) is therefore very reasonable and strongly supports our assignment as the Cu(111) Bragg peak.

In contrast to the Bragg peak, which remains fixed at 29 eV, a prominent peak (red circles) does show a clear shift from about 23 to 21 eV with increasing temperature. This is attributed to a temperature dependent outward relaxation of the height of the Bi-layer above the exposed Cu layer in the \( \sqrt{3} \)-BiCu\(_{2} \) surface alloy [23]. Here we find that the peak position relative to the Bragg peak is consistent with a Bi-relaxation that ranges from about 0.47 Å at 515 K to 0.60 Å at 695 K. However, note that the exact values of the relaxation also depend upon the phases of electrons that back scatter from Bi and Cu atoms. These phases are likely to be different but they are not known nor taken into account in the estimate above. A grazing incidence x-ray diffraction study reports an interplanar distance of 1 Å between Bi and Cu at room temperature [20]. A phase shift of the electrons, which scatter from Bi- and from Cu-atoms, respectively, that would differ by 120° suffices to account for the apparent discrepancy. This is reasonable by all means. We derive from the DWFS plot for this peak in the temperature range 500–600 K a reasonable Debye temperature of 107 K (for bulk Bi, the Debye temperature amounts to 119 K at room temperature [31]).

The peak feature at 16 eV is much harder to understand than the straightforward interpretation of the peaks at about 22 and 29 eV. Most likely, this spurious peak is rather the result of an intensity dip at its low energy side superimposed on the strongly decreasing intensity feature with increasing energy away from mirror reflection at 0 eV. This intensity dip located at about 13.5 eV is tentatively attributed to resonant scattering into the first and/or second (or higher) order level(s) of the image potential via diffraction into the just opened \( G_{10} \) and equivalent channels with in-plane periodicity of 3.83 Å, see equation (1). (With just opened we mean that the radius of the Ewald sphere after consideration of the inner potential just passes 1/3.83 Å \(^{-1} \).) The reciprocal space indices are defined with respect to the diffraction peaks of the \( \sqrt{3} \)-BiCu\(_{2} \) structure. Note that this would correspond to the \( \sqrt{3} \)-peaks of the diffraction pattern based on the (1 \times 1) Cu(111) lattice. We emphasize that the energy position of resonant scattering does obviously not depend on temperature because the in-plane lattice constant is fixed. Indeed the position of the dip is found to be temperature independent, even when the neighboring peak at 21–23 eV, associated with strong Bi relaxation, does shift. A careful inspection of the (I, E) curves reveals another intensity dip at about 27.2 \( \pm \) 0.2 eV. This feature is weakly present in the raw intensity data at lower temperature, but is clearly visible in the second derivative of the (I, E) curves, also shown in figure 3. The position of the inflection points does not depend on temperature. This intensity dip is also tentatively attributed to resonant scattering of electrons via \( G_{11} \) and equivalent channels, with a periodicity of 2.21 Å, i.e. \( \sqrt{3} \) times smaller than 3.83 Å.

The involved energies are hard to establish exactly but are estimated in a straightforward fashion. The image state levels \( n = 2 \) and 1 are at only 0.2 and 0.6 eV below the vacuum level. From figure 3, we derive incident energies of 13.5 and 27.2 eV for resonant scattering via \( G_{10} \) and \( G_{11} \), respectively. To account for resonant scattering in both channels quantitatively we need to introduce effective electron masses of, respectively, \( m^* = 0.76 m_0 \) and \( m^* = 1.13 m_0 \), with \( m_0 \) the rest mass of a free electron. The effective mass is coupled to the electron wave length by: \( \lambda = h \cdot (2m^*E)^{-1/2} \), where \( h \) is Planck’s constant and \( E \) the electron energy. The obtained effective masses deviate less than 25% from the free electron mass and are well within the usual frame [e.g., 28, 32]. The quantitative understanding of these dips provides convincing evidence for the importance of resonant electron scattering from the \( \sqrt{3} \)-BiCu\(_{2} \) structure. Giesen et al [33] concluded from their phase shift analysis that an effective mass larger than unity is predicted if the image state is located near the top of the (surface projected) bulk band gap and smaller than unity near the bottom of a gap, as is the case here for Cu(111). At large values of the parallel wave vector, \( k_{//} \), the effective mass is shifted to higher values as the state approaches more closely the top of the surface projected bulk band gap further giving rise to higher effective masses. These results are very satisfactory which corroborates further the assignment above: the intensity dips at around 27.2 and at 13.5 eV bear clear signature of resonant scattering into image states.

We concentrate now on the temperature dependence of the intensity dip occurring at incident energy of 13.5 eV. It is the result of electrons captured into \( n = 1, 2, \ldots \) image states through a diffraction process (equation (1)) and subsequently (partly) lost from the specularly reflected beam due to scattering from elastic (defects, domain boundaries) or inelastic interactions. The exact magnitude of this dip is hard to establish since it is superimposed on a strongly varying ‘background’. Still a rough estimate (difference between maximum at its right hand and minimum intensities) of the depth can be made and the result has been plotted in figure 5 as a function of temperature.

A prominent increase of this depth with temperature is found. We mention that this intensity increase not only counteracts the expected Debye-Waller behavior according to equation (2) (left part), but even overwhelms it completely. We remind that resonant scattering into the image state (equation (1)) involves in-plane diffraction from the \( \sqrt{3} \)-BiCu\(_{2} \) structure. The increase of the magnitude of the resonant dip must then be attributed to an increase of the cross section for diffraction from the \( \sqrt{3} \)-BiCu\(_{2} \) structure. In fact, the latter is a natural consequence of the increased corrugation amplitude due to the outward relaxation of Bi relative to the...
outer-most exposed Cu-layer with increasing temperature as discussed above. In conclusion, from the measured LEEM ($I, E$)-curves and their thermal behavior we obtain firm evidence for the importance of ordinary resonant scattering from the $\sqrt{3}$-BiCu$_2$ structure into image states. The strong and counterintuitive deepening of the intensity dips with increasing temperature is probably the most convincing evidence for resonant scattering. The increasing relaxation of the Bi-plane with growing temperature renders this system pre-eminently suited for revealing resonant scattering features.

We now focus on unexpected features in the very low energy part of the LEEM ($I, E$) curves shown in figure 6. The normalized intensity is shown on a logarithmic scale. Irrespective of the temperature, two distinct intensity dips in the flank of the steeply falling specular intensity are pertinent: one at incident energy of about 3 eV and another at about 7 eV. Evidence of a weaker third one is present at about 1 eV. We argue below that the presence of these intensity dips too is a natural and direct consequence of resonant electron scattering discussed above. In an attempt to relate these dips to resonant scattering as well, it is noted that these features lie well below the horizon set by the Ewald sphere for $\sqrt{3}$-BiCu$_2$ and diffraction is forbidden for an ideal (i.e. infinitely large) crystal at these energies. Hence, bound state resonance of the electrons with the energy levels of the image potential is not anticipated at first sight. Below we argue that these features are due to the presence of domain boundaries and thus to finite size effects, even on top of an otherwise defect-free crystal. For this purpose we consider various diffraction situations illustrated in figure 7. We emphasize that here we discuss the geometry and the diffraction directions explicitly in real space. The directions are expressed in base vectors of the $\sqrt{3}$-BiCu$_2$ structure. The nearest neighbor Bi distance equals 4.42 Å. We have more or less arbitrarily chosen to consider diffraction along ($-1, 0$), ($-1, 1$), ($-1, 2$), ($-1, 3$), and ($-1, 4$) directions. Note that 6 symmetry-equivalent geometries are available for the first two directions and 12 for the latter four, which become active simultaneously due to the normal incidence of the probing electrons. The first-order diffraction peaks emerge (position of the Ewald sphere!) at energies $E_1$ of about 30.8, 10.3, 216, 398 and 72 eV, respectively. (Of course resonant scattering into image states becomes available at slightly lower energies due to the involved energy gain $\varepsilon_n$.) This implies that then adjacent equi-phase lines (see figure 7) scatter in-phase under these emergent
The size of the domains has been chosen in unit cells: 91 perpendicularly wave vector change. All curves were calculated for domains consisting of 182 Bi-atoms. The basic distance between adjacent atoms on a given equi-phase line. The calculations are one-dimensional and the kinematic approximation. For each geometry, we introduce a new rectangular unit cell with a length given by the probability for supernumerary diffraction. It is noted that calculations for domains elongated along the scattering from adjacent lines leads to destructive interference. Then scattering from next-nearest equi-phase lines leads to constructive interference, while scattering channels is available below 10 eV. What happens if the electron wave length equals twice the elemental line distance? Then scattering from next-nearest equi-phase lines leads to constructive interference, while scattering from adjacent lines leads to destructive interference.

As a result complete extinction will occur for an ideal infinite lattice. This is true for any sub-Bragg condition, i.e. diffraction for electrons with a wave length equal to an integer number times the elemental line distance. So far, this is all well-known from basic diffraction theory.

However, it must be remembered that the lattice is not ideal in the realistic situation at all. Let us consider the situation of a hard hexagon model \[24, 25\]. Baxter has calculated the configurational entropy and the distribution of atoms over each of the three sub-lattices as a function of coverage \[26\]. At low coverage, the Bi atoms are distributed equally over each of the three equivalent sub-lattices. At a coverage exceeding \((5 - \sqrt{5})/10 = 0.276\ldots\), the occupation of one of the sub-lattices starts to prevail, while the occupation of sites belonging to each of the other two sub-lattices decreases sharply. At the maximum coverage of one-third, all of the Bi atoms are contained in only a single sub-lattice, while the occupation of the two other sub-lattices is zero. On a local scale of a few nm, as studied by Girard et al \[34\], this may well be true but for more macroscopic surfaces this requires ordering to occur over macroscopic distances and this may be kinetically limited and take a prohibitively long time, especially close to the ideal Bi coverage of \(\frac{1}{2}\) in the \(\sqrt{3}\)-BiCu\(_2\) surface alloy. So macroscopically, the surface is expected to be comprised of finite size domains of the \(\sqrt{3}\)-BiCu\(_2\) structure for an extended period of time. In practice, the interruption of the ideal lattice by domain boundaries will necessarily lead to supernumerary diffraction peaks and resonant scattering below the threshold energies \(E_1\), referred to above, as a result of incomplete extinction for scattering from the various equi-phase lines in figure 7. The strength of the supernumerary diffraction peaks depends on both the number of equi-phase lines as well as on the number of adjacent atoms present on each particular equi-phase line within a given domain.

In an attempt to relate the intensity dips in figure 6 to supernumerary resonant scattering, we have calculated diffraction from finite domains and the results are shown in figure 8. The calculations were made in the kinematic approximation. For each geometry, we introduce a new rectangular unit cell with a length given by the length of the arrows parallel to the diffraction direction (figure 7) and a perpendicular width given by the distance between adjacent atoms on a given equi-phase line. The calculations are one-dimensional and the profiles shown in figure 8 thus represent the situation for in-plane diffraction corresponding to zero perpendicular wave vector change. All curves were calculated for domains consisting of 182 Bi-atoms. The basic size of the domains has been chosen in unit cells: \(91 \times 1, 91 \times 1, 13 \times 1, 7 \times 1\) and \(13 \times 1\) for the \((−1, 0), (−1, 1), (−1, 2), (−1, 3)\) and \((−1, 4)\) directions, respectively. The influence of the width of the domains was assessed by adding sequentially lines of, respectively 91, 91, 13, 7 and 13 atoms parallel to the given scattering directions, such that the domain widths vary between \(≥1\) and \(<2\) unit cells. The number of calculated curves from top \((−1, 0)\) to bottom \((−1, 4)\) in figure 8 is then, respectively, 2, 2, 14, 26 and 14. All individual curves have been normalized at unity for \(E = 0\). The height of the supernumerary peaks is then taken as a measure of the probability for supernumerary diffraction. It is noted that calculations for domains elongated along the \((−1, 0)\) and the \((0, 1)\) directions lead to identical results, which should be the case for symmetry reasons.

The positions of the supernumerary peaks along the real space \((−1, 0)\) and \((−1, 1)\) directions correspond nicely to the observed intensity dips at about 7 eV and 3 eV, respectively. The strongest peak of the green \((−1, 2)\) lines up with the about 1.0 eV intensity dip, while the strong(est) ones from the red \((−1, 3)\) and blue \((−1, 4)\) direction reinforce the dip at about 3 eV obtained for the \((−1, 1)\) direction. Therefore, supernumerary resonant electron scattering along high-symmetry and non-high-symmetry directions is consistent with the experimental
very low energy specular intensity data and provides a powerful interpretation platform for the observed intensity dips in this very low energy window.

For completeness we mention that in these calculations we have considered only diffraction parallel to the chosen scattering direction at the surface. (The finite size of the domains perpendicular to this direction gives rise to interference fringes but their effects are canceled by the applied normalization.) Transient capture in different image potential states for states $n = 1, 2, \ldots$ would give rise to slightly different (lower) energies, which we cannot resolve due to the energy spread of the electrons from our thermal electron source. The lower values of the incident energies of the involved electrons by an amount $\varepsilon_n$ are counteracted by a sub-unity effective mass. As a result we consider the used energy scales in figure 8 as a fair approximation of reality.

A natural trait of supernumerary diffraction is its dependence on the exact choice of the domain shape. This is surely true for the calculated intensities but is much less important, if at all, for the position of the peaks. This statement applies for the main diffraction peaks and thus the onset of the resonant electron scattering. The subsidiary peaks between the main peaks apparent in the calculations originate from the finite domain size chosen parallel to the scattering directions. Both the strength and the frequency of these subsidiary peaks depend strongly on the size of the domain: their frequency increases and their amplitude decreases with growing domain size parallel to the scattering direction. However, the ratio of the supernumerary peak height and that of the $E = 0$ peak (see figure 8) does not depend on the length of the domains, parallel to the scattering direction. Due to the normalization the latter ratio does not depend on the domain width perpendicular to the scattering direction either. This opens a way to make an estimate of the relevant domain sizes.

To this goal, we have calculated the intensity of the resonant peak at $2.77$ (eV)$^{1/2}$ along the $(-1,0)$ direction as a function of the perpendicular domain width. (Please note once more that an infinite perpendicular domain width would give rise to complete extinction and thus no intensity at this location.) Here we make the reasonable assumption that the height of the main supernumerary peak is a valid measure of the cross section to diffract parallel to the surface and thus to resonantly scatter into an image potential state. First we established that the relative peak height and thus the resonant scattering dip at $7.7$ eV does not depend on the length of the domain parallel to the diffraction direction in real space as long as one chooses an integer number of unit cells. A variation by an order of magnitude only leads to an order of magnitude higher frequency of the fringes and a stronger decay of their amplitude away from the main supernumerary peak as well, but importantly the intensity (height) of the supernumerary peak remains unaffected. On the other hand, an increase of the width of the

---

**Figure 8.** The LEEM $(I, E)$ data from figure 6 are replotted in the upper panel as $\ln I$ versus incident energy $E$ (upper scale) and $\sqrt{E}$ (lower scale). In the panels below, the peak height is calculated for finite domain size for diffraction along the real space directions $(-1, 0)$, purple; $(-1, 1)$, magenta; $(-1, 2)$, green; $(-1, 3)$, red; and $(-1, 4)$ blue. The numbers of calculated curves (from top to bottom) are then, 2, 2, 14, 26 and 14, respectively. Individual curves have been normalized at unity for $E = 0$. (See text for more details of the calculations.)
domain perpendicular to the diffraction direction does lead to a decrease of the main peak height. This was anticipated since for an infinite domain size the peak should disappear completely.

The height $H$ of the supernumerary peak is approximated well by $H = H_0 h^{-0.81}$ with $h$ the dimensionless width of the domain in number of unit cells. Identical results have been obtained for supernumerary diffraction along the other azimuths. For simplicity we assume that the domain widths $w$ obey a Poisson distribution $P(w)$ with mean $\lambda$.

$$P(\lambda, w) = \frac{e^{-\lambda} \lambda^w}{w!}.$$  

The cross section for supernumerary scattering is then:

$$H_{ss}(\lambda) = \sum_{w=0}^{\infty} \frac{H_0 h^{-0.81} w P(\lambda, w)}{\lambda}.$$  

The result is shown in figure 9 as a function of $\lambda$. Given the fact that the depth of the minimum at 7.7 eV is about 6 times $1.6 \times 10^{-3}$, taking into account that 6 equivalent $(-1, 0)$ directions are available simultaneously for resonant scattering we estimate the mean domain size in our experiment to be of the order of 10 nm. An STM image selected and published by Girard [34] indicates that indeed such domain sizes do occur.

A consequence of these rather small domains is that domain boundaries suppress the diffraction of electrons from an image state back into the specular channel. This is probably the reason why the bound state resonances we estimate the mean domain size in our experiment to be of the order of 10 nm. An STM image selected and published by Girard [34] indicates that indeed such domain sizes do occur.

LEEM is well suited to observe resonant scattering of low energy electrons. First, the elastic scattering cross section of electrons from atoms is highest at low energies [38]. Another crucial factor is the higher cross section

Figure 9. $H_{ss}$ expressed as the logarithm of the peak height at 7.7 eV for the $(-1, 0)$ direction (equation (4)) versus the natural logarithm of the domain size $\lambda$, expressed in Å.
for wide angle scattering, as needed here, is also highest at low energies [39]. Probably the most favorable property is the fact that one can conveniently measure specular diffraction at normal incidence in LEEM, in contrast to tilted incidence needed to observe the specular beam in conventional LEED. This implies that multiple equivalent channels involving elastic diffraction into a resonant level of the image potential (these could be 6 or 12 equivalent ones for an fcc(111) sample) are simultaneously opened as a function of incident electron energy. A similar favorable multiplication factor would also be present for an fcc (001) surface (4 or 8 x) and even for an fcc (011) surface (2 or 4 x). An additional advantage of LEEM is its ability to control the energy down to zero, without additional measures to render magnetic stray fields harmless for very low energy electrons.

From the position of the peak at around 22 eV relative to the Bragg peak we concluded, based on kinematic approximation considerations, that the vertical position of the Bi atoms differs from that of the copper atoms in the outmost (alloy) layer by an amount \( \Delta x_{\text{Bi-Cu}} \) of 0.47 Å at 515 K. This positive relaxation is in qualitative agreement with glancing incidence x-ray diffraction data [18]. Quantitatively however, the x-ray data arrive at a value of 1 Å. This difference is tentatively attributed to different phase shifts of electrons backscattered through an angle of 180° from Bi and Cu atoms. The difference between our rough estimate of the apparent height and the more reliable x-ray results would amount to 0.53 Å. This corresponds to a phase difference of about 70°, which is in the realm of the phase shifts reported for Bi and Cu [39, 40]. A more definite phase shift value requires a full LEED \((I, E)\) analysis. Such a full analysis is cumbersome, if not impossible, for several reasons, among which is the presence of resonant scattering described here. However, it is clear from the shift of the relevant peak towards lower energies that the relaxation of the Bi atoms increases with temperature. This is in qualitative agreement with an earlier report also based on LEEM measurements [23]. In the current case, the data are obtained from a single experimental run in which severe caution was exerted to maintain constant experimental conditions that affect intensity measurements, e.g. incident beam current and detector settings. As such, the confidence in the results of the present case is much more profound.

Supernumerary diffraction phenomena are reported for the first time. The relative positions of the quite strong intensity dips at low energies provide a powerful confirmation of this assessment. This is even more corroborated by the fact that LEEM \((I, E)\) curves provide an internal check for the energies of the participating electrons from the location of the transition from mirror mode towards more complex interaction of electrons with matter. We have given solid evidence for the potential importance of resonant scattering in LEEM. The evidence of supernumerary features below 10 eV is compelling, because of the success with the description of ordinary dips combined with the consistency of modeling of supernumerary dip positions.

Finally we note that in principle intensity dips (maxima) will also occur in the \( \sqrt{3} \) ‘integer’ order curves of the \( \sqrt{3} \) BiCu surface alloy. Dips in \((I, E)\) curves originate in ordinary resonant scattering into bound states of the image potential, involving the reciprocal vectors \( \mathbf{G}_{10} \) and \( \mathbf{G}_{11} \) of the \( \sqrt{3} \) BiCu superstructure at incident energies of 13.5 and 27.2 eV, respectively. Intensity dips also arise from strong supernumerary resonant scattering of electrons at very low energy, below 10 eV, due to incomplete extinctions in scattering from finite size domains. LEEM is inherently suited for observing these two rarely recognized features. Resonant scattering of (very) low energy electrons is a so far often neglected but highly likely process, particularly in specular diffraction at normal incidence in LEEM. When not properly accounted for, it may undermine efforts to extract the rich information about atomic positions and unoccupied electronic states that is encoded in electron diffraction intensities in this energy range.

Conclusions

We conclude that strong evidence is reported for the importance of resonant scattering of electrons in LEEM data taken from the ordered \( \sqrt{3} \) BiCu surface alloy. Dips in \((I, E)\) curves originate in ordinary resonant scattering into bound states of the image potential, involving the reciprocal vectors \( \mathbf{G}_{10} \) and \( \mathbf{G}_{11} \) of the \( \sqrt{3} \) BiCu superstructure at incident energies of 13.5 and 27.2 eV, respectively. Intensity dips also arise from strong supernumerary resonant scattering of electrons at very low energy, below 10 eV, due to incomplete extinctions in scattering from finite size domains. LEEM is inherently suited for observing these two rarely recognized features. Resonant scattering of (very) low energy electrons is a so far often neglected but highly likely process, particularly in specular diffraction at normal incidence in LEEM. When not properly accounted for, it may undermine efforts to extract the rich information about atomic positions and unoccupied electronic states that is encoded in electron diffraction intensities in this energy range.

Acknowledgments

M S A gratefully acknowledges financial support from the Hong Kong Research Grants Council under grant HKUST600113.

References

[38] Frank D G and Hubbard A T 1997 J. Phys. Chem. A 101 894