THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF PHYSICS

A FEASIBILITY STUDY OF INTENSITY VERSUS ENERGY ANALYSIS AS A MEANS OF TESTING LOW ENERGY ELECTRON DIFFRACTION TECHNIQUES ON THE AU(111) CRYSTAL

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Spring 2010

A thesis
submitted in partial fulfillment
of the requirements
for baccalaureate degrees
in Physics and Electrical Engineering
with honors in Physics

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Abstract

Experimental studies on the atomic arrangement of crystals are necessary in order to understand and predict the properties and interactions of the structures. The crystal of focus in this experiment, the Au(111) crystal, was chosen for its long-range order. This long periodicity approximates the structure of quasicrystals, materials of ordered structure that lack true periodicity. Using the process of Low-Energy Electron Diffraction (LEED), and comparing the results to a known crystal structure, the structure of the surface atoms can be inferred. Using the HotLEED program, the intensities of a LEED file are extracted, and the Intensity vs. Incident energy curves are analyzed. This experiment is a feasibility study of the use of HotLEED to determine the surface structure of the Au(111) crystal. It will be considered feasible if the Pendry-r factor is less than 0.2.

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Acknowledgements

I would like to thank my thesis advisor, Dr. Renee Diehl, for her support and patience in throughout the thesis process. Also. I would like to thank Dr. Richard Robinett for serving as my honors adviser during my stay in the Schreyer Honors College. Finally, I'd like to extend my gratitude to Dr. Mellita Caragiu of Ohio Northern University for her help performing data analysis.

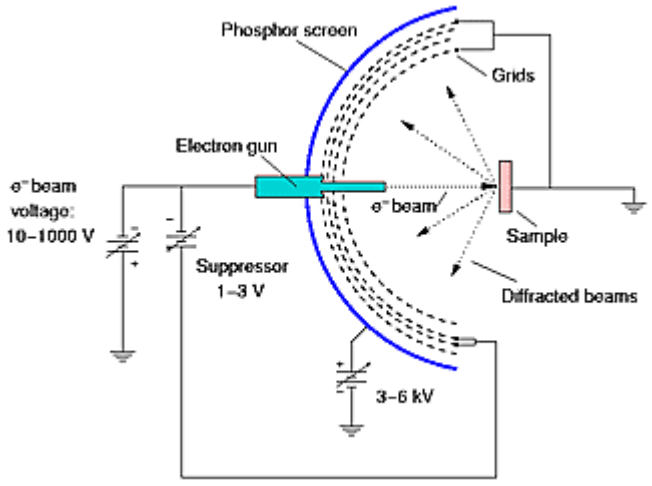
1. Introduction

1.1 Low Electron Energy Diffraction

The study of surface atoms in a crystalline structure is necessary because many forces and interactions at the surface of a crystal tend to differ from this in the bulk of the material. The surface structures of crystals are necessary to understand their physical properties and chemical interactions with other materials, as well as thermodynamics and dynamics of particles.

Low energy Electron Diffraction (LEED) is a means of determining the structure of surface and near-surface atoms in a crystal. It is the most widely used technique for the experimental determination of surface structures in the last several decades. Low-energy electron diffraction involves probing a surface with directed electrons in the 40 – 500 eV energy range. The crystalline structure acts as the diffraction grating, and the electrons display wavelike characteristics. These electrons then elastically scatter in the reverse direction, where they are collected. Figure 1 depicts a diagram of a simplified LEED setup.

Figure 1: Typical LEED hardware setup



The typical wavelength of these incident electrons is in the 0.5Å – 2Å range.

Typically, the energy distribution of intensity involves a rounded peak at low energies (below 50 eV) and a more pronounced, sharper peak at a higher energy, known as the elastic

peak. With LEED, only the electrons that scatter elastically are recorded and measured. This is typically about 1% of the total number of scattered electrons.

1.2 Quasicrystals

The crystal being used in this experiment, the Au(111) crystal, was selected for its long-range periodicity. It is used to approximate the structure of a quasicrystal. Quasicrystals are solid structures with order (similar to crystals) but they lack periodicity. There is no translational symmetry in quasicrystals, which makes them harder to characterize. Rotational symmetry, which is limited to 2-, 3-, 4-, and 6-fold in normal crystals, can appear as numerous other folds in quasicrystals. Quasicrystals have several interesting physical, electrical, and chemical properties. They typically have a low surface energy, as well as a low coefficient of friction. They are resistant to oxidation, and have a low thermal conductivity. Finally, quasicrystals have a tunable band structure, which can be controlled by changing the lattice constant.

1.3 Au(111) Crystal

While not a quasicrystal, the Au(111) crystal approximates a quasicrystal due to its large unit cell. Previous studies (STM, x-ray diffraction, LEED) have shown that the close packed (111) structure of Au reconstructs itself into a herringbone structure. This large unit cell is due to the herringbone reconstruction that occurs when a layer of gold atoms is applied to the surface of the gold. Studying surfaces like that of the Au(111) crystal helps researchers develop capabilities for studying quasicrystals due to its large unit cell. The surface of the gold crystal has a unit cell sized $\sqrt{3}$ by 23. In *Scanning Tunneling Microscopy Observations on the Reconstructed Au(111) Surface: Atomic Structure, Long-range Superstructure, Rotational Domains, and Surface Defects*, the unit cell of the bulk layer was suggested to be $\sqrt{3}$ by 22. However, the top reconstructed layer of gold atoms showed 23 surface atoms in the unit cell. The unit cell is

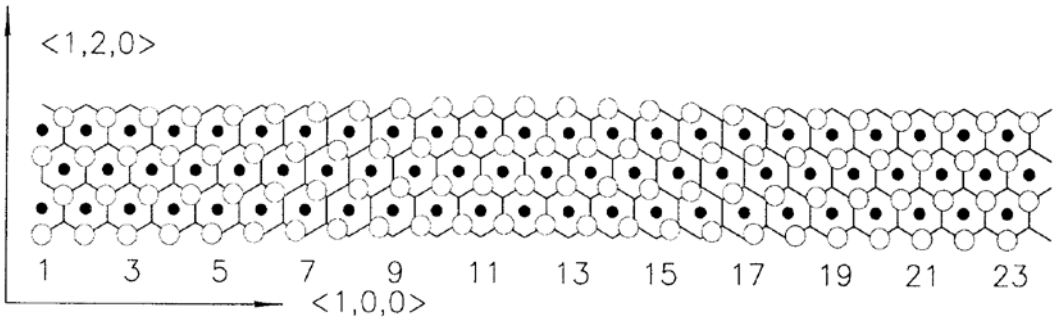
treated as √3 by 22 in this case because 22*2.885 Å = 63.47Å, which matches the proposed unit cell length of 63 Å better than a unit cell 23 atoms long. The actual position of the surface atoms in a unit cell according to an x-ray diffraction study can be found in Figure 1. The crystal has a face-centered cubic structure.

Figure 2: Atomic position in the unit cell of Au(111)

Atom	x_m (Å)	y_m (Å)
0	0.0000	0.0000
1	-0.0301	0.0054
2	-0.0612	0.0212
3	-0.0941	0.0462
4	-0.1298	0.0786
5	-0.1688	0.1160
6	-0.2113	0.1555
7	-0.2575	0.1944
8	-0.3072	0.2296
9	-0.3599	0.2585
10	-0.4149	0.2791
11	-0.4714	0.2898
12	-0.5284	0.2898
13	-0.5849	0.2791
14	-0.6400	0.2585
15	-0.6927	0.2296
16	-0.7424	0.1944
17	-0.7887	0.1555
18	-0.8313	0.1160
19	-0.8703	0.0786
20	-0.9060	0.0462
21	-0.9390	0.0212
22	-0.9701	0.0054

These positions were determined by the equations for the fractional coordinates of the m^{th} atom in the 22 x √3 unit cell. The surface atoms, shown here as white hollow circles, are shown to obey a sinusoidal behavior. Because of this, in the space of 22 subsurface Au atoms, the applied surface layer has 23 atoms present. This causes the top surface to buckle in an upwards fashion, and creates the zigzag patterning seen on the surface of Au(111) crystals.

Figure 3: Surface structure of the Au(111) crystal



The previously mentioned sinusoidal behavior can be observed in the equations for the atomic coordinates. In the following calculations, the second-order values for x and y position were ignored, as they were small enough to be considered negligible. The formulas are as follows:

$x_m = -m/23 + (a_1/2\pi)\sin(2\pi m/23) + (a_2/2\pi)\sin(4\pi m/23) + \ldots$

$y_m = b_1[1-\cos(2\pi m/23)]/(4\sqrt{3}) + b_2[1-\cos(4\pi m/23)]/4\sqrt{3} + \ldots$

According to Barth et al, the unit cell of the reconstructed layer would have dimensions of 63Å by 4.7Å. This is determined by using the nearest neighbor distance of fcc gold at 300K to be 2.885 Å.

2. Previous Work

This experiment relied on the previous measurement of LEED patterns of Au (111) crystals using the method of low-energy electron diffraction. Initially, the Au (111) crystal had to be prepared. It was placed in an Ultra High Vacuum (UHV) chamber, where the pressure was reduced to approximately $5x10^{-11}$ Torr. This was necessary to ensure that gas particles and dust did not adsorb to the surface of the crystal. The sample was then bombarded with a stream of Argon ions to ensure that the sample's surface was clean of impurities. The sample is then annealed to restore the solid's crystalline structure. In order to produce quality results, the sample is cooled to -194ºC, which reduces thermally-induced lattice vibrations.

Through the LEED process, an electron gun was used to direct energized electrons toward a sample crystalline piece of Au (111) keeping a constant angle of incidence. These electrons were sent through a potential near the energy of the electrons. This potential barrier repelled any electrons that had previously scattered inelastically. Only roughly 1% of the electrons, those that have been scattered elastically, were allowed through the grid. These elastically scattered electrons were the ones that had been diffracted off the Au(111) surface. After striking the crystal, the electrons were diffracted off the outermost several levels of atoms. They were then accelerated through an electric field, and struck a hemispherical energy-analyzing grid on a phosphorous screen. This method allowed for an easily visible pattern of intensities where the electrons hit the grid. However, in order to perform signal processing on the outputted intensity patterns, photometers or video cameras are needed to measure the signals.

In order to efficiently capture the outputted signals such that they were easily measurable, a program was developed to carry out the data acquisition and Intensity vs. Energy analysis. This program, HotLEED, was used extensively throughout the research process. Dynamic acquisition

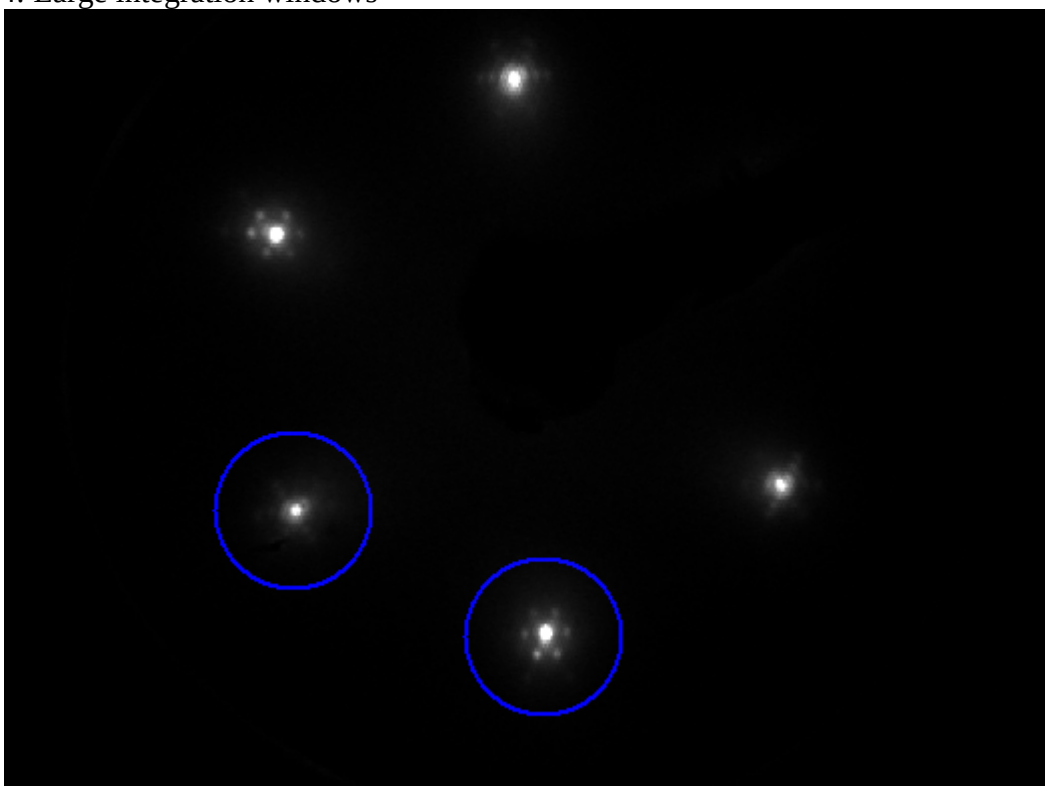
was used to collect a set of frames that were a function of the incident beam's energy. Then, the I(E) spectra were extracted for each diffraction beam. Using the HotLEED program, during the extraction process the incident energy was varied with a slider. The energy range of extraction was then specified. The initial energy pattern then had to be selected as the "anchor pattern," such that HotLEED would start the acquisition with this frame. After the acquisition options were established, the program was ready to acquire the pattern intensities.

3. Methods

Much of the experimental analysis also relied heavily on the HotLEED program. After the diffraction patterns were acquired from the experimental setup, they had to be analyzed. This profile analysis was performed with stored images frames that had been acquired in the past. In order to perform I(E) analysis, in which the program would plot curves of intensity versus energy, the files mode had to be specified. This introduced a spot list onto the screen, in which the position of integration windows can be controlled. These integration windows are circles in which the intensity of the pattern is collected. At this point, the set of images was opened, starting with the initial image, labeled IVframe1.img. Due to the symmetry of the sample crystal, the 6 groups of spot intensities were actually 2 separate groups of 3 identical intensities. Therefore, only 2 groups of intensities needed to be profiled. The HotLEED program worked by averaging several frames at a time and taking the intensities as a function of the energy.

It was decided that due to the unique structure of the Au(111) crystal, several different spot samples would be analyzed. One set of analyses would focus on the 2 groups of intensities. This can be seen in figure 4.

Figure 4: Large integration windows

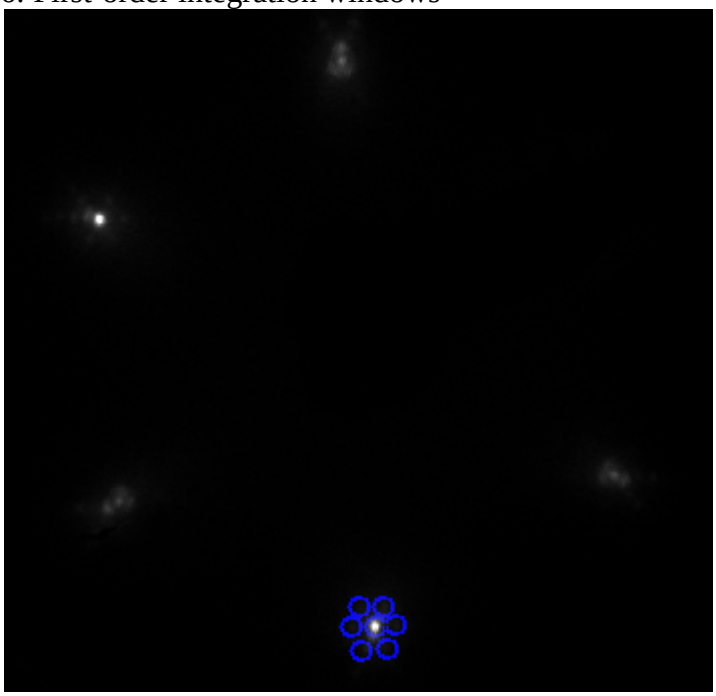


Integration windows were formatted to fit around each group of intensities. The integration circles were chosen with a diameter size of 80 in order to completely encircle the individual groups of intensities. Also, a separate analysis was performed to extract the intensities of only the central maxima. This can be observed in Figure 5.

Figure 5: Small integration windows

For each group of intensities, it was hypothesized that the central maximum, which was the brightest by far, would behave almost identically to the group of intensities as a whole. The I(E) curves would be similarly shaped, it was thought, but the total intensity of the group of spots would be higher. A third analysis performed was on the bottom group of intensities. This can be observed in Figure 6.

Figure 6: First-order integration windows



Because the individual spots were well defined, 6 integration windows were chosen to analyze the first order diffraction spots immediately surrounding the central intensity. Also present were some half-order intensities, but the limiting screen resolution prevented these intensities from being correctly encompassed by the integration windows. These 6 intensities were converted into I(E) curves, but due to time constraints, were not compared to any theoretical data. Curve 1 is located at 1 o'clock, and the numbering continued clockwise for the other 5 curves.

Starting with the first applicable image, the integration circles were placed such that they surrounded the intensity locations of interest. At this point, the intensities had to be locked in place for that frame, and it had to be made the initial frame for intensity extraction by clicking on an "anchor" icon. The next frame was then chosen, and the integration windows had to be repositioned, since the intensities moved as the incident energy changed. This process was

repeated for all of the frames in the file. After this was completed, the frames were reviewed to make sure that the integration windows were perfectly placed.

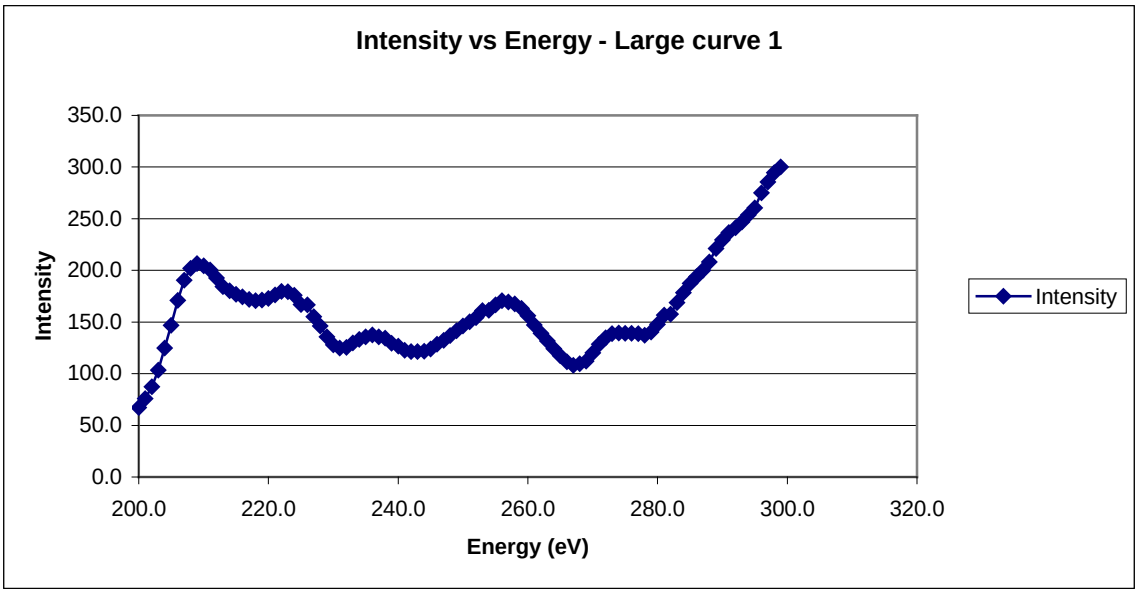
At this point, the program was run, and I(E) curves were outputted. This data was converted to an Excel format and sent to an outside researcher to be analyzed by calculating the Pendry R-factor of these experimental curves to the theoretical curves generated by an outside researcher. These theoretical curves were based on an assumed structure model. Using the program SATLEED, the intensity curves are calculated. SATLEED calculated the scattering potential for the electrons scattering from the Au(111) atoms. The structure model was then inputted, and the program calculated the diffracted intensities, taking into account the inelastic effects, temperature effects, and multiple scattering. The program then compared them to the experimental spectra using the Pendry R-factor. If needed, the model structure was adjusted, and the same iteration was used until the best fit was found.

Several notes about the program and files being used are necessary. The IVframes.img files were partially damaged, so the first 80 of the 180 files in the set appeared to have no present diffraction pattern. This problem was addressed by only analyzing the latter portion of the data set. The “curved screen” option had to be set, because the screen used in the previous experimental procedure was curved. When taking intensities of individual spots, an integration window size of 10 was used. Circular integration windows were used because they easily encompassed the circularly shaped intensity spots without taking up an extra amount of area.

4. Results

The results from these data runs came in the form of output curves showing the I(V) relationships of the diffraction beams. For the first large curve data set, the curve is show below in figure 7.

Figure 7: Large curve 1



This is the relevant portion of the I(E) curve. Because of a bug in the files, the images labeled "IVframe1.img" through "IVframe8.img" did not accurately record the intensities of the given incident energies. These initial data points were discarded and not considered in the subsequent analysis. The curves were converted into excel files and then analyzed by comparing them to a known curve.

The other I(E) curves are given below.

Figure 8: Large curve 2

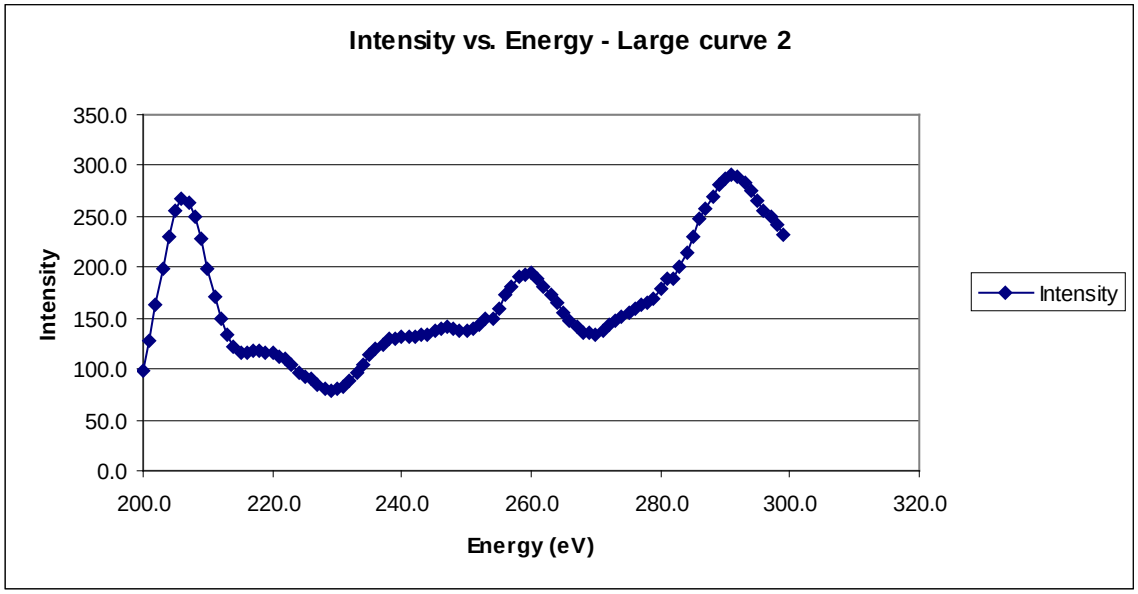


Figure 9: Small curve 1

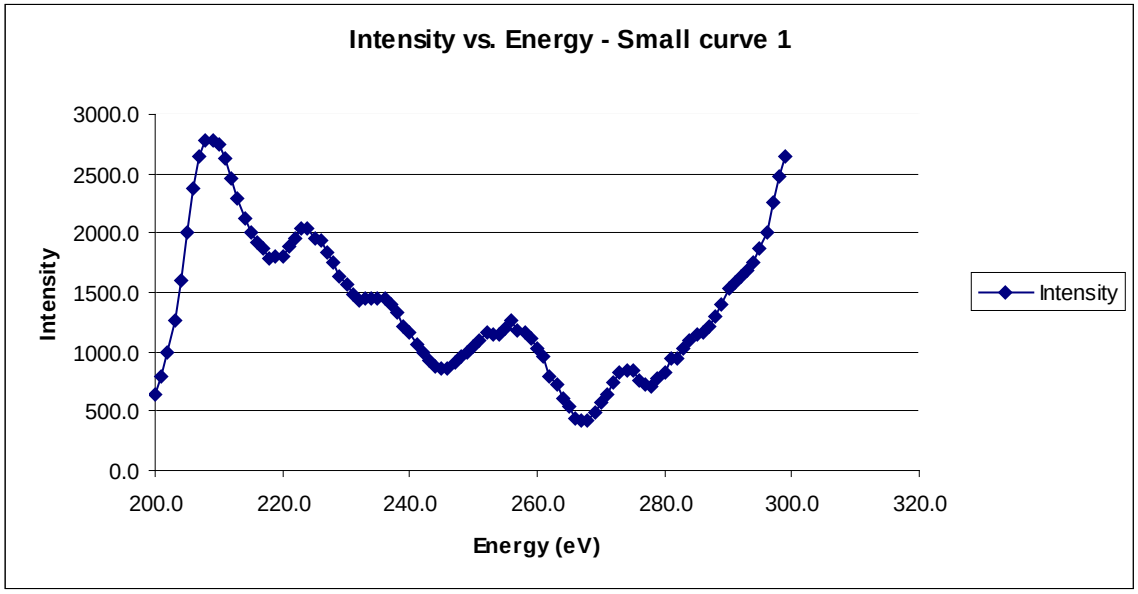


Figure 10: Small curve 2

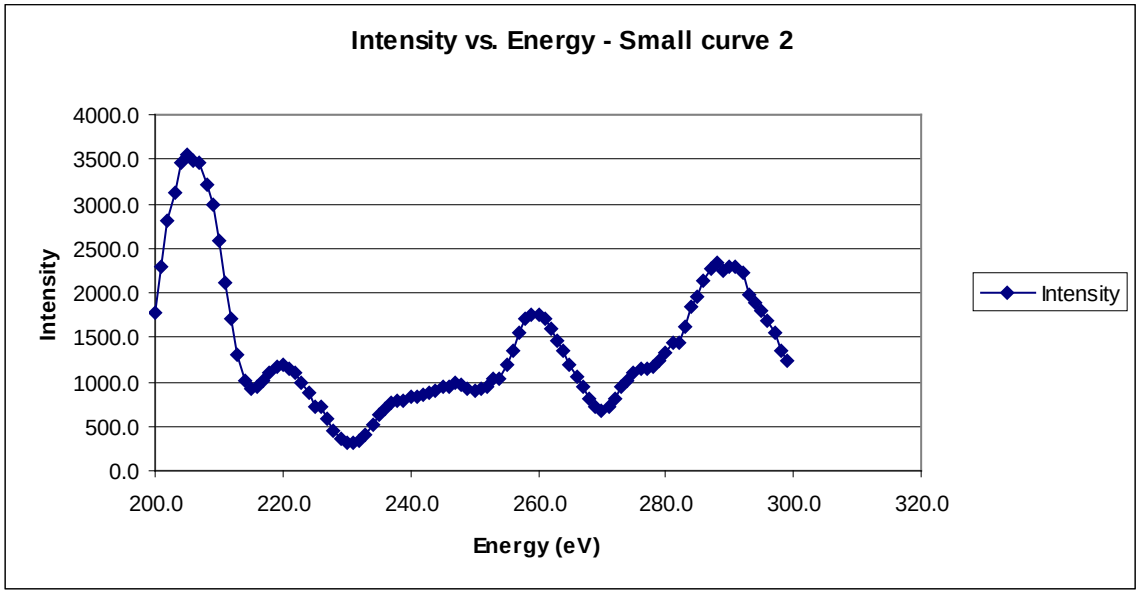
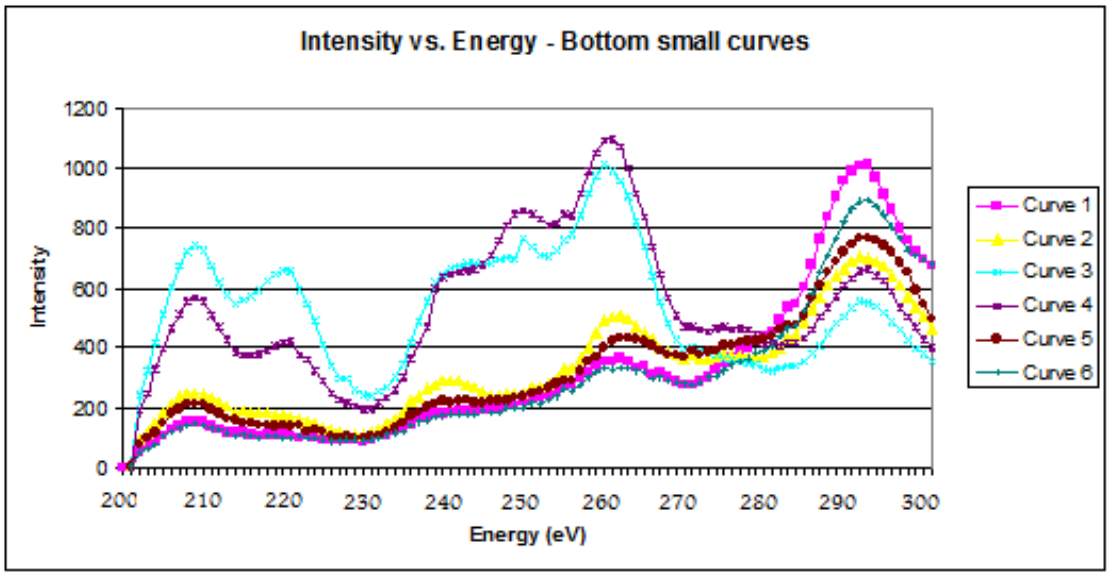


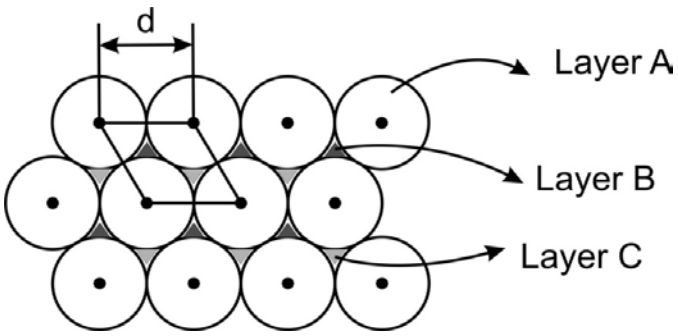
Figure 11: Bottom small curves



5. Analysis

The fcc structure of Au(111), shown in figure 10, indicates the hexagonal geometry present in the crystal.

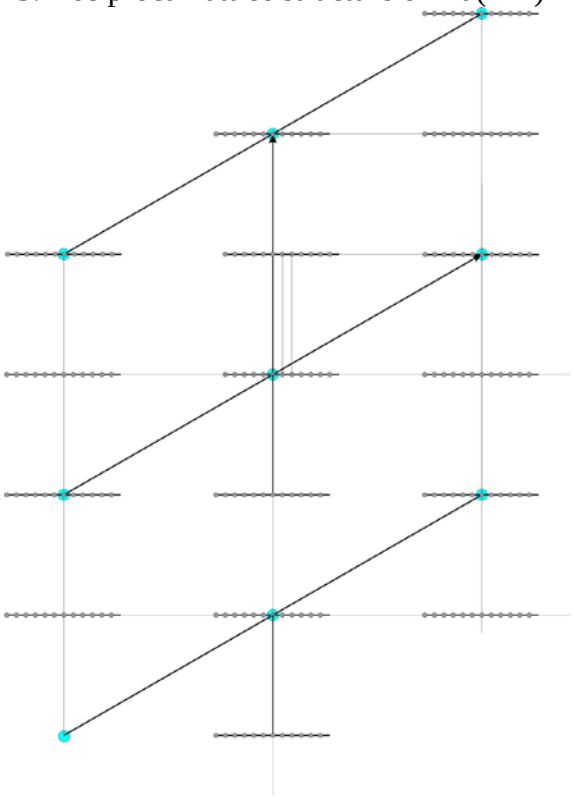
Figure 12: FCC structure



Here, d = 2.885 Å, the nearest neighbor distance. Because SATLEED does not operate with an overlayer large enough to cover the 22 x √3 unit cell, the program was set to a smaller overlayer unit cell dimension.

Due to the LEED program showing the diffracted electron intensities, the pattern of the intensities was expected to adhere to the reciprocal lattice structure of the crystal. And as expected, the intensity pattern closely matched this reciprocal structure, shown in figure 12. This figure was determined from the structure of the unit cell in figure 10.

Figure 13: Reciprocal lattice structure of Au(111)



Using the I(E) curves from the 2 central beams as well as an unreconstructed Au(111) calculation, the intensities could correctly be attributed to the orthogonal directions in the unit cell. The intensities in the 12, 4, and 8 o'clock positions were referred to as the (1,0) beams, while the intensities in the 6 and 10 o'clock positions were referred to as the (0,1) beams.

Analysis of the I(E) curves was performed by Mellita Caragiu of Ohio Northern University's physics department using the SATLEED program. SATLEED (Symmetrized Automated Tensor Low Energy Electron Diffraction) is a GUI package used to determine crystalline surface structure by analyzing experimental and theoretical diffraction data in the form of I(E) curves. For the following 2 figures, the red curves indicate the experimental data, while the blue curves are from the theoretical data.

Figure 14: Experimental (red) and Theoretical (blue) I(E) curves for the reconstructed Au(111)

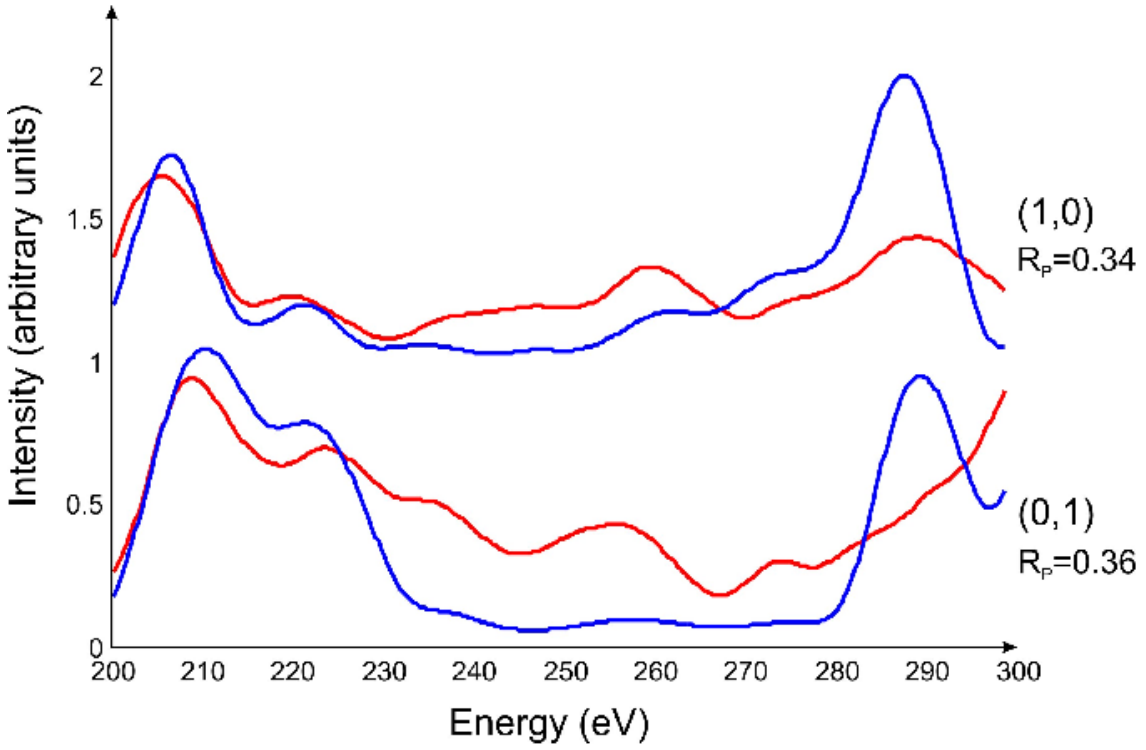
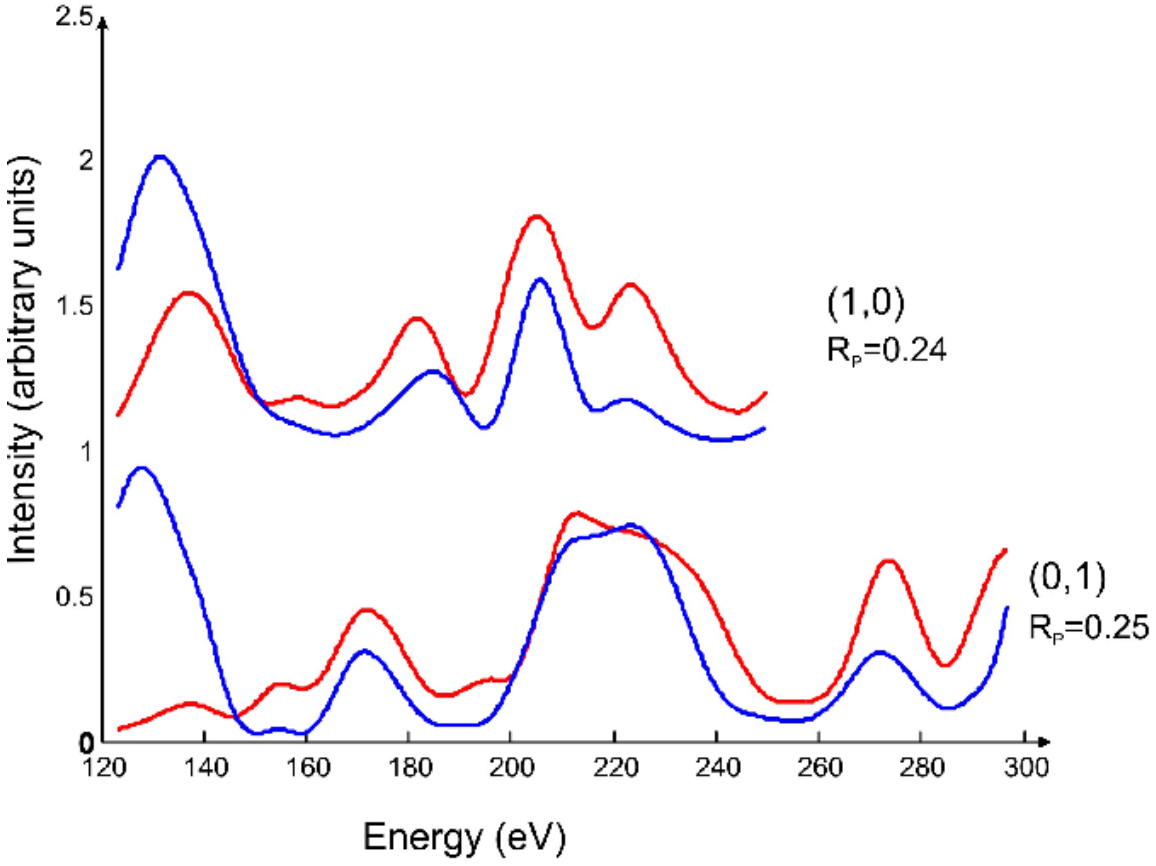
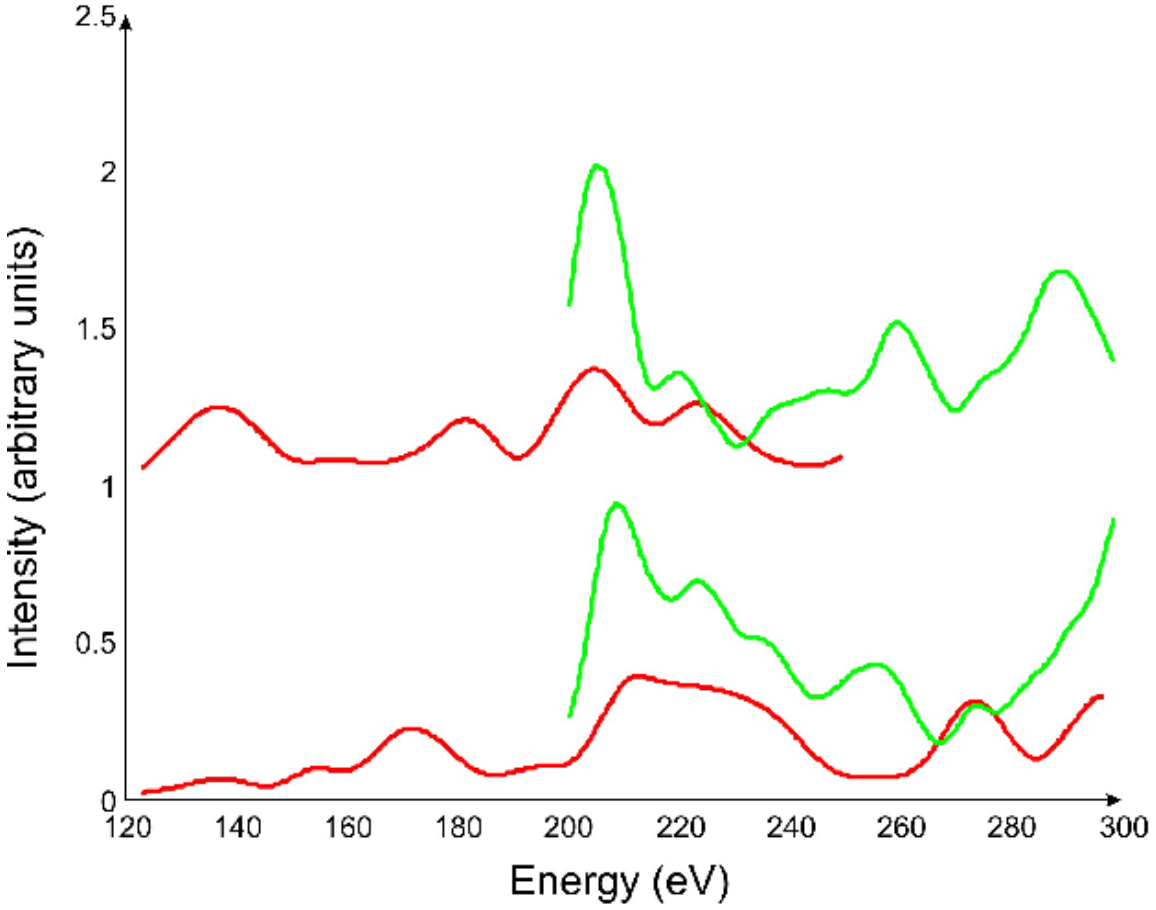


Figure 15: Experimental (red) and Theoretical (blue) I(E) curves for the unreconstructed Au(111)



For the following figure, the red curves indicate data from the unreconstructed crystal, while the green curves indicate data from the reconstructed crystal.

Figure 16: Experimental I(E) curves for reconstructed (green) and unreconstructed (red) Au(111)



The analysis technique accounts for many factors that contribute to a loss in accuracy of the electron diffraction. These include the presence of a scattering potential, inelastic effects during the electron-lattice collisions, and thermal effects on the lattice, which causes lattice vibrations. Also, the presence of multiple scattering by electrons, in which electrons may diffract off several layers of the crystal, complicates the results. Because of all of these complications, the calculation of atomic position in the crystal is not as simple as taking the reverse transformation of the intensity vs. energy data. These complications can be partially mitigated, however, by lowering the temperature of the crystal, having a better surface quality, and using a higher resolution, which can be attained by using better LEED instrumentation.)

The Pendry r-factors are measures of agreement between the experimental and theoretical I(E) curves. In *Reliability Factors for LEED Calculations*, Pendry states that values of 0.2 or less show good agreement, numbers near 0.35 show mediocre agreement, and values of 0.5 or greater show bad agreement. Our reconstructed data had Pendry r-factors near 0.35, and the unreconstructed data had values near 0.25.The contributing factor to the large scale of these metrics was mostly the large weight of the gold atoms used, which affected the scattering potential calculations. This shows that the reconstructed experimental data did not match the theoretical data as well as the unreconstructed data. Therefore, it can be said with confidence that the method of I(E) extraction for the reconstructed experimental data is not a reliable method, and that a better method is necessary to feasibly achieve results similar to the unreconstructed data set.

Overall, the reconstructed and unreconstructed curves agreed when comparing the experimental and theoretical data. The theoretical curves for the reconstructed Au(111) were made using a small overlayer in the SATLEED modeling, so using a larger overlayer (the size of the unit cell) in the future will most likely lead to greater agreement in the curves in figure 13. When comparing the data in figure 15, it can be seen that there are disparities at about 240 – 260 eV between the reconstructed and unreconstructed curves. It is thought that this corresponds to a difference in the surface structure of the reconstructed and unreconstructed surfaces, which was initially expected.

Comparing the I(E) curves shows close similarity between the small and large extraction areas, which agrees with the hypothesis that the small central beam behaves similarly to the whole set of intensities in the beam.

6. Future Work

Several improvements could be made to the study in order to gain deeper insight into the experimental study of the reconstructed Au(111) surface. Using a full set of I(E) data for energy below 200 eV would allow for a more complete analysis between the experimental and theoretical data, which would produce a more reliable Pendry-R factor. Also, the disparity between the experimental and theoretical curves is more pronounced at lower energies, indicating that a better method of extracting intensities at lower energies may be necessary, which would also help lower Pendry-R factor if the disparity were decreased.

7. References

Barth, J. V., H. Brune, G. Ertl, and R. J. Behm. "Scanning Tunneling Microscopy Observations on the Reconstructed Au(111) Surface: Atomic Structure, Long-range Superstructure, Rotational Domains, and Surface Defects." *Physical Review B* 42.15 (1990). Print.

Sandy, A. R., S. G. J. Mochrie, and D. M. Zehner. "Structure and Phases of the Au(111) Surface: X-ray-scattering Measurements." *Physical Review B* 43.6 (1991). Print.

Leatherman, Gerald S., Nicola Ferralis, and Renee D. Diehl. "HotLEED User Guide." Rev. of *HotLEED*. 22 Apr. 2004. Print.

Diehl, Renee D. "Adsorption Studies Using Low-Energy Electron Diffraction." *The Time Domain in Surface and Structural Dynamics*. Kluwer Academic, 1988. 439-65. Print

Thompson, James L., Heekeun Shin, and Renee D. Diehl. *Surface Characterization and Thermal Properties of Au (111) Using LEED*. Thesis. Lincoln University University, 2009. Print.

Pendry, J. B. "Reliability Factors for LEED Calculations." *Journal of Physics: Condensed Matter* 3 (1980): 937-44. Web.

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