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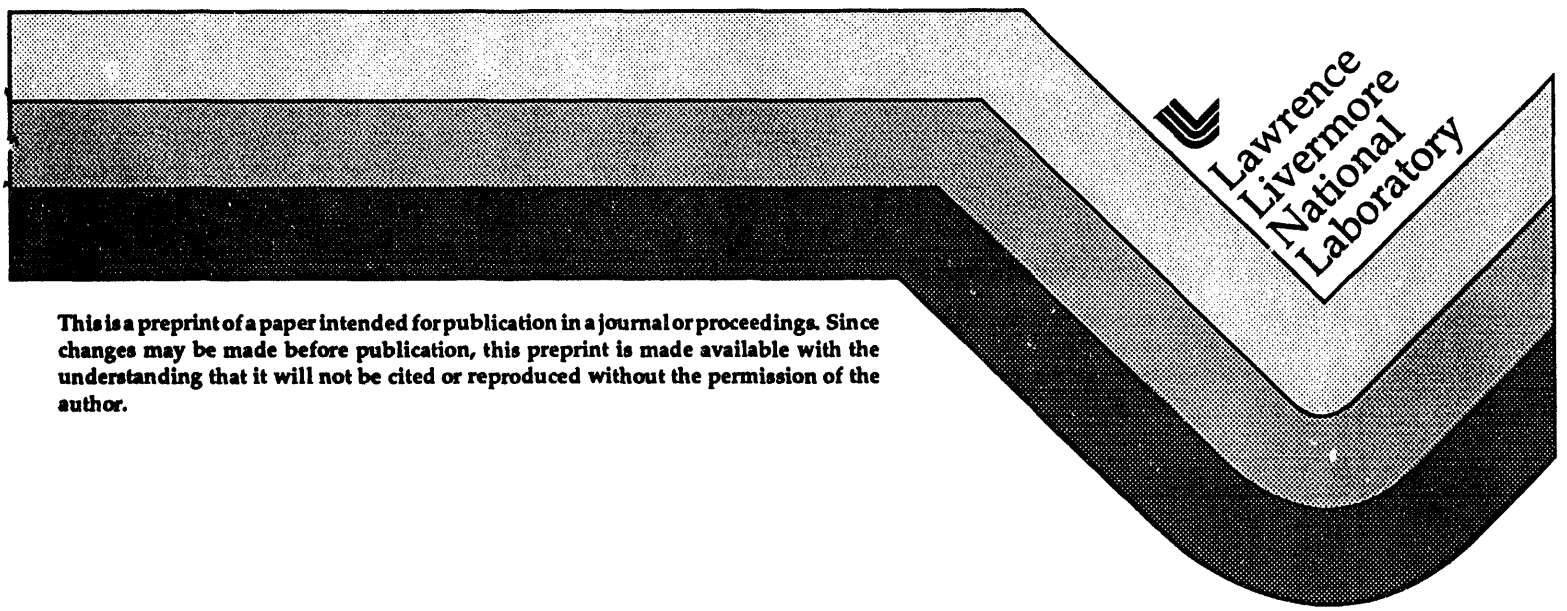

DISCLAIMER

HOLOGRAPHIC ATOM IMAGING FROM EXPERIMENTAL PHOTOELECTRON ANGULAR DISTRIBUTION PATTERNS

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ABSTRACT

One of the most challenging areas of materials research is the imaging of technologically relevant materials with microscopic and atomic-scale resolution. As part of the development of these methods, near-surface atoms in single crystals were imaged using core-level photoelectron holograms. The angle-dependent electron diffraction patterns that constitute an electron hologram were two-dimensionally transformed to create a three dimensional, real-space image of the neighboring scattering atoms. We have made use of a multiple-wavenumber, phased-summing method to improve the atom imaging capabilities of experimental photoelectron holography using the Cu(001) and Pt(111) prototype systems. These studies are performed to evaluate the potential of holographic atom imaging methods as structural probes of unknown materials.

INTRODUCTION

In the hopes of developing new, direct methods for probing the structure of novel materials, the atom imaging technique of photoelectron holography has generated much interest as a probe of single crystal materials and, eventually, more challenging abrupt interfaces. Suggested by Szöke,[1] and subsequently formulated by Barton,[2] the electron holography technique has undergone a series of refinements to improve the quality and reliability of the atom images. Most of these improvements - such as scattering factor compensation, reduced angular windowing, and Gaussian elimination methods[3-5] - have been demonstrated mainly on simulated data, but some of the experimental demonstrations to date of the holography technique have also benefited.[6-10] However, most of these image improvement methods require *a priori* knowledge of the system being studied to achieve image improvement, particularly the suppression of conjugate atom images.

Another method for improving the quality of holographically derived atom images was developed by Barton.[11,12] He showed with simulated holograms that a third-axis transform-approximation - a phased-sum of multiple-wavenumber holograms - can suppress twin images and multiple scattering artifacts that are a natural consequence of hologram inversion. It was later demonstrated with experimental work[13,14] that this approach for near surface atom imaging held much promise. We show in this work the application of this image improvement method on experimental holograms and have chosen the Cu(001) and Pt(111) bulk systems using the photoejected Cu 3p and Pt 4f core-states as the coherent wave source for atom illumination. This method is well served by vacuum ultra-violet and soft x-ray synchrotron radiation because of the tunability of the monochromatic light. One attractive

feature of the multiple-wavenumber, phase-summing formalism is that it requires only experimentally observable information (the hologram and its energy) to create a higher fidelity atom image.

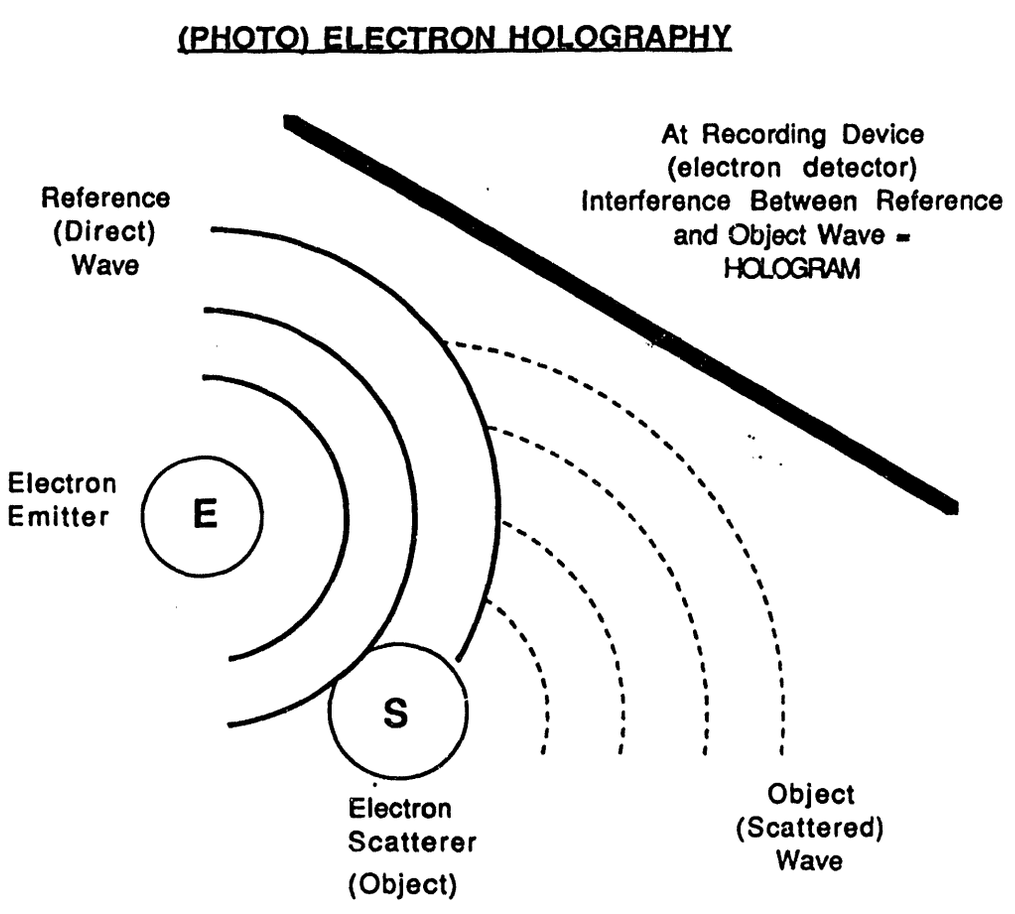

Figure 1: A schematic that illustrates the diffraction process that forms an electron hologram is shown. A localized electron is ejected from an atom (electron emitter) at some fixed kinetic energy and propagates towards an angle resolved electron detector. Part of that same electron wave scatters off of neighboring atoms *en route* to the electron detector. The interference between these two waves contains the structural information in the form of the path length difference incurred during the scattering process.

BACKGROUND

The electron scattering physics that produces a photoelectron hologram is experimentally the same as photoelectron diffraction.[15] This technique for probing the atomic structure of surfaces, adsorbates, epitaxial overlayers, and interfaces examines the photoelectron intensity measured from ordered materials in order to isolate the structurally significant modulations in intensity that arise from local diffraction. Several excellent reviews of this now well established and utilized technique have been written.[16] When electron emission is measured as an electron angular distribution, the diffraction (interference) between the core-level electron measured directly from the emitter (i.e., the reference beam), and the same

photoelectron wave that has scattered off neighboring atoms (i.e., the object wave), form a true hologram. The electron scattering physics that forms a hologram is shown schematically in Fig. 1. A hologram's chemical specificity is a consequence of using element-specific core-level photoelectrons, and oxidation-state and interfacial sensitivity can be achieved when high-resolution, synchrotron-radiation photoelectron spectroscopy is used to select the oxidation-state or interfacially shifted core-level electron.

The elegance of the holography technique permits the multiple-angle photoelectron interference pattern to be two-dimensionally transformed[2] to produce a real-space, three-dimensional intensity map of the electron-scattering atoms neighboring the photoemitter.[5-8] Even without transforming the holograms, the electron forward scattering, which is implicit in patterns measured from buried systems, yields important structural information. The powerful combination of synchrotron radiation and photoelectron holography also enables higher resolution images of atoms to be created through multiple-energy filtering of the resultant images.[12-14]

EXPERIMENTAL

We measured copper 3p photoelectron holograms from a clean, Cu(001) crystal face using well established cleaning and annealing procedures.[17] The surface was checked with core-level photoelectron spectroscopy for contaminants, and the Cu valence-band photoemission features were used to orient the sample with respect to the analyzer. All photoemission spectra were recorded using an Eastman ellipsoidal mirror analyzer that has been described previously.[18] This angle-resolving, energy-band-pass electron analyzer characterized the Cu sample as an angle-integrating detector and also measured the 3p photoelectron holograms in an angle-resolved mode.

Measuring the Cu 3p multiple-energy electron angular distribution patterns at several energies mandated the use of monochromatic synchrotron radiation as the excitation source so that photoelectron holograms over a wide kinetic energy range could be obtained. We conducted these measurements at the National Synchrotron Light Source on the IBM/U8 beamline[19] This facility provided the 316 - 560 eV photons needed for ejecting the Cu 3p core electrons. Electron angular distributions were measured at nine kinetic energies ranging from 244 to 477 eV. This range had several experimental advantages over a higher energy which could produce better resolution:[6] the cross section for Cu 3p photoemission is well matched with the flux throughput of the monochromator, and non-forward scattering intensities are large in this region of k-space.[20] This implies that electron back scattering atoms as well as forward scatterers may be observed through this choice of energy range.

The Pt(111) sample was prepared using well established cleaning procedures[14] and was examined for cleanliness using photoelectron spectroscopy. Initial spectra were measured and continually compared to spectra taken during the experiment in order to monitor the cleanliness of the sample. The sample normal was positioned directly into the center of the angle-resolving analyzer and resulted in the synchrotron radiation polarization vector being 45^{o} with respect to the sample surface. Crystal positioning was done by observing the symmetry of the Fermi surface map obtained from angular distribution patterns.

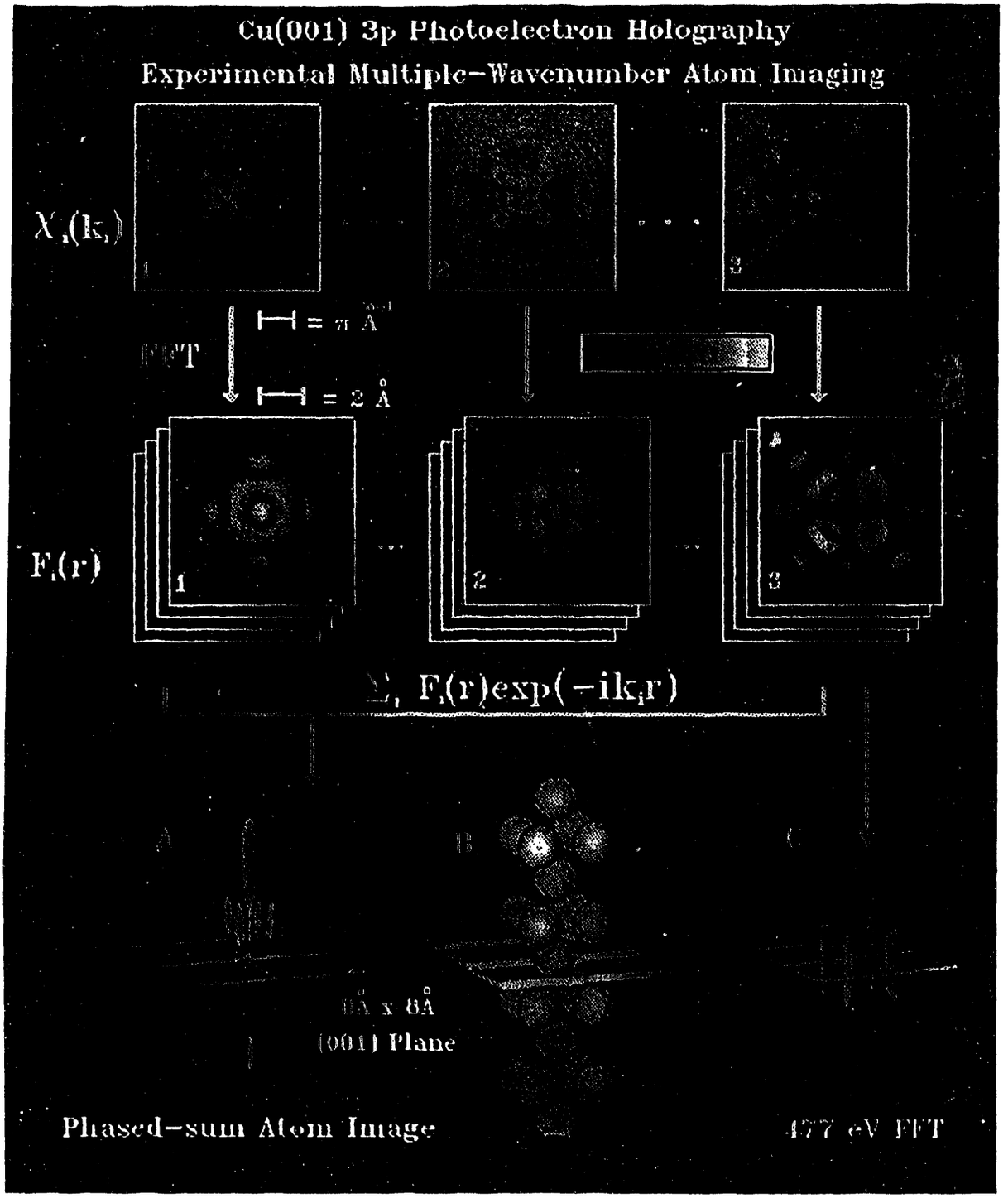

Figure 2: Several steps in the experimental multiple-wavenumber atom imaging method are shown. A series of holograms (Cu 3p $\chi_i(ki)$) measured at several wavenumbers k_i, 1 = 244 eV, 2 = 322 eV, 3 = 477 eV) are numerically inverted to form a series of real space atom images $F_i(r)$. The amplitude of a nine wavenumber phase-summed reconstruction for Cu(001) is shown in panel A. This iso-contour volume rendering has an 8 x 8 Å reference plane parallel to the (001) face passing through the emitter and is shown next to an ideal atom rendering of the Cu(001) lattice (Panel B) with an identical reference plane. The volume contour depiction of the atom image intensity for 3 is shown in Panel C.

Electron emission patterns of the Pt $4f_{5/2}$ photoelectron were measured at eight equally spaced wavenumbers from k=8.8Å^{-1} to 10.2Å^{-1}. Background spectra were taken at the high energy side of the photoelectron peak and were used for analyzer signature and photon flux normalization. We found that the backgrounds were interchangeable and it was sufficient to measure a few at well chosen energies. All eight images were taken at the same sample position. The method of extracting the structural information from the electron angular distribution patterns from Pt(111) were similar to those used for the Cu(001) sample.

RESULTS

Simple, two-dimensional background removal methods were used for each electron angular distribution pattern to isolate the holographic interference information from the raw data. It should be noted that many aspects of our background removal also eliminate the strong forward peak upon which the structure-containing interference fringes reside,[8] which improved the image quality. Each Cu hologram was then four-fold symmetry averaged and multiplied by a Gaussian window to eliminate truncation errors. The Cu(001) hologram measured at 322 eV is shown in the inset to Fig. 2. Each of the nine copper holograms were then two-dimensionally transformed.[2] The resultant volume of Fourier-like intensities ideally have local maxima that are located at scattering atom positions, but in practice, the reconstructed atom intensities appear shifted from their ideal position by as much as 1Å. Other work has shown that this result of direct transformation of the hologram, without any other treatment, also produces shifted atom images.[5-7] It is only a fortunate selection of energy that produces unshifted atom images.[14]

From the raw electron angular distribution patterns, holograms were extracted using methods that have been described elsewhere.[21] Three of the holograms measured in this work are pictured in Fig. 2 where χ_1 was measured at 244 eV, χ_2 at 322 eV, and χ_3 at 477 eV. Fourier-like, two-dimensional transforms were used to invert all nine holograms into three-dimensional, real-space, atom intensity volumes. The numerical inversions of the three holograms pictured in Fig. 2 are shown schematically below their respective source data. The visible slice in each case is a cut through the Fourier volume taken through the first layer of electron forward scatterers. Note the four high intensity spots around the center (the surface normal) that can be assigned to the four scatterers. Also note that going from lower to higher kinetic energy, the lateral resolution of each atom image improves.

Phase-summing of the hologram reconstructions was achieved using the simple, multiple-energy transform approximation presented by Barton.[12] Briefly, this approximation can be described as:

$$A(\mathbf{r}) = \sum_i F_i(k_i,\chi_i,\mathbf{r})e^{-ikir}$$

where the resultant real-space $\mathbf{r}$ scattering atom intensity, $A(\mathbf{r})$, is given by a sum over the individual atom reconstructions $F_i(k_i,\chi_i,\mathbf{r})$ - which were computed from the holograms χ_i measured at each wave vector value k_i times exp(-ikr)- the phase term that isolates the real, single-scattering contribution to the reconstruction. The phase-dependence as a function of wavenumber is different for the conjugate image than the true image thereby leading to suppression of the twin image.

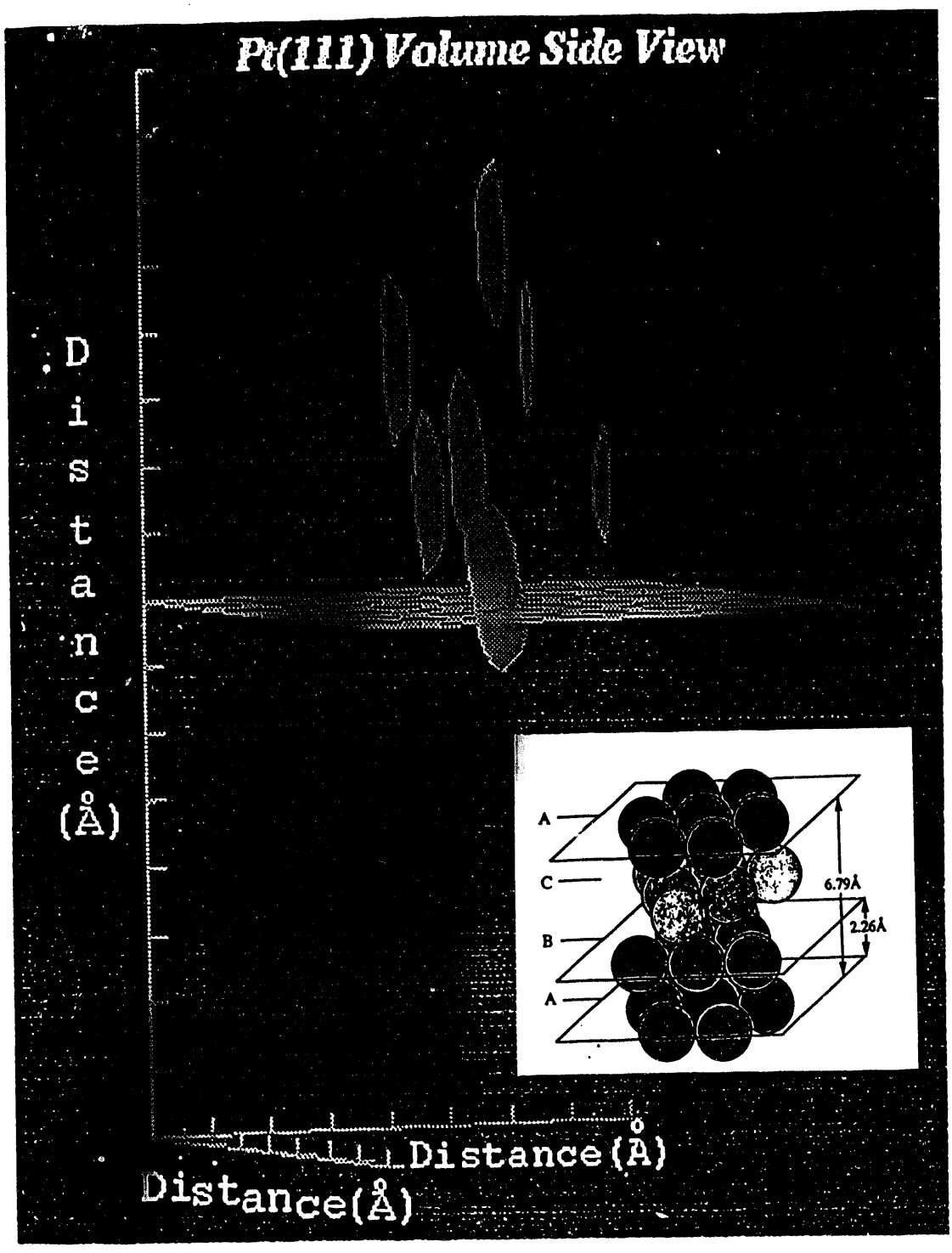

Figure 3: Multiple-wavenumber symmetry averaged volume side view of the Pt(111) $4f_{5/2}$ hologram reconstructions. Atoms are shown as iso-density surfaces in a three-dimensional space above the photoelectron emitting atom. Seven atoms are shown in their expected atomic positions. Each tick mark is 1 Å. The inset depicts the ideal atom geometry with the black sphere representing the emitter atom (bottom layer).

The result of the Cu(001) nine-energy phased sum is shown as a volume contour at 70 % of maximum in Panel A of Fig. 2. The five atoms directly above the emitter are visible in this image and are the highest intensity features. When compared to the ideal atom image of the Cu(001) lattice in panel B, and to the 477 eV result in Panel C, it is apparent that the quality of the atom imaging has been improved mostly through suppression of the conjugate image below the reference plane. In the phase-summed image we also note that the conjugate image is approximately 0.1 the intensity of the real image.

Scattering atoms appear shifted from their nominal lattice location in the multiple-energy (A) and all single-energy images[6,8,22] because of the additional phase introduced by the scattering physics. This has been observed in earlier experimental electron holography studies[6] and Fourier-transformed, energy-dependent, photoelectron diffraction.[15,23] Forward scattering amplitudes are greater than back scattering intensities throughout the structurally-useful range of wavenumbers and determines why atoms that lie between the emitter and the detector dominate the Fourier reconstruction. In our multiple-energy, phase-summed image, we obtain a radial shift of 0.4 Å for the first layer atoms, and a 0.9 Å shift for the second layer atom located directly above the emitter.

The results obtained from the Pt(111) multiple wavenumber phased-summing procedure are even more striking.[14] Figure 3 shows an iso-density, three-dimensional image of atoms above a given Pt emitter, which is shown in the center of the reference grid. Three atoms are seen near their ideal location one layer above the emitter, three more two layers above, and one three layers up, directly above the emitter. This image was generated by phase-summing eight patterns together in the fashion described above.[2] Notice, that compared to the Cu(001) results, there is some improvement in Z-resolution for the Pt(111) image with the main effect being a loss of twin images and artifacts. We note that all of the information shown here has been averaged rotationally for ease of presentation, and that most of the information can be realized without averaging. Variations in position intensity for different directions due to final state wave effects encourage this method of presentation.

CONCLUSIONS

We have shown that the recently developed technique of photoelectron holography can be used to image single-crystal materials with atomic resolution. Using the prototype, single-crystal surfaces of Cu(001) and Pt(111), we can improve upon the early accomplishments in the field by using a multiple-wavenumber phase-summing algorithm that suppresses the conjugate images that are a result of the numerical transform. This method also acts to suppress the multiple-scattering contributions to the resultant reconstructed atom images.[2] In our examples, it is not clear that the intensity below the emitter in Figure 2, Panel A is entirely attributable to the twin image of the second layer, (forward scattering) atom above the emitter, or to the second layer (back scattering) atom below the emitter; the expected intensities for both should be the same. However, we see that in Figure 3, the twin image problem can almost entirely be removed. When the multiple-wavenumber, phase-summing method can be coupled with an adsorbate system imaging demonstration, we can then consider using photoelectron holography on challenging abrupt interfaces, such as buried heterojunctions.

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