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A NEW RAPID AND ACCURATE METHOD TO MEASURE LOW-ENERGY ELECTRON DIFFRACTION BEAM INTENSITIES. THE INTENSITIES FROM THE CLEAN Pt(111) CRYSTAL FACE

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ABSTRACT

The intensities of the low-energy electron diffraction beams back-scattered from the clean platinum (111) surface are measured by a photographic technique. The fluorescent screen in a conventional low-energy electron diffraction (LEED) chamber is photographed at various incident electron energies in electron volt intervals in the range of 20-200 eV. The film is then machine developed and scanned using a computer-controlled, digital-output microdensitometer. The intensity profiles of all of the diffraction beams can be obtained simultaneously this way in ten minutes and these are identical to those measured by telephotometer. The film can readily monitor three orders of magnitude change in intensity. The photographic diffraction beam intensity measurement is particularly useful when time-dependent changes in the beam intensities due to adsorption, chemical reactions or electron beam-surface interactions occur or when many diffraction beams are present as in the case of coincidence lattices or reconstructed surfaces. The diffraction beams from the clean platinum (111) crystal face have been measured by both photography and telephotometry and the intensity profiles necessary to carry out surface structure analysis are reported.

I. INTRODUCTION

The development of surface crystallography in the past several years has required the accurate measurement of low-energy electron diffraction beam intensities as well as the evolution of the theory of low-energy electron diffraction from clean solid surfaces and from surfaces with adsorbed layers. Important advances in theory have made surface structure determination of clean monatomic solids possible wherever adequate experimental data has become available. In fact, the lack of accurate diffraction beam intensity data appears to be the major obstacle at present to the development of the field of surface structure analysis.

There are good reasons for the slow accumulation of precise intensity data in the published literature. The low-energy electron diffraction apparatus that is presently commercially available is not well-suited for accurate determination of scattering angles because of the presence of stray magnetic fields and crystal holders lacking precise control of crystal position. In an ultra-high vacuum system there are always time-dependent changes in surface conditions due to the adsorption of unwanted gases from the ambient. Therefore, it is imperative to measure diffraction beam intensities emanating from the sample surface as rapidly as possible. The reasons for the rapid obtainment of intensity data multiply when the structure of adsorbed gases is to be determined. Competition of various gases for adsorption sites, interactions of adsorbates with the electron beam, and the easy transformation of certain surface structures to disordered layers or other structures are factors that make diffraction beam intensity determination difficult. In addition, the refinement of the

calculated surface structure necessitates the availability of intensity data from several diffraction beams over a wide range of scattering angles and electron energies.

A rapid and accurate method of taking diffraction beam intensities is needed that permits measurement of all of the various order diffraction beams simultaneously, and over wide ranges of angles and electron energies. The presently available and more frequently used techniques that utilize spot photometer or Faraday cups cannot carry out this task.

In this paper we report on the development of a new photographic method to obtain low-energy electron diffraction beam intensities accurately and rapidly and on the application of this technique to measure the beam intensities from the platinum (111) crystal face. The technique involves photographing the fluorescent screen using a fast film of suitable sensitivity to obtain all of the diffraction beam intensities simultaneously. We can measure the diffraction beam intensity over three orders of magnitude range. Photographs are machine developed for uniformity and calibrated for point-by-point conversion from digitalized optical density to intensity. This is followed by computer analysis of the integrated intensities and background correction. The diffraction beam intensities from the clean platinum (111) crystal face that were obtained this way have not been reported previously. The surface structure analysis based on this data is provided in the paper following this manuscript.

Using this photographic technique the structure analysis of complex coincidence lattices and reconstructed surfaces has become possible. In order to facilitate wide-spread adoption of this technique of surface

structure analysis, we compare the experimental intensities obtained by photography and by spot photometer and describe in detail how to obtain a relationship between the diffraction beam current and the measured optical densities. It should be noted that the photographic technique yields only the relative intensities of the various diffraction beams which is certainly sufficient data to carry out surface structure analysis.

II. EXPERIMENT

A. Apparatus

A modified Varian UHV LEED-Auger apparatus was used for these measurements. The stainless steel chamber was maintained at a background pressure of 1×10^{-9} torr by an Ultek 200 ℓ/sec ion pump and a Varian, water jacketed titanium sublimation pump. Selected gases could be introduced into the vicinity of the sample through a hypodermic syringe needle separated from a bakable gas manifold by a Varian adjustable leak valve.

The LEED-Auger system had a Varian four grid LEED optics which uses an ~5 kV post acceleration to display the diffraction pattern on a fluorescent screen coated with P-11 phosphor. The electron gun was a Varian off-axis gun with a direct heated tungsten filament. A Varian Electron Gun Power Module with a LEED Control Module provided either a beam current or filament voltage regulated electron beam with a voltage range from -2.5 V to -1.5 kV in the LEED mode and from -5 V to -3 kV in the Auger mode. The electron beam current was determined by measuring the total current returning to the electron gun from ground and was measured to the 0.001 μamp level using a Kiethley model 160 Digital Multimeter.

The platinum crystal sample was cut from a 99.9999% purity single crystal rod purchased from Materials Research Corporation. It was spot welded to high purity polycrystalline platinum strips to avoid possible contamination. The sample which could be heated resistively was mounted on a Varian High Precision Manipulator modified so that the "Flip Mechanism" would provide rotation about the incident beam axis.

In addition to heating and chemical treatment, crystal cleaning was facilitated by sputtering using a Varian Ion Bombardment gun mounted at a right angle to the LEED optics.

One of the most important considerations involved in making accurate intensity measurements was creating a field-free drift region for the incident electron beam. Electric fields were eliminated by shielding with conducting materials, usually tantalum foil. Shielding from external magnetic fields was accomplished by surrounding the LEED optics and the drift region from the end of the electron gun to the viewing window with a normalized μ-metal shield. This reduced the magnetic field perpendicular to the incident electron beam to less than 10 milligauss, which will deflect a 20 eV electron beam by no more than 0.2 degrees.

The degree to which an electric or magnetic fields might effect the intensity profiles was checked by two methods. In the first method the azimuthal angle of the Pt(111) crystal was chosen so that an equatorial rotation in either direction from normal incidence by the same amount would give the same specular intensity profile. The second method made use of the fact that for the Pt(111) surface the first-order non-specular diffracton beams exhibit a three-fold degeneracy when the incident beam is normal to the surface. At ±10°, the specular intensity profiles were identical from 10 eV to 50 eV, and from 50 eV to 85 eV the intensities of the three-fold degenerate first-order beams were identical (Figure 1).

The cutting, polishing, and cleaning of platinum single crystal has been previously described.[1] The cleanliness of the surface was determined using Auger electron spectroscopy. Auger spectra

were always taken both before and after taking an intensity measurement.

Accurate crystal positioning was achieved by first establishing a condition where the incident electron beam was normal to the crystal surface as evidenced by the threefold degeneracy of the first-order Pt(111) diffraction features. The crystal was then rotated to the desired angle of incidence by means of the angular scale on the manipulator. A vernier on this scale implied that measurements could be made to the nearest 0.1°, but the accuracy was not justified due to mechanical play in the manipulator. The azimuthal angle was determined by measurement from a photograph, and the accuracy was within 0.5°.

B. Telephotometer and Photographs

Diffraction intensities were measured from the fluorescent screen in two ways, by telephotometer and by analyzing photographs. The telephotometer used in these studies was a Gamma Scientific Model 2000 Telephotometer employing fiber optics with an accuracy of ±4% of full scale and with the capability of measuring intensities over a range of better than three orders of magnitude at a given aperture setting. The photographs were taken using a Nikon F camera using an 85 mm lens with a K3 + K4 + K2 extension ring, and a motor drive. The film used was Kodak Tri-X emulsion #SO-265. The film was machine developed using Dupont extra fast x-ray developer (XPD). The developing, fixing, and washing times were all 150 sec at a temperature of 83°F. The developed film was scanned using a computer controlled, digital output, microdensitometer. The film was advanced from one frame to the next by a motorized advancing mechanism, also under computer control.

When taking intensity measurements using the telephotometer an aperture was used which detected light from a solid angle of 20'. This corresponds to an area on the fluorescent screen of approximately 4 mm. All measurements were taken with the LEED power supply in the Constant Beam Current mode. However, for incident electron energies less than ~50 eV the incident current was no longer held constant, but the beam current was measured as previously described, and the intensities were normalized to the constant value maintained above 50 eV. All intensity measurements were made from 20 eV to 200 eV in 2 eV intervals. The position of the telephotometer was checked periodically throughout the series of measurements to insure that the maximum intensity was recorded at each energy.

When taking intensity measurements photographically an exposure time of 1 sec was used with an aperture of either f/4.0 or f/2.8 depending upon whether the diffraction feature of interest was the (00) beam or a non-specular beam respectively. A portion of the same film batch was exposed to a calibrated continuous gray wedge by light filtered through a #48 Wratten filter and developed along with each film strip. This "sensi-strip" was used for calibrating the density on the film to the intensity which created it as described in the next section. The developed film was scanned, and the output analyzed by computer to determine the diffraction intensities.

C. Conversion of Density to Intensity

In order to measure intensities photographically the darkened, negative image on the film has to be related quantitatively to the light intensity, I, which created that image. The conventional quantitative measure for the darkening of a film negative is the optical density which is defined as the negative logarithm of the transmission (O.D. = -log T, $T = I/I_o$).[4] For fixed conditions of film emulsion, developing and spectral distribution in the incident light, the optical density is a monotonic function of the exposure where the exposure, E, is defined as $E \equiv \int I dt$.[4] For incident light intensities which remain constant in time, which is the case here, the exposure reduced to E = It. If the exposure times are all the same, then the optical density is a monotonic function of the intensity, and a calibration between the O.D. and the intensity is possible.

The calibration from density to intensity was done in the following way: A piece of film from the same emulsion batch as was used in photographing the diffraction pattern was exposed to the image of a calibrated, continuous neutral density wedge. This wedge was calibrated so that the logarithm of the relative intensity of the light transmitted varied linearly over the length of the wedge. Thus, the $\log(I_{rel})$ of the light incident on the film varied linearly over the length of the image. This image was the "sensi-strip" referred to in the previous section. By measuring the optical density of the film along this image a relation was obtained between the optical density and the incident relative intensity. By using the same emulsion batch any non-uniformity between emulsion batches was eliminated. The light used to expose the wedge was

filtered through a Wratten #48 filter which has nearly the same transmission spectrum as the emission spectrum of P11 phosphor.[2,3] This was done because the film response depends upon the spectral distribution of the incident light. Finally, the calibration wedge was exposed, and the film strip was developed along with each set of diffraction pictures taken. This minimized the effect of changes that may occur during developing.

Under exposure conditions where either I is large and t is small, or vice versa, the exposure may no longer obey the relationship E = It. This is called reciprocity failure.[4] The exposure time when taking photographs is 1 sec, but the strobe which was used to expose the density wedge has a flash time of 1/100 sec. To check for reciprocity failure a plot of density vs. log(relative intensity) was generated by taking pictures of a gray card through a series of neutral density filters and at the same time measuring the intensity of the light transmitted through the filters using the telephotometer. A comparison of the density vs. log(relative intensity) curve generated by the calibrated wedge to that generated by the camera showed no significant differences (Figure 2).

Using the photographic technique of intensity measurement 90 frames are generated at a given polar angle, θ, and azimuthal angle, ϕ, by a single electron energy scan. Since accurate structure analysis requires taking intensities at several values of θ and ϕ, it is imperative to scan the film automatically.

The mechanics of the scanning microdensitometer makes use of the "sensi-strip" calibration a routine operation. The instrument scans a rectangle of selected dimensions in a series of lines. Each line consists of a series of steps where the film optical density is measured

and recorded on magnetic tape. The spacing between lines and steps is precision regulated through micrometer linkages driven by two stepping motors. The minimum step distance or line spacing is 0.0005 inches. All mechanics are under computer control. This generates a grid of density values corresponding to the positions in the rectangle scanned, i.e. a two dimensional density map.

When scanning the "sensi-strip" each step in the scan corresponds to a change in the intensity determined by the calibrated density wedge. By averaging several lines together to eliminate the graininess in the film image, a table is generated of measured densities and the corresponding relative intensities.

All of the data including the scanning of the "sensi-strip" is recorded on magnetic tape for computer analysis. The analysis consists of four parts. First, the data from scanning the "sensi-strip" is averaged and smoothed to generate a table of density vs. the corresponding relative intensity. Next the data from scanning the diffraction pictures is searched for diffraction spots. When a spot is found, the relative intensity is computed by converting the density of each point within a fixed radius of the maximum density into an intensity, subtracting a locally determined background value and summing the intensities for all points with intensities greater than the background. The number of points used in the integration is a measure of the spot size but also depends upon the distance chosen between steps and lines when scanning. Finally, the spots found in each scan are numbered and plotted within a rectangular boundary representing the border of the film frame. The spot numbers and their intensities are listed next to the plot, and a

deck of cards is punched to be used as data for a Cal Comp plot of the I-eV curve.

III. RESULTS AND DISCUSSION

The diffraction intensities from a clean Pt(111) surface were recorded at normal incidence and at polar angles of 4°, 10°, and 16°. The diffraction beams as well as the azimuthal angle, ϕ, are defined following the convention established by Jona[5] (Figure 7). Figures 3 and 4 show the normalized relative intensity profiles as a function of polar angle for the (00) beam and the $(\bar{1}0)$ beam respectively. Figure 5 shows the normalized I vs. eV curves for the first-order non-specular beams at normal incidence. Figure 6 shows the $(\bar{1}1)$ beam and the (01) beam at a polar angle of 4°. The intensity scales between beams are not consistent so that the intensities of different beams cannot be compared directly.

The intensities determined photographically are in excellent agreement with those determined using the telephotometer as can be seen in Figure 3. The photographic measurements were taken with the LEED power supply in the Constant Beam Current mode which causes the diffraction intensities at higher energies to fall below the threshold for detection by the photographic film, and since the theoretical analysis of the intensities could not be carried past 100 eV due to computational limitations,[6] no effort was made to analyze photographic data at energies above 120 eV. However, with the LEED power supply in the Constant Filament Voltage mode the beam current increases with the incident beam energy so that there is no significant decrease in the overall diffraction intensity allowing photographic determination of the intensity profiles at higher energies. The intensities may then be normalized to unit beam current during the computer analysis. If the intensity profile terminates below 100 eV, this

was due to the diffraction beam being blocked from view by the sample holder. A more compact crystal holder is currently being designed to minimize this problem. Finally, since all measurements were taken with the first grid at ground potential, the non-specular beams were not observable at their emergence energy.

It is important to note that due to the nature of the calibration from density to intensity only relative intensities can be determined photographically. In addition, no attempt was made to relate the intensity scales from one beam to another. Despite this limitation and the limited range of incident beam energies for which data was available the data was sufficient for a crystallographic characterization of the surface.[6]

The value of the photographic technique comes into play when the data must be recorded swiftly due to time dependent changes in the surface condition as a result of adsorption or chemical reactions on the surface or of interaction with the electron beam. All of the data available on the display screen may be recorded permanently on film within 10 minutes, then analyzed at leisure. When coincidence lattices are present or in the case of surface reconstruction (for example, the Si(111) or the Pt(100)) there are so many diffraction beams present at a given electron energy that photographic detection and storage of their relative intensities appears to be the only way to compile sufficient data for surface structure analysis. The photographic detection of low-energy diffraction beams is likely to remain the most versatile technique to collect intensity data for surface structure analysis until a new display and rapid scanning techniques are designed for use in a drastically modified LEED chamber.

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6. L. L. Kesmodel and G. A. Somorjai, subsequent paper.
7. Designed and built by the Remote Sensing Group of the School of Forestry, University of California, Berkeley.

FIGURE CAPTIONS

Fig. 1. (a) Normalized relative I vs. eV profiles for Pt(111), (00) beam, $\theta = \pm 10°$, $\phi = 30°$. (b) Non-normalized relative I vs. eV profiles for Pt(111), (10), $(0\bar{1})$, $(\bar{1}1)$ beams, $\theta = 0°$, $\phi = 0°$.

Fig. 2. Film density vs. log relative intensity generated by the "sensi-strip" (heavy circles) and by the camera (open circles).

Fig. 3. Normalized relative I vs. eV profiles for Pt(111), (00) beam as a function of the polar angle, θ. The intensity scales for different polar angles are not comparable.

Fig. 4. Normalized relative I vs. eV profiles for Pt(111), $(\bar{1}0)$ beam as a function of the polar angle, θ. The intensity scales for different polar angles are not comparable.

Fig. 5. Normalized relative I vs. eV profiles for Pt(111), (10) beam and (01) beam at normal incidence. The intensity scales between beams are not comparable.

Fig. 6. Normalized relative I vs. eV profiles for Pt(111), $(\bar{1}1)$ beam and (01) beam, $\theta = 4°$, $\phi = 0°$. The intensity scales between beams are not comparable.

Fig. 7. Diffraction beam labelling for the Pt(111) diffraction pattern following the convention of Jona (Ref. 5).

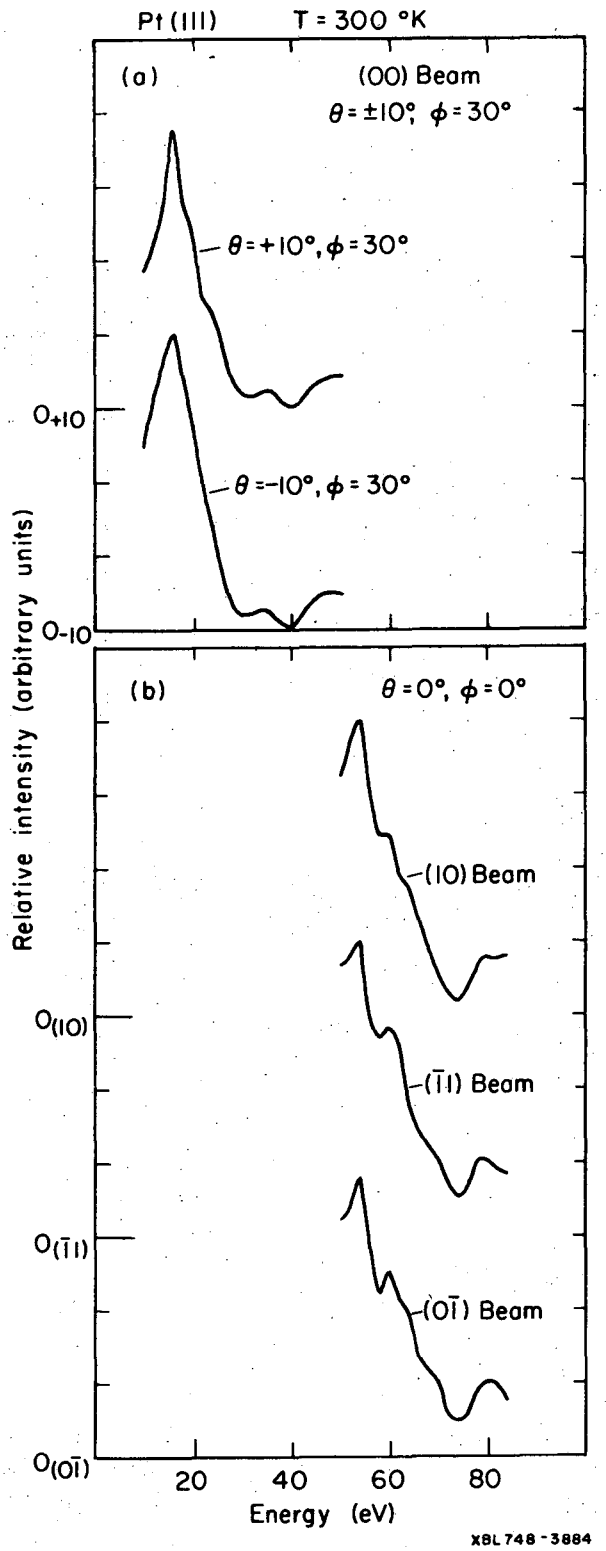
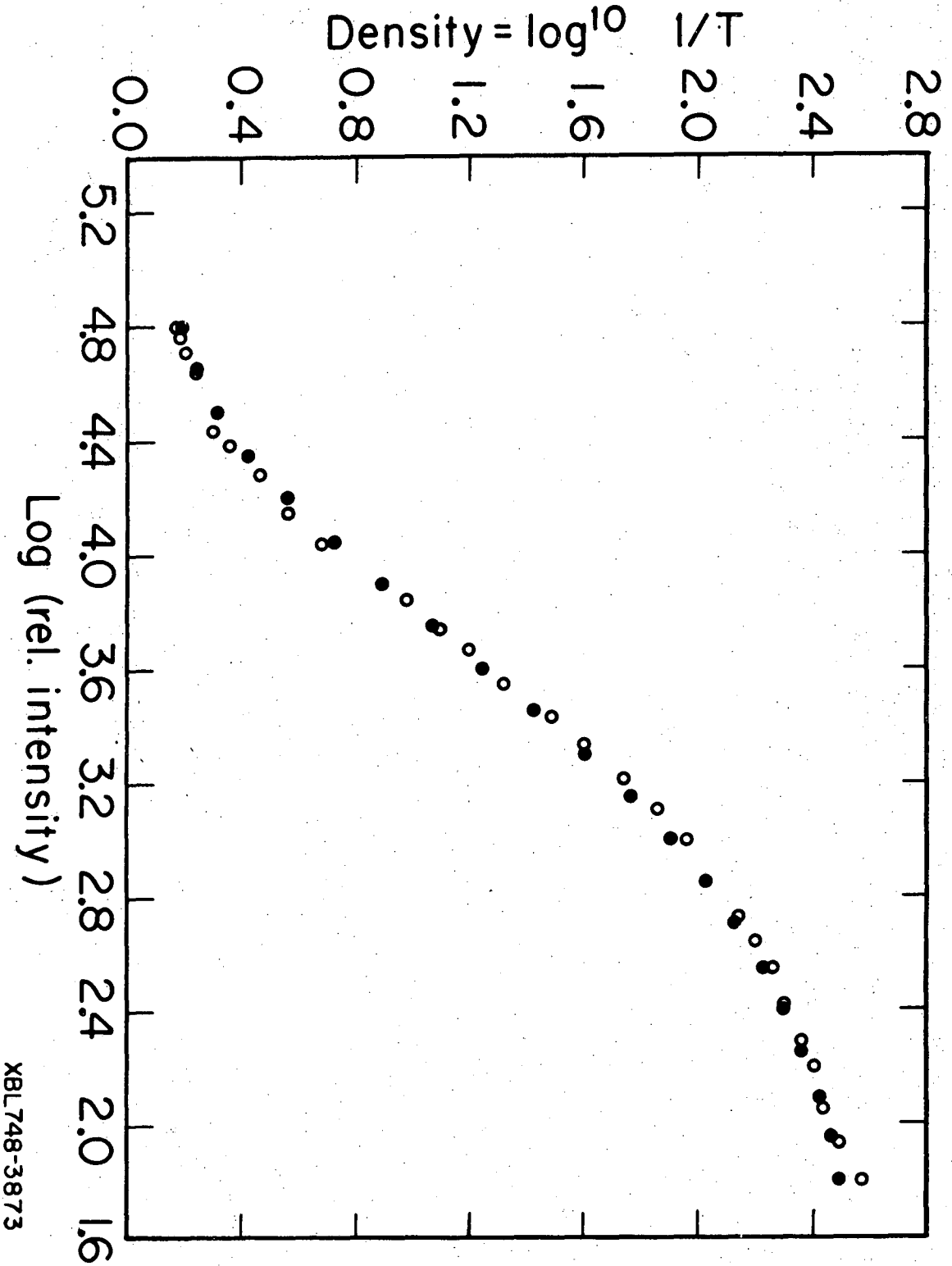

Pt (111)
T = 300 °K
(a)
(00) Beam
θ = ±10°, φ = 30°
θ = +10°, φ = 30°
θ = −10°, φ = 30°
0+10
0-10
(b)
θ = 0°, φ = 0°
(10) Beam
(1̄1) Beam
(01̄) Beam
0(10)
0(1̄1)
0(01̄)
Relative intensity (arbitrary units)
20
40
60
80
Energy (eV)
XBL 748-3884

Fig. 1



XBL748-3873

Fig. 2

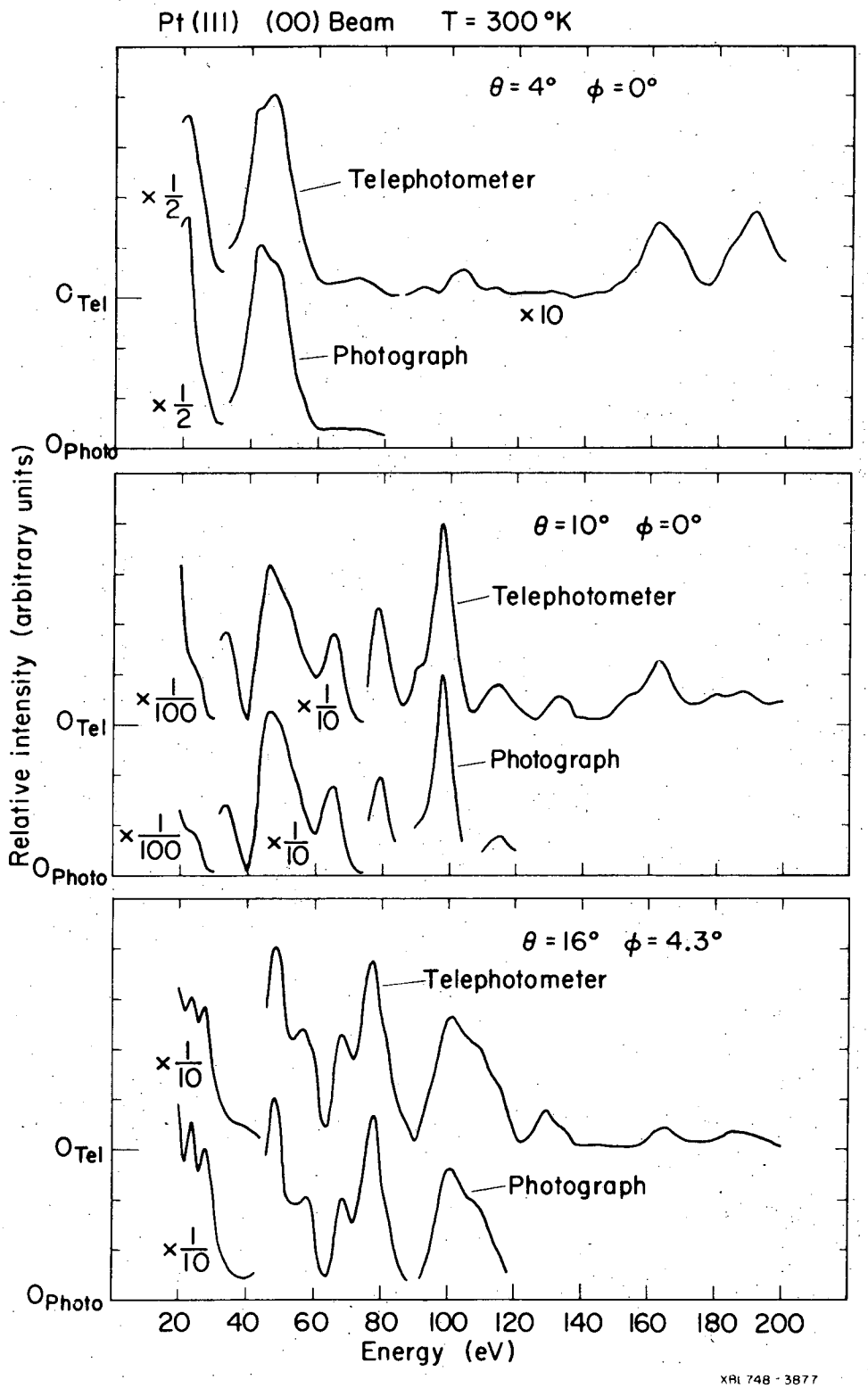

Pt (111) (00) Beam T = 300 °K
θ = 4° φ = 0°
Telephotometer
Photograph
× 1/2
× 10
O Tel
O Photo
θ = 10° φ = 0°
× 1/100
× 1/10
θ = 16° φ = 4.3°
Relative intensity (arbitrary units)
20 40 60 80 100 120 140 160 180 200
Energy (eV)
XBL 748 - 3877

Fig. 3

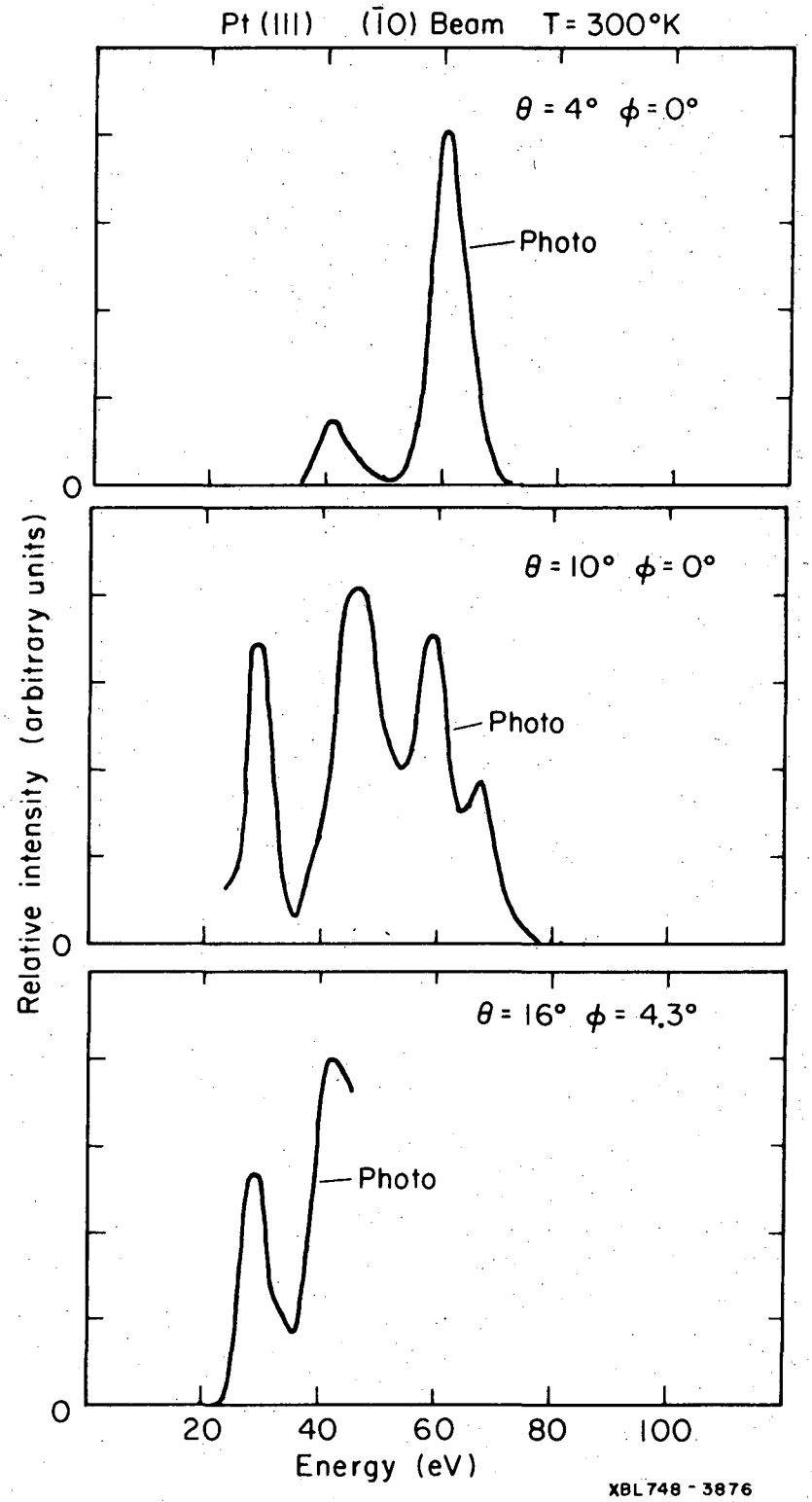

Pt (111) (1̄0) Beam T = 300°K
θ = 4° ϕ = 0°
Photo
θ = 10° ϕ = 0°
Photo
θ = 16° ϕ = 4.3°
Photo
0
0
0
Relative intensity (arbitrary units)
20
40
60
80
100
Energy (eV)
XBL748-3876

Fig. 4

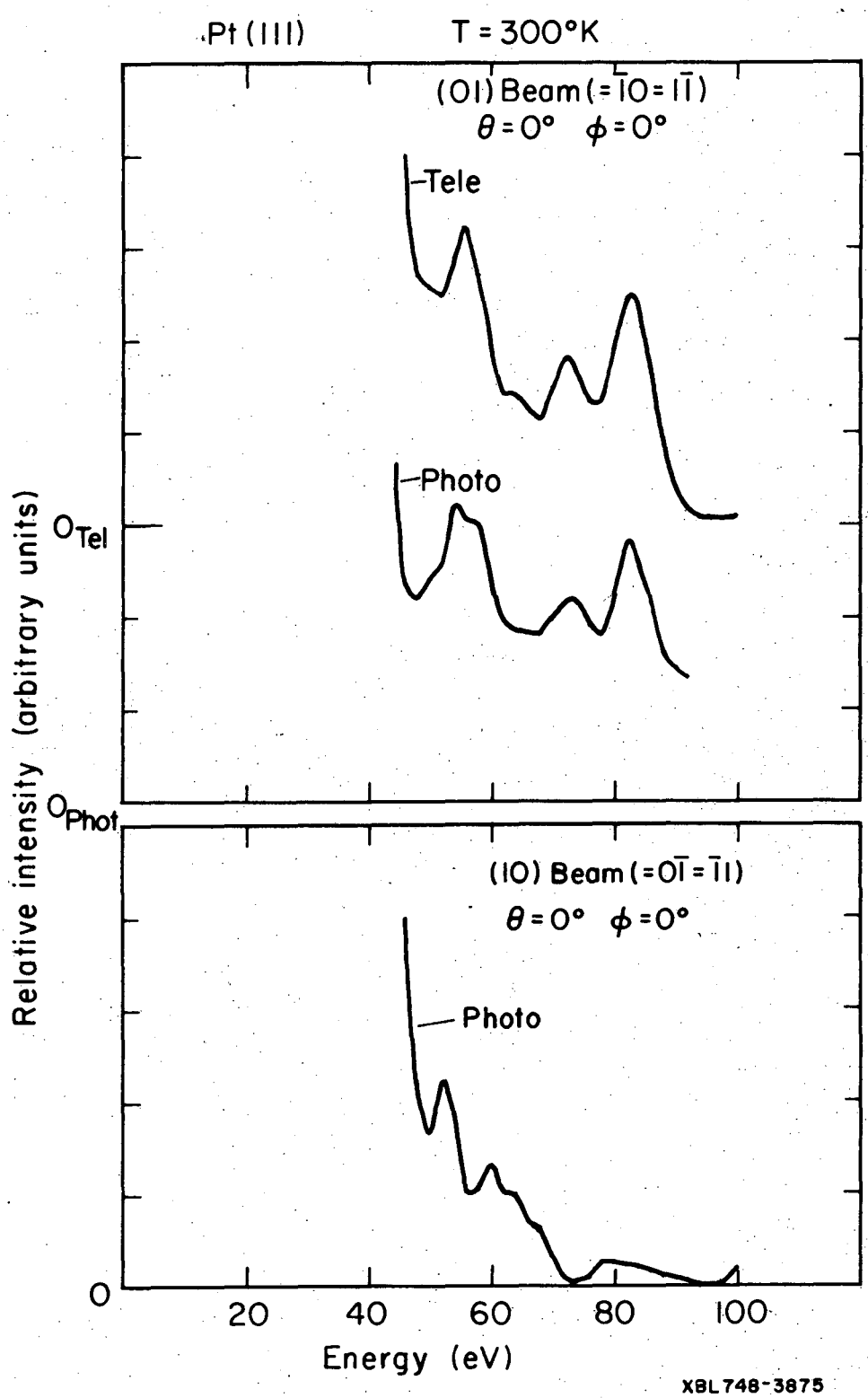

Pt (111)
T = 300°K
(01) Beam (= $\bar{1}0$ = $1\bar{1}$)
θ = 0° ϕ = 0°
Tele
Photo
O_{Tel}
O_{Phot}
Relative intensity (arbitrary units)
(10) Beam (= $0\bar{1}$ = $\bar{1}1$)
θ = 0° ϕ = 0°
Photo
0
20
40
60
80
100
Energy (eV)
XBL748-3875

Fig. 5

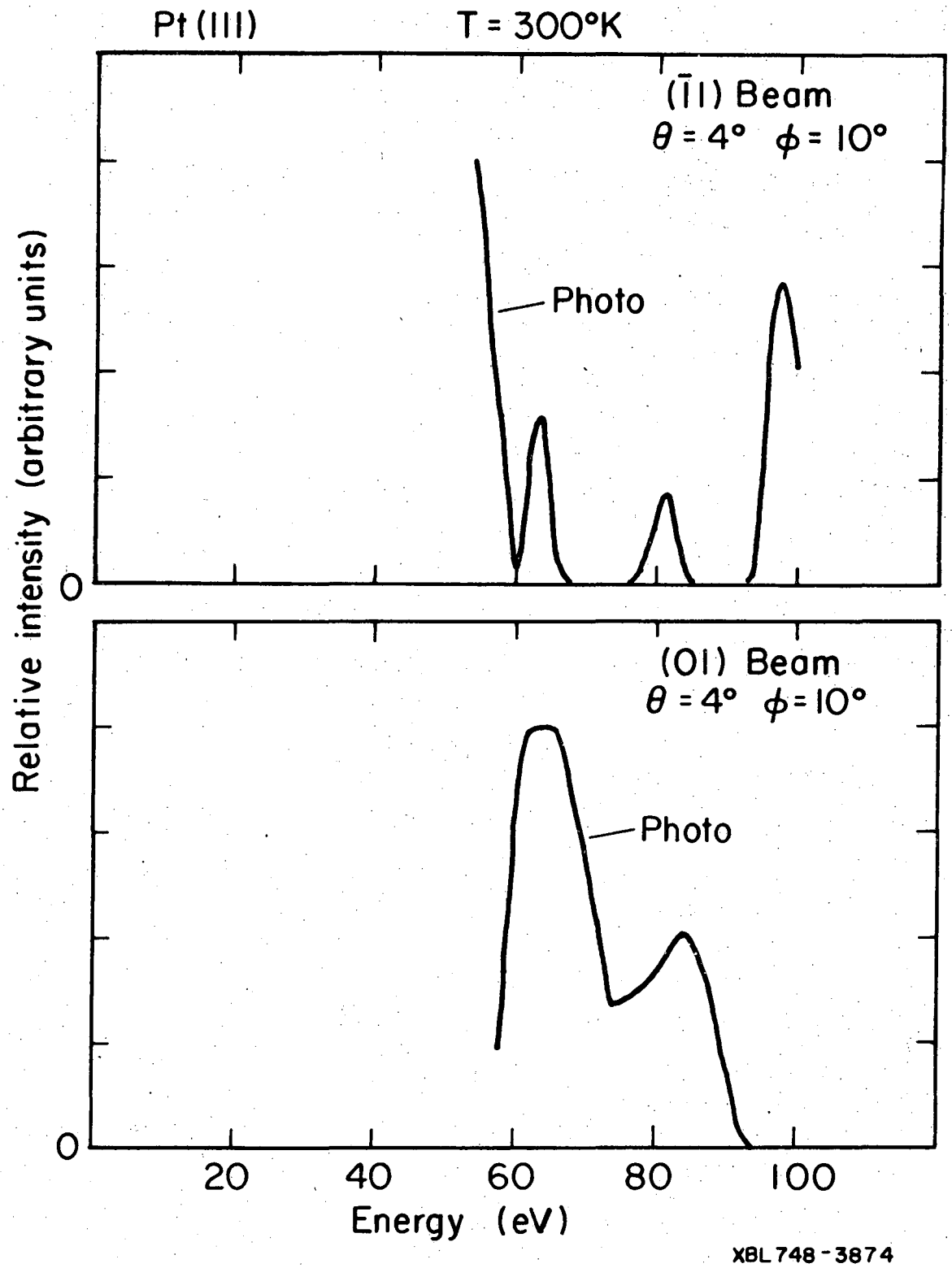
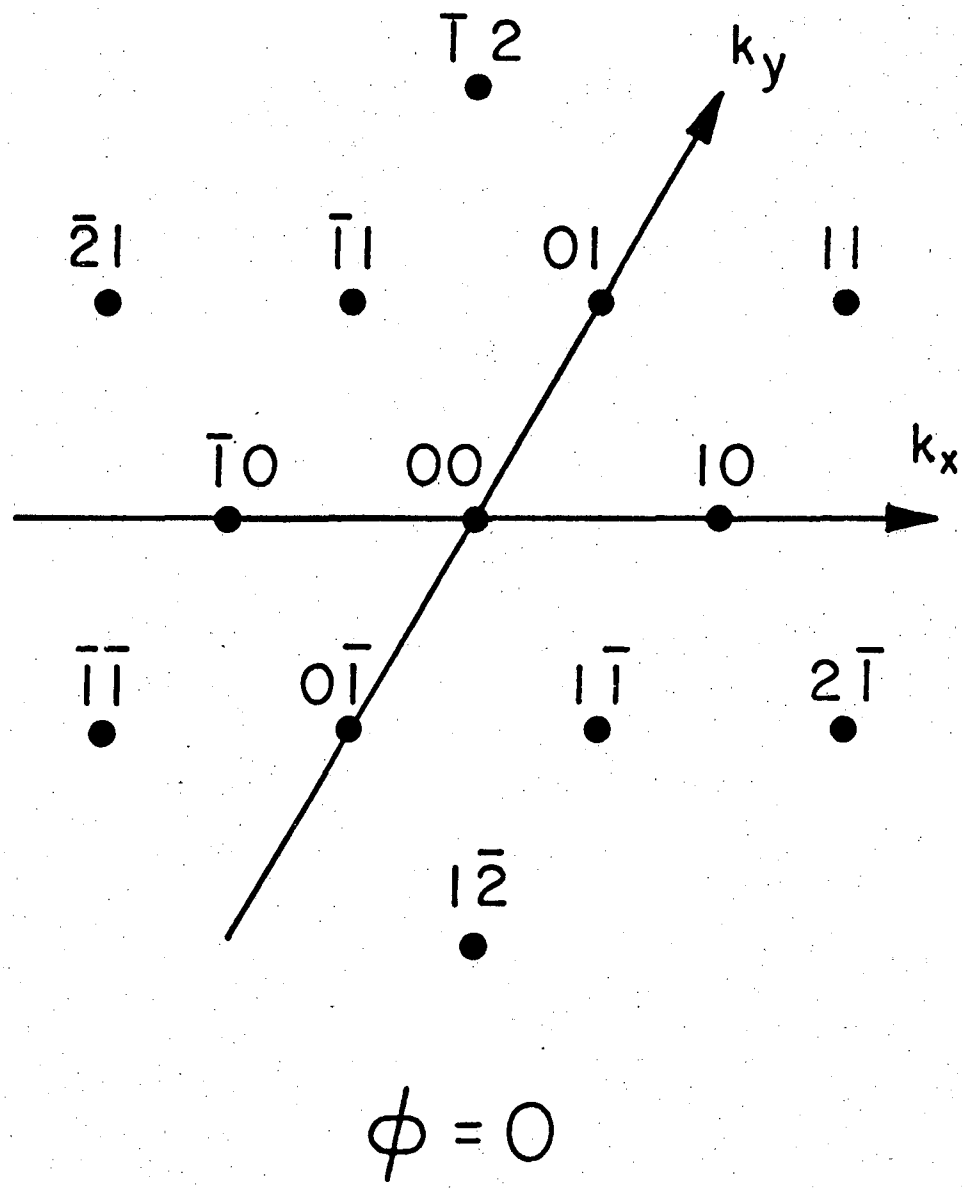

Pt (111)
T = 300°K
($\bar{1}$1) Beam
θ = 4° ϕ = 10°
Photo
(01) Beam
θ = 4° ϕ = 10°
Photo
Relative intensity (arbitrary units)
0
0
20
40
60
80
100
Energy (eV)
XBL 748-3874

Fig. 6



XBL 748 - 3885

Fig. 7

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