# Determination of azimuth angle, incidence angle, and contact-potential difference for low-energy electron-diffraction fine-structure measurements

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Low-energy electron-diffraction fine-structure data can often have relatively large inconsistencies associated with the electron-beam incidence conditions. This is in part due to the difficulties associated with working with electrons in the range 0–40 eV and in part due to the crystal being oriented azimuthally before being put in the vacuum system. The angle of incidence is often measured optically, but the optical and electron paths need not coincide if residual magnetic fields are present. We describe a technique for determining the angles of incidence and azimuth from the data themselves. This relies upon two factors: the ability to vary the azimuth angle continuously and the ability to see two sets of fine-structure features on one $I$-$V$ scan. This technique is applied to fine-structure data obtained from clean Cu(001) and O/Cu(001) surfaces. We hope that the technique described will help give confidence to those collecting such data that these angles can be uniquely determined and that the data can be usefully analyzed. The uncertainty of not having a technique for this purpose has prevented groups from publishing such data in the past.

## INTRODUCTION

The fine-structure features that appear on low-energy electron-diffraction (LEED) $I$-$V$ profiles at low energies (typically $<40$ eV) have been shown to be valuable in testing models of the surface potential barrier.[1] These features are due to the interference between the beam under observation (usually the specular beam) and a preemergent beam that is internally reflected by the potential barrier.[2] The success with which this modeling can be applied depends on a number of factors that relate to the precision with which the experimental data can be collected.[3] Amongst the parameters that must be known consistently are the angles of incidence and azimuth.

Techniques for determining these angles when using a fluorescent screen in conventional LEED apparatus have been presented previously.[4–6] These techniques, however, cannot be used with high-resolution spectrometers as the diffracted beams are not visible.

One problem with working with very low-energy electrons is that the path of the beam may not be equivalent to the "straight-line" path due to slight deflections by residual magnetic fields. Difficulties also arise in using surfaces that cannot be cleaned by flash heating. It is then usually necessary to move the crystal to a position where it can be cleaned by ion bombardment and then repositioned back in front of the spectrometer.

Measured fine-structure emergence energies always differ from the theoretical predictions by around 1–2 eV. This is due to the contact-potential difference (CPD) between the electron-gun filament and the crystal surface, a quantity that is difficult to measure directly. We present a technique for determining the absolute incidence and azimuth angles and CPD from measurements of fine-structure profiles over a range of azimuth angles.

## I. EXPERIMENT

The ultrahigh vacuum (UHV) system and crystal preparation have been described previously.[7] The apparatus used for the collection of fine-structure data has also been previously described.[8] It consisted of a 127° cylindrical deflecting analyzer as an electron monochromator and a three grid retarding field analyzer as a detector. This assembly could be rotated about a common axis via a rotary feedthrough that was calibrated in degrees. This allowed the azimuth angle to be varied. It was also possible to alter the angle of incidence with the crystal manipulator.

It should be noted that with the experiment set up in this manner, the incidence angle varied as the azimuth angle was changed, if the crystal surface was not perpendicular to the axis of rotation. Also, the azimuthal movement seen by the crystal differed slightly from the movement of the rotating arm. Our analysis allowed for this effect.

The oxygen adsorbed Cu(001) surface was produced by leaking in high purity $O_2$ through a gas handling line. The clean Cu(001) surface was given an exposure of 300 L, which produced the $c(2\times2)$ structure.[9]

## II. METHODOLOGY

### A. Azimuth angle

We have shown[10] that there are interesting symmetry points on a graph of emergence energy versus azimuth angle, at a fixed angle of incidence. This is true of all crystal surfaces. These can be used to determine the directions of the crystallographic axes. As an example, Fig. 1 shows such a graph for Cu(001) at an incident angle of 60°. Note that the $\bar{1}\,\bar{1}$ beam emergence has a minimum at an azimuth angle of 45° (i.e., the $\langle 11 \rangle$ direction). This fact could be used to find this azimuth by observing when the fine structure due to the emergence of this beam moved to its lowest energy.

Another symmetry point is the "crossover" of the $0\bar{1}$ and $\bar{1}0$ beams at the $\langle 11 \rangle$ azimuth. Although it is unlikely to be able to see features arising from these beams, due to the "equivalent resolution" argument of Gaubert

 

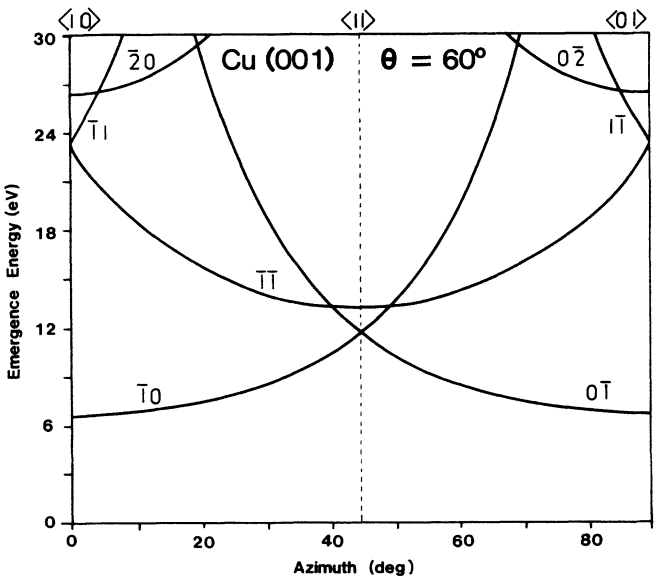


FIG. 1. Theoretical emergence energy versus azimuth for various diffracted beams of Cu(001). Note the symmetry point at $\phi = 45°$.

*et al.*,[3] if they were visible then the ⟨11⟩ direction could be found quite easily.

### B. Emergence energy

Before one can usefully compare the predicted theoretical emergence energy with the measured one, it is essential to find a technique for estimating the emergence energy from an experimental *I-V* curve. If fine structures could be measured with infinite resolution then the emergence energy would correspond to the highest energy at which the feature affects the spectrum. In fact, one would observe peaks of ever decreasing width converging towards a fixed position, this being the emergence energy. For an instrument of finite resolution, the feature will be seen to extend one FWHM beyond this energy.[3] This suggests that a technique for estimating the emergence energy is to subtract one FWHM from the energy at which the fine structure last affects the *I-V* curve.

The problem with this is that the FWHM of the instrument varies as the diffraction conditions change. Hence, to produce an experimental curve similar to Fig. 1 it is necessary to find the appropriate resolution for each angle of azimuth. We have shown previously[10] how these quantities can be calculated for Cu(001), based on the work of Gaubert *et al.*[1]

It should be noted that the emergence energy is independent of the inner potential and the barrier shape.[10] It depends only on the incident diffraction conditions and the two-dimensional geometry of the surface.

### C. Incident angle

Once the azimuth angle is known it should be possible to calculate the angle of incidence by estimating the experimental emergence energy and matching this with the theoretical predictions. However, as mentioned earlier, there is an unknown CPD that translates the energy scale of the *I-V* scan. The theoretical lines of emergence energy versus azimuth for a particular beam at different incidence angles, although differing in absolute energies, are closely parallel to each other over a large range of incidence angles. It is thus impossible to differentiate between the different choices for $\theta$. However, if two fine-structure features are visible together over a range of azimuth angles then it is possible to determine the angle of incidence by comparing the emergence energy differences of the two beams with the theoretical values. As these are differences, they are independent of the CPD. This emergence energy difference is a much stronger function of $\theta$ and the choices of angles can be narrowed considerably.

### D. Contact potential difference

When the angles of incidence and azimuth have been determined it is a simple matter to find the energy translation necessary to match the experimental emergences with the theoretical ones. This then is the CPD. When dealing with adsorbed species on a surface it should be noted if there is any change in apparent experimental emergence energy of the fine structure, when compared with the clean surface, and allowance made for this.

### E. Incidence angle for other spectra

Once the CPD has been found it is possible to adjust all other experimental scans, taken under the same system conditions, by this amount and then deduce $\theta$ from the emergence energy ($\phi$ is known from the calibration technique described earlier). If the system is altered in any way (e.g., opened to atmosphere, new gun filament, different crystal, etc.) then the process of angle and CPD determination should be repeated.

## III. APPLICATION TO Cu(001)

### A. Clean surface

For the clean Cu(001) surface the most prominent fine-structure feature near the ⟨11⟩ azimuth was due to the $\bar{1}\,\bar{1}$ beam emergence. No structure due to the $0\bar{1}, \bar{1}0$ beams was visible.[10] It was possible to calibrate the azimuth to within 0.5° by observing when the fine structure moved to its lowest energy. Once this symmetry point was found it was assumed that the angular markings on the azimuthal feedthrough were accurate and thus any other azimuth angle was known. Close to the ⟨10⟩ direction features due to both the $\bar{1}\,\bar{1}$ and $\bar{2}0$ beams were visible over a range of around 5° in azimuth.[10]

By estimating the emergence energies of these two features over this range it was possible to determine the angle of incidence using the method described in the previous section. It was found that $\theta$ was 65.5° and hence the CPD was 1.3 eV. It was estimated that the degree of uncertainty in incidence angle and CPD was about ±1.5° and ±0.05 eV, respectively. Figure 2 compares the theoretical emergences for 65.5° (full curve) and the experimental ones (crosses, translated by the CPD).

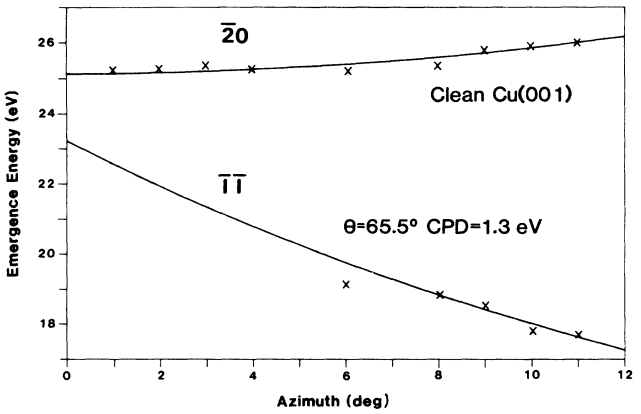


FIG. 2. Theoretical (solid curve) and experimental (crosses) emergence energies for clean Cu(001) at $\theta=65.5°$. The experimental points have been translated by the CPD.

The CPD was used to translate other spectra and the angles of incidence deduced from the emergence energies. Figure 3 shows the fine structure due to the $\bar{1}\,\bar{1}$ beam along the $\langle 11\rangle$ azimuth ($\phi=45°$) at different incident angles. Note that the third peak is being better resolved with increasing angle of incidence, even though the fine structure feature is narrowing. This is analogous to the effect observed previously[10] in which the total equivalent resolution of the spectrometer varied with azimuth angle.

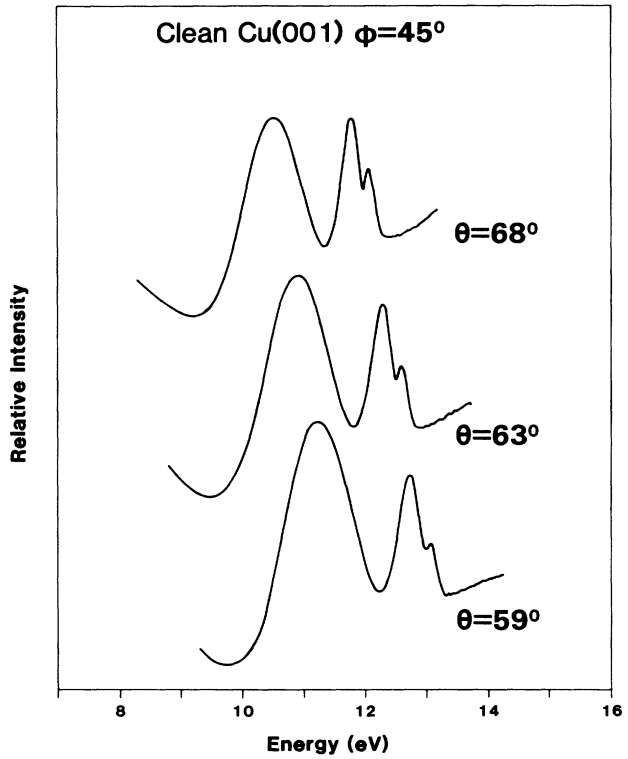


FIG. 3. Fine-structure feature from clean Cu(001), due to the $\bar{1}\,\bar{1}$ beam emergence, at different angles of incidence, near the $\langle 11\rangle$ azimuth. Note the apparent increase in resolution as $\theta$ increases.

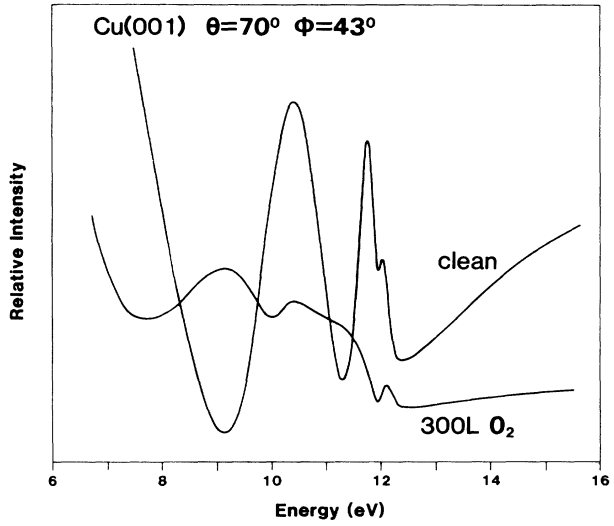


FIG. 4. Comparison of the fine-structure profile for the clean Cu(001) and the $c(2\times2)$-O/Cu(001) surfaces.

In this case, the resolution became better as the incident angle increased. Assuming the angular half-widths to be $\Delta\theta=\Delta\phi=1°$ and the energy half-width to be $\Delta E=70$ meV the total resolution was around 150 meV at 59° and 110 meV at 68°. These values were calculated using the equations of Gaubert *et al.*[3]

### B. Oxygen $c(2\times2)$ surface

It is interesting to note the change in fine-structure profile when oxygen is adsorbed onto the Cu(001) surface. Figure 4 shows the $\bar{1}\,\bar{1}$ feature for the clean surface and for an exposure of 300 L. The angle of incidence was 70° and the azimuth 43°. For the $c(2\times2)$ oxygen surface the fine structure was modified to the large "three peak" structure seen in other experiments.[9] It has not previous-

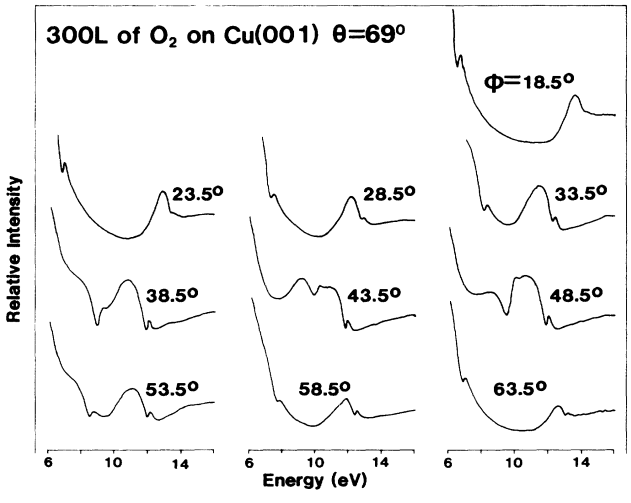


FIG. 5. Change in the fine-structure profile for the $c(2\times2)$-O/Cu(001) surface as the azimuth angle is varied. Note how it splits into different components as the azimuth moves away from $\phi=45°$.

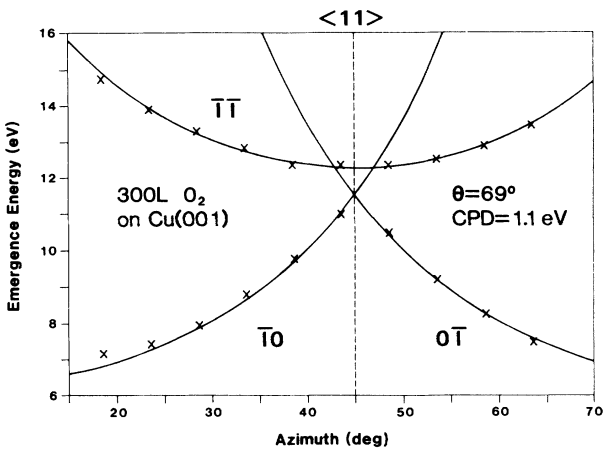


FIG. 6. Theoretical (solid curve) and experimental (crosses) emergence energies for the $c(2\times2)$-O/Cu(001) surface at $\theta=69°$. The experimental points have been translated by the CPD.

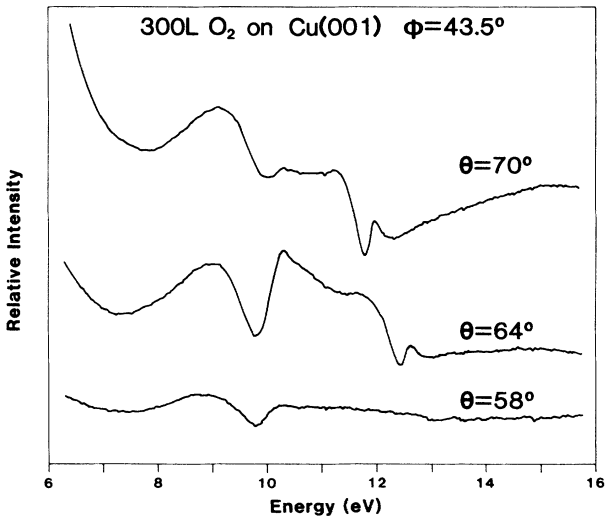


FIG. 7. The fine-structure profile for the $c(2\times2)$-O/Cu(001) surface at different angles of incidence, near the ⟨11⟩ azimuth.

ly been clear exactly what was causing this feature to change. However, by varying the azimuth angle we were able to see that this profile was, in fact, the superposition of three fine-structure features. These were the original $\bar{1}\,\bar{1}$ feature plus the $0\bar{1}$ and $\bar{1}0$ features, which were not visible for the clean surface. It can be seen from Fig. 1 that the emergence energies of these three beams are grouped closely together near the ⟨11⟩ azimuth. Figure 5 shows how the feature split into its separate components as the azimuth angle moved away from the ⟨11⟩ direction. The fine structure due to the $0\bar{1}, \bar{1}0$ beam emergences was very weak on the high-energy side of the "crossover point" at $\phi=45°$.

In a manner analogous to the method used for the clean surface we were able to calibrate the azimuth and then determine the incidence angle and the CPD. We did this as these spectra were taken several months after the ones obtained for the clean surface and system conditions could have changed. The introduction of oxygen also affected the CPD. The values obtained were $\theta=69°$ and CPD$=1.1$ eV. Figure 6 shows a plot of theoretical emergence energies for $\theta=69°$ (solid curve) and estimated experimental ones (crosses, translated by the CPD).

Again, we were able to use this CPD to translate other spectra taken under the same conditions and hence determine their angle of incidence. Figure 7 shows the fine-structure profile (due to three beams) for different angles of incidence near the ⟨11⟩ azimuth.

When oxygen was introduced to the system there was an apparent shift in emergence energy of the $\bar{1}\,\bar{1}$ feature of about 0.2 eV. Thus the CPD for the clean surface of Fig. 4 was 1.3 eV, which corresponded to the value obtained in the previous section. This was despite the time difference of several months and seemed to suggest that the CPD remained relatively constant. We still think, however, that the CPD should be recalibrated after such a time interval.

## SUMMARY AND CONCLUSION

Progress in the field of fine-structure analysis has been somewhat impeded by a lack of data in which the angles are known with some consistency. While this may not have been a problem for the examination of tungsten, which can be cleaned by flash heating, it has prevented progress on those surfaces which must be cleaned by ion bombardment. We have found changes in incidence and azimuth angles by up to 2°, for the same apparent mechanical alignment, following cleaning and repositioning of the sample.

We have shown a technique for determining the angles of incidence and azimuth and the CPD for fine-structure features from the data itself. We then applied this method to the clean and oxygen covered surfaces of Cu(001). This technique relied upon two factors:

(1) being able to continuously vary azimuth angle;

(2) being able to observe two sets of fine-structure features, on the one scan, over a range of azimuth angles.

This technique provided a precision of around $\pm0.5°$ in azimuth angle, $\pm1.5°$ in incidence angle and $\pm0.05$ eV in the CPD. This precision reflected the angular divergence of the electron beam as this largely determined the total resolution of the system and so set the precision with which the azimuthal angle and all other derived quantities could be measured. It was reassuring that the precision of the angles was of the same order as the divergence of the electron beam.

The method was a self-consistent one that did not rely on geometric, line-of-sight alignment. It may not be a technique applicable in all cases, but it is hoped it will provide data for which there can be some confidence in the quoted angles. This analysis, and that done previously,[10] gives a very complete picture of the experiment, fixing not only the angles of incidence and azimuth and the CPD but also the divergence of the electron beam and the energy resolution of the spectrometer. We hope that data of this quality can be used to help tie down, beyond doubt, the surface potential barrier for Cu(001).

## ACKNOWLEDGMENTS

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