Investigation of Certain Effects Accompanying the Diffraction of Low Speed Electrons

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Influence of surface action. A test was made for the effect of density and arrangement of atoms in the surface plane on the fine structure of electron diffraction beams from a silver single crystal. This was done by observing the structure of the diffraction beams corresponding to Bragg reflections from a (210) and a (520) set of planes for two different boundary planes of the crystal ((100) and (110) planes). For the second-order beam from the (210) planes at about 200 volts, and the first-order beam from the (520) planes at about 300 volts, the changes in fine-structure characteristics due to a change in the surface atomic layer of the amount indicated are small compared to the differences in fine structure characteristics of the beams from different sets of atomic planes. **Directional effects.** A new type of directional effect was observed which shows a dependence of beam structure on the direction of the diffracted beam in the crystal. Further observations on deviations from the surface grating formula also indicate the presence of directional effects. Etching of the type obtained by Sproull was observed. A sensitive method of observation for determining what crystal facets are present is described.

SURFACE ACTION

M. v. LAUE[1] has estimated the voltage range in which there should be an appreciable effect on the diffraction of electrons due to the gradual transition of the field across the boundary of a crystal. He concludes that this surface action may be neglected for electrons with energies greater than 200 electron volts, but that for lower speed electrons it is doubtful if such a treatment is permissible.[2] Because we[3] have observed unexpected fine-structure characteristics in the diffraction of low speed electrons by metallic single crystals, it is important to determine if these characteristics are due to or in any way influenced by such surface action. We have previously pointed out that there appear to be several methods of obtaining such information, and some evidence on this point has already been reported.[3]

The object of the present investigation is to ascertain if the fine structure characteristics are greatly affected by a change in the density and arrangement of atoms in the surface layer. v. Laue's final formula for the effect of the surface layer contains, among other things, the density of the atoms in this layer, i.e., a change in the surface density alters the voltage below which the effect of the surface layer becomes appreciable. Hence, if the fine structure depends on surface action, the maximum voltage at which it is present should depend on the spacing; and presumably the exact form of the fine structure, at any voltage for which this structure appears, should be altered by a change in the surface density of atoms.

METHOD

A change in the atomic density of the surface layer may be realized in the following manner. With a silver crystal having a surface boundary parallel to a (100) set of planes, diffraction beams may be obtained which correspond to Bragg reflection from a (210) set of planes. Bragg reflection from this same set of (210) planes may be obtained also from a second silver crystal whose boundary is parallel to a (110) set of planes. The difference between the two cases is that the incident and emergent beams of electrons pass through a (100) boundary plane in one case and a (110) boundary plane in the other case. Hence, a comparison of the results for these two cases should reveal any effect due to the difference in the boundaries of the two crystals. Clearly, this experiment requires that the surfaces of the two crystals shall be made up *entirely* of facets of atomic planes parallel to the surface boundary planes. Silver crystals are suitable

[1] M. v. Laue, Phys. Rev. **37**, 53 (1931).

[2] In obtaining this value, v. Laue considers a simple cubic lattice equivalent to hydrogen atoms of spacing 4×10^{-8} cm. (Also see Ehrenberg, Phil. Mag. **18**, 878 (1934).) Since the scattering of high speed electrons by atoms of atomic number Z is proportional to $(Z-F)^2$ where F is the atom form factor for x-rays, it follows that the effect of the surface atomic layer will be greater in the case of the heavier atoms. Although this formula does not hold for low speed electrons, it is to be expected that the scattering effect of the surface atomic layer will be greater for the heavier atoms in this case also.

[3] H. E. Farnsworth, Phys. Rev. **40**, 684 (1932).

because either (110) or (100) planes can be developed exclusively by proper etching in nitric acid.* The concentration of the acid determines the type of facet developed. Thus two silver crystals were cut and etched so that only (110) facets were developed on a (110) face of one, and only (100) facets on a (100) face of the other. After etching, both of these surfaces were smooth and mirror-like. Tests by optical and by electron-diffraction methods showed in each case no observable amount of etching parallel to other sets of planes.

In order to obtain the same angle of incidence on the (210) set of planes for the two cases, different angles of incidence at the two crystal surfaces are required, as shown in Fig. 1. Normal incidence on the (100) surface corresponds to an angle of incidence of 26.56° on the (210) set of planes. For the same angle of incidence on these planes when the primary beam passes through the (110) surface, the angle of incidence on this surface must be 8.12°, assuming unit refractive index. For a refractive index greater than unity, a larger angle of incidence on the (110) surface is required. Similarly, normal incidence on the (100) surface corresponds to an angle of incidence of 21.8° on the (520) set of planes. For the same angle of incidence on these planes when the primary beam passes through the (110) surface, the angle of incidence on this surface must be −1.4° (minus sign indicates that incident and emergent beams are on the same side of the normal to the surface), assuming a unit refractive index.

The apparatus and procedure have been described previously.[3] Under best vacuum conditions the pressure was of the order of 10^{-8} mm Hg as measured by an ionization gauge. After the usual initial outgassing of the whole tube, the crystal was cautiously heated for a few hours by bombardment from the rear at a very dull red heat such that no observable evaporation occurred. This was very important since previous observations had shown a very marked tendency for the (110) surface to etch parallel to (111) and (100) sets of planes during evaporation, as indicated by the presence of Bragg-type beams from the facets etched during evaporation. In accord with previous observations with silver crystals this relatively small amount of outgassing was sufficient to eliminate observable effects of surface gas layers. Briefly the procedure was as follows: Beginning with observations on the various diffraction beams for normal incidence, the primary voltage was varied in small steps, and for each voltage we obtained the beam maximum by adjusting the angular position of the Faraday collector, while keeping the total primary current constant for the entire set of observations. This gave the intensities of the beams as a function of voltage. By repeating this procedure for different angles of incidence, we obtained the beam intensities as a function of angle of incidence.

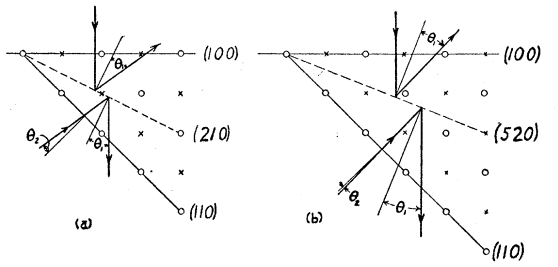

FIG. 1. (a) Cross section of the silver lattice normal to a [001] direction. The (100), (210) and (110) planes are normal to the plane of the paper, and their traces on this plane are indicated in the figure. (b) The same as (a) except that it shows a trace of the (520) plane on the plane of the paper.

RESULTS

Fig. 2 shows the observations of the first and second-order reflections from the (210) set of planes and the first-order reflection from the (520) set of planes, for each of the two silver crystals. The upper curves were obtained when the primary electrons were incident on the (100) face (these have been published previously[3]), and the lower ones when the primary electrons were incident on the (110) face. The lower curves and their scales of abscissae for the (210) set of planes have been displaced about 8° to the left with respect to the upper ones. This is the difference in the external angle of incidence required to make the internal angles of incidence on the (210) set of planes the same in each case, assuming no inner potential. A positive inner po-

* Reference 3, p. 699.

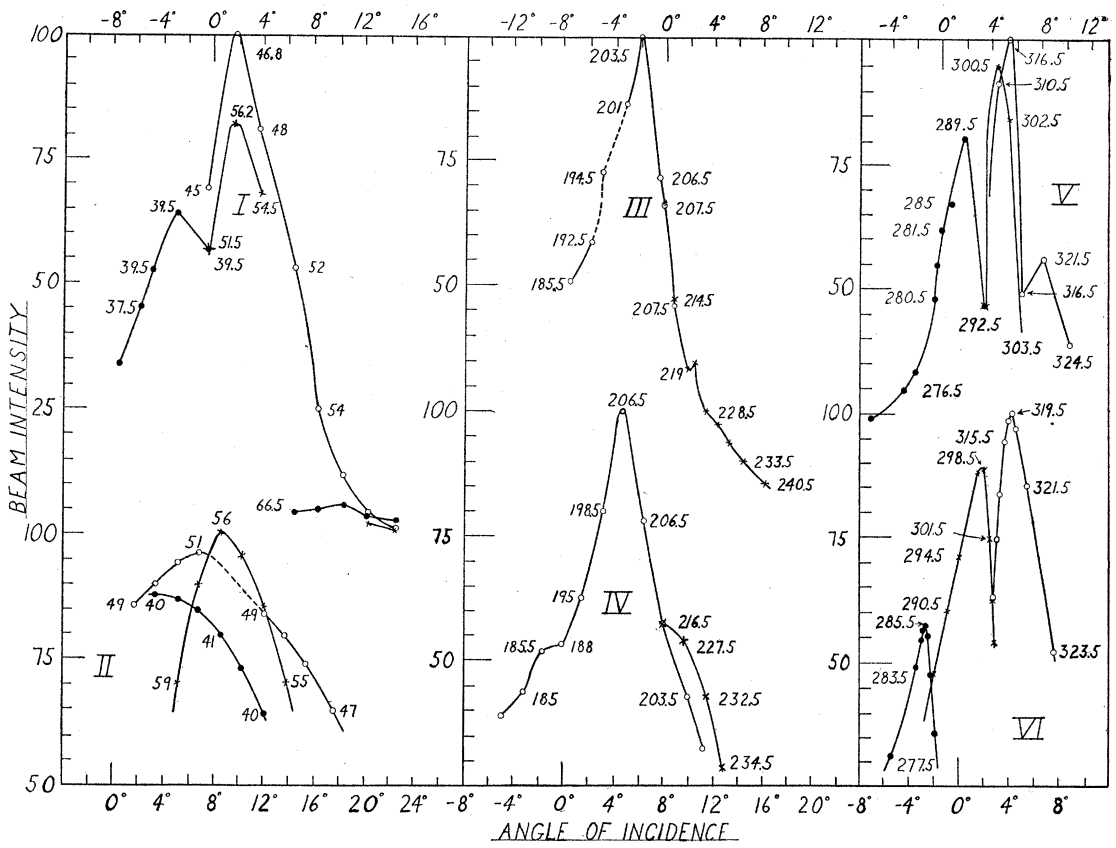

FIG. 2. Curves showing relative intensities of beam components as a function of angle of incidence for a silver crystal. I, first-order reflection from the (210) set of planes with the primary beam entering the (100) face. II, first-order reflection from the (210) set of planes with the primary beam entering the (110) face. III, second-order reflection from the (210) set of planes with the primary beam entering the (100) face. IV, second-order reflection from the (210) set of planes with the primary beam entering the (110) face. V, first-order reflection from the (520) set of planes with the primary beam entering the (100) face. VI, first-order reflection from the (520) set of planes with the primary beam entering the (110) face.

tential would make the shift somewhat larger. For the (520) set of planes the corresponding shift of the lower curves is about 1.4° to the right.

When comparing the curves in Fig. 2, it should be kept in mind that they are obtained from a *series* of experimental curves. Each point of the curves shown represents the maximum of an experimental curve. In addition to the number of components, the significant features of the fine-structure characteristics are the rapid changes of intensity and the shifts in voltage with change in angle of incidence. Referring to the second-order beams from the (210) planes, we note a correspondence in general appearance and voltages. The maxima occur at 203.5 and 206.5 volts, respectively. There is an indication of an unresolved component on the low voltage side, and also a more prominent component on the high voltage side of each curve. The most striking similarity, however, is in the great change of intensity of several hundred percent for a change in the angle of incidence of a few degrees, with the maximum of intensity coming at nearly the same angle of incidence and voltage in the two cases. The first-order beams from the (520) planes also show similarity with three main components having approximately the same relative intensities in the two cases. The components from the (110) surface are separated more in both angle of incidence and voltage than those from the (100) surface. A very weak com-

ponent on the high voltage side for the (100) surface was not found for the (110) surface, but all components from this latter surface are much weaker than those from the former. The similarity of these curves appears even more striking when one considers the great differences in fine-structure characteristics of the beams from different sets of atomic planes as shown in Fig. 9 of a previous publication.[3] The correspondence between the first-order reflections from the (210) planes is not so close as that of the ones just considered, although there are three major components in each case.[4]

Before attributing the above differences to surface action, other possible causes should be considered. (1) The atoms on the two sides of a (210) reflecting plane are not symmetrically arranged with respect to this plane. Since the primary electron beams in the two cases considered are incident on opposite sides of the (210) planes, a possible directional effect might introduce a difference in the results for the two cases. A test for a directional effect which might be responsible for the differences just mentioned is described in the following section of this paper. While a type of directional effect was observed, none was found to be present which would account for the difference in question. (2) As mentioned above, in order for the angles of incidence on the (210) planes to be the same in both cases, the angles of incidence on the crystal boundaries must be different. This will cause a different dispersion effect in the two cases if the crystal has a positive inner potential ϕ. This is because the refractive index is given by

$$\mu=\frac{\sin i}{\sin r}=\left(\frac{V+\phi}{V}\right)^{\frac{1}{2}}=\frac{\lambda\text{ (outside)}}{\lambda\text{ (inside)}},$$

and, with a constant external angle of incidence other than zero, the direction of the beam inside the crystal is changed as the primary voltage V or wave-length λ is changed. Since the fine-structure characteristics, which are obtained by varying the primary voltage, are very sensitive to changes in angle of incidence, they should be altered by this dispersion which would be a different function of the primary voltage in the two cases considered. This effect should also be greatest in this low voltage region and decrease as the voltage is increased since the ratio of $(V+\phi)/V$ decreases as V increases.

Although there is no obvious method of distinguishing between an effect of dispersion and that due to surface action, it appears probable that the first is appreciable for the low voltage beam. While the differences in the higher voltage beams may be attributed to surface action, it is significant that the changes in the fine-structure characteristics due to a change in the surface atomic layer of the amount indicated are small compared to the differences in fine-structure characteristics of the beams from different sets of atomic planes. This seems to indicate that the surface action does not play a major part in the determination of fine-structure characteristics. However, because of the low penetration even at 300 ev (see the following paper) one expects the surface action to be appreciable over the whole voltage range of the observations. Similar observations on other diffraction beams would be highly desirable, but unfortunately the number of available beams on which a test can be made is very limited. The third-order reflection from the (210) set of planes occurs at about 500 volts where the intensity of reflection is small, and the fine-structure characteristics are less pronounced and are difficult to observe.

Directional Effects

In the previous section we indicated the importance of determining whether directional effects exist when electrons are reflected from atomic planes, such as the (210) set, with respect to which the atoms on opposite sides are arranged unsymmetrically. Since the atoms are also arranged unsymmetrically with respect to a plane perpendicular to both the (210) planes and the plane of Fig. 1, a directional effect might also be expected to appear when comparing two beams reflected from the same side of the (210) plane, but which are incident at equal angles on opposite sides of the normal to the plane. To eliminate dispersion effects the reflecting plane must be a boundary plane of the crystal. The

[4] In a preliminary abstract (Phys. Rev. **43**, 778 (1933)) written before complete observations were made, it was stated that there is an unsymmetrical reflection from opposite sides of an atomic plane.

(111) planes of a face centered cubic crystal possess similar unsymmetrical characteristics and are preferable for experimental reasons. Although such directional effects are not to be expected from simple diffraction theory, one type of directional effect for high speed electrons diffracted by single crystals of sodium chloride and sodium fluoride has been reported by G. A. Morton.[5] In the present case a possible connection is sought between such an effect and the fine structure of the diffraction beams.

A silver crystal was cut and ground parallel to a (111) set of planes. It was then etched in a solution of nitric acid of such strength (60 to 65 percent by vol. of acid in distilled water at room temperature) that only (111) facets were developed.*

Fig. 3 shows the arrangement of the atoms in the plane of incidence. The crystal was mounted so that Bragg reflection curves could be taken for various angles of incidence between 8° and 45° (measured from the normal) in both the (100) and (111) azimuths.

The Bragg-type curves for the same angles of incidence in these opposite azimuths checked so closely that no directional effects of the type sought were detected. However, an unsymmetrical effect of another type was observed. When the regular Bragg reflection curve was taken in the (111) azimuth at about 41° angle of incidence it was found that all of the beams showed a double maximum in colatitude. But for

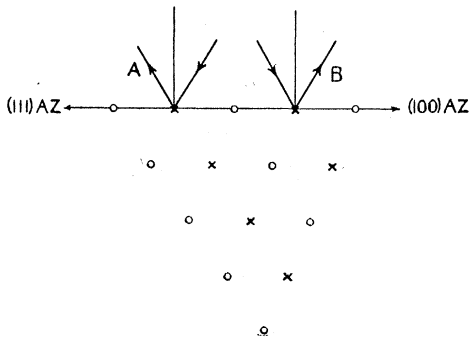

FIG. 3. Cross section of the silver lattice normal to a [01$\bar{1}$] direction. The (111) boundary plane of the crystal is normal to the plane of the paper, and its trace on this plane is indicated by the solid horizontal line.

[5] G. A. Morton, Phys. Rev. **44**, 952 (1933).
* Reference 3, p. 699.

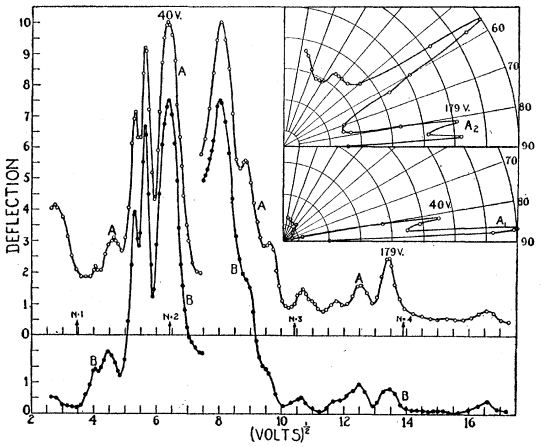

FIG. 4. Intensity of regular reflection from the (111) set of planes for angles of incidence of 41°. Curves A and B are for the (111) and (100) azimuths, respectively. Curves A_1 and A_2 are colatitude curves (angle, measured from primary beam, is twice the angle of incidence) corresponding to the 40 and 179 volt peaks of curve A.

the same angle of incidence in the opposite (100) azimuth only single maxima were observed. Fig. 4 shows two Bragg reflection curves which were both taken at a 41° angle of incidence but in opposite azimuths. The two curves check as closely as may be expected. The two colatitude curves illustrate the double maxima obtained at this angle of incidence in the (111) azimuth. The colatitude angles are measured from the primary beam, and hence a single beam maximum is to be expected at twice the angle of incidence or at 82°. This is the position of one maximum but there is another maximum at approximately 87°. The relative intensities of the two components of the various maxima are not the same and do not vary in the same manner as the angle of incidence is changed. Both components are present over a range in angle of incidence of about 3° on either side of 41°. Outside of this range only single maxima are present. This appears to be one manifestation of the fine-structure characteristics but no reason has been found for the particular angle at which it occurs.[6]

[6] The direction of the diagonal of the cube face, which is the direction of the most densely populated rows of atoms in the crystal, makes an angle of 35.3° with the normal to the surface. The difference of 5.7° between this direction and that of the emergent beam within the crystal would be decreased by a positive inner potential of the crystal, but there is no apparent reason for a correlation of this sort if it does exist.

Deviations from the Surface Grating Formula

In a previous paper[7] we have reported observations on this subject. The procedure was to plot sin ϕ against $(150/V)^{\frac{1}{2}}$. This plot contained theoretical curves giving the plane grating conditions for waves diffracted, in a particular azimuth, from certain atomic planes. Thus for the surface grating one obtains straight lines (one for each order of diffraction) while for an atomic plane not parallel to the surface one obtains a set of curved lines which were referred to as depth grating lines. The points of intersection of the different sets of lines correspond to the expected diffraction beams from the three dimensional grating. However, due to the fact that the experimental diffraction beams are present over a considerable range of colatitude angle ϕ and primary voltage V, a series of points was plotted for each observed diffraction beam showing its growth and decay with change of primary voltage. Since the surface plane of atoms has a predominating effect because of the high absorption, one expects the experimental points to follow the surface grating lines. In the paper referred to it was shown that this is frequently not the case. In many cases a depth grating formula is more nearly followed. Also a dependence on the angle of incidence of the primary beam was noted. The experimental points for some of the beams follow one grating formula for one angle of incidence and a different grating formula for another angle of incidence. This suggested a type of *directional* effect, but it was pointed out that if a portion of the surface is etched parallel to a set of atomic planes other than the one coinciding with the geometric boundary, we may expect the parts of the beam reflected from this portion of the surface to follow a grating formula for this surface. In terms of the plot referred to above this means that a set of the curved lines, which was used to represent a depth grating of the crystal, also represents a surface grating for any facets which are etched parallel to the corresponding set of atomic planes.

It was possible to obtain further information regarding this question during the present investigation of surface action while using a silver crystal cut and etched parallel to a (110) set of planes. Evaporation from such a silver crystal due to heating in a vacuum causes marked etching parallel to (111) and (100) sets of planes. Observations on the variation of colatitude angle with primary voltage were obtained both before and after this etching. Typical results are shown in Fig. 5. Proceeding as in Fig. 4 of the earlier paper,[7] the lines were plotted from plane grating formulas obtained by considering certain rows of atoms which are perpendicular to the plane of the insets that are shown for the (100) and (111) azimuths on the left and right, respectively. These rows pass through the points indicated in the insets and the trace of an atomic plane (containing these rows) on the plane of the paper is indicated by the same type of line as that used for the associated plane grating lines for that particular azimuth. The (100) azimuth is such that the trace of its plane on the (110) surface plane coincides with the direction of a face diagonal of the unit cell. The (111) azimuth is in a plane at right angles to this. The equations of the lines in the plots for the (100) azimuth are the following, where the length of a cube edge of the unit cell is represented by a.

$$n_1\lambda=(a/2^{\frac{1}{2}})\sin\phi,$$
$$n_2\lambda=(a/8^{\frac{1}{2}})+(a/2)\cos(\phi+45°),$$
$$n_3\lambda=(a/2^{\frac{1}{2}})(1+\cos\phi).$$

For the plots in the (111) azimuth the following equations apply.

$$n_1\lambda=a\sin\phi,$$
$$n_2\lambda=(a/8^{\frac{1}{2}})+(3/8)^{\frac{1}{2}}a\cos(\phi+54°45'),$$
$$n_3\lambda=(a/2^{\frac{1}{2}})(1+\cos\phi),$$
$$n_4\lambda=(a/8^{\frac{1}{2}})+(3/8)^{\frac{1}{2}}a\cos(54°45'-\phi).$$

Referring to Sets 1, 2, and 3, it is seen that the solid line curves correspond to a plane of atoms containing the points 0 and 2 in the left-hand inset and normal to the plane of the paper. This is a (100) plane. Similarly for Sets 4 and 5, the solid line curves correspond to a plane of atoms containing the points 0 and 2 in the right-hand inset. This is a (111) plane. Since the normals to (100) planes lie only in (100) azimuths while normals to (111) planes lie only in (111) azimuths, it follows that electron beams corresponding to Bragg reflection from crystal facets

[7] H. E. Farnsworth, Phys. Rev. **43**, 900 (1933).

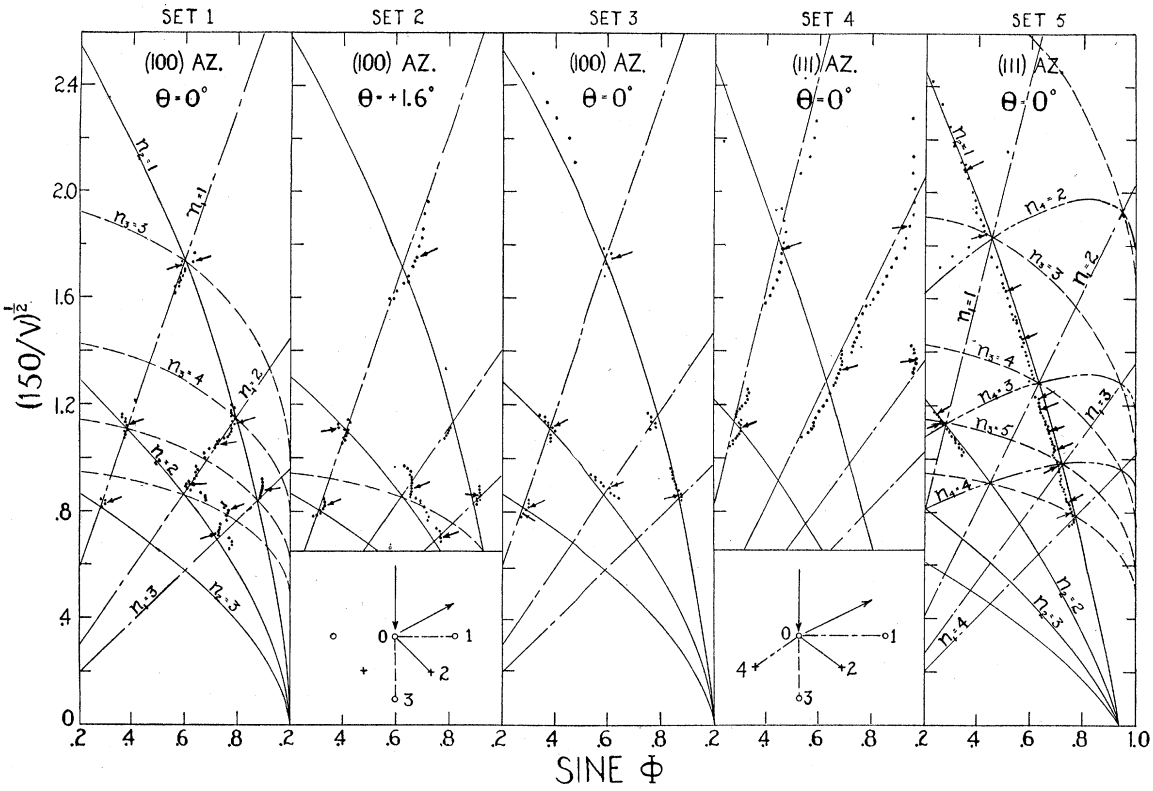

FIG. 5. Plots of sine ϕ against $\lambda=(150/V)^{1/2}$, ϕ = colatitude angle measured from the normal. θ = angle of incidence of primary beam. The points are experimental observations, and the arrows indicate which ones correspond to maxima. The lines are plotted from grating formulas obtained by considering the corresponding rows of atoms shown in the insets for the two azimuths, respectively. Sets 1, 2 and 4 were obtained before evaporation from the crystal due to heat treatment. Sets 3 and 5 were obtained after considerable evaporation.

etched parallel to (100) planes will be observed only in (100) azimuths, and beams corresponding to reflection from facets etched parallel to (111) planes will be observed only in (111) azimuths. The observations in Sets 1 and 2 show the effect of changing the angle of incidence. The experimental points for some of the beams show a decided shift in their relative positions. The observations in Set 3, which were taken after considerable evaporation, show that (100) facets exposed by evaporation now largely determine the grating followed by the experimental points in this azimuth (except for the highest voltage beam shown). The original (110) surface planes have practically disappeared. Other observations, not shown, were taken during the progress of the etching and show the experimental points characteristic of both the (100) and (110) surface planes. These observations reveal the significant fact that, as long as (110) facets are present, the presence of (100) facets has no effect on the positions of the experimental points due to (110) facets, as given in Sets 1 and 2, Fig. 5. The presence of the (100) facets is revealed by the appearance of *additional* experimental points which follow the grating lines corresponding to (100) planes. This supports the view that the effect illustrated in Sets 1 and 2, Fig. 5 is a real *directional* effect, and is not due to the presence of facets which are not parallel to the geometric boundary of the crystal. The observations in Sets 4 and 5, respectively, were obtained before and after evaporation which exposed (111) facets, and illustrate how completely the surface layer of atoms predominate under these conditions. The presence of the experimental points over ranges greater than those in the (100) azimuth is probably due to the greater area of the etched (111) facets compared with that of the (100) facets. This etching is of the type observed

by Sproull[8] for a tungsten crystal. With a (112) surface plane of tungsten and the azimuth perpendicular to the cube diagonals, beams which obeyed a depth grating formula corresponding to rows of atoms in the (011) plane were found by Sproull at every primary voltage tried. We[9] have previously pointed out that these observations can be explained by assuming the presence of etched facets parallel to (011) planes resulting from evaporation during heat treatment of the crystal. G. P. Thomson[10] has also suggested a similar interpretation. The above observations from a silver crystal are seen to be of just this type. We have further verified this interpretation by checking the positions of the diffraction beams shown in Set 5 of Fig. 5 when using a silver crystal cut and etched parallel to a (111) set of planes, and set at the proper angle of incidence in the (111) azimuth to correspond to these observations.

The fact that no beams characteristic of the (100) or (111) facets were obtained with the silver crystal which was chemically etched parallel to a (110) set of planes proves the effectiveness of the method in etching parallel to only one set of crystal planes. It may also be noted that it was found possible to heat the silver crystal for many hours at temperatures up to about 650° or 700°C without the appearance of diffraction beams characteristic of (100) or (111) facets, thus indicating that there was no appreciable evaporation at this temperature.

The sensitivity of this method of detecting what crystal facets are present should be of value in any experiment which is concerned with the surface properties of particular crystal facets such as the photoelectric characteristics.

Messrs. E. C. Bray, C. R. Lewis, A. E. Hastings, J. C. Turnbull, and Dr. B. A. Rose have aided at various times in taking the numerous observations.

[8] W. T. Sproull, Phys. Rev. **42**, 904 (1932); **43**, 516 (1933).
[9] H. E. Farnsworth, Phys. Rev. **43**, 906 (1933); **44**, 417 (1933).
[10] G. P. Thomson, Phys. Rev. **44**, 417 (1933).

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Penetration of Low Speed Diffracted Electrons

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A known number of atomic layers of one metal was deposited on the surface of a single crystal of another metal by evaporation in a high vacuum. Direct results on depth of penetration were obtained from measurements on electron diffraction as a function of the thickness of the surface layer. A silver film having a thickness up to 15 atoms does not form in a single crystal when deposited on the (100) face of a copper crystal. A monatomic layer reduces the maxima of the beams from the copper lattice by at least 70 percent for energies up to 300 ev. A number of foreign silver atoms equal to a few hundredths of that contained in a monatomic layer can be detected by this method. A silver film forms in a single crystal when deposited on the (100) face of a gold crystal. At least 50 percent of the maximum of each diffraction beam from a thick silver crystal is contributed by the surface atomic layer of silver, for energies as high as 300 ev, while at least 90 percent is contributed by a surface layer two atoms thick. A possible selective effect was observed for low voltage reflection from a film 2 atoms thick.

INTRODUCTION

ALTHOUGH it is known that low speed electrons are diffracted by only a small number of atomic planes at the surface of a metal crystal, there have been no direct quantitative data on the exact number which is effective in special cases.

Davisson and Germer[1] calculated a rate of extinction for 54-volt electrons in a direction perpendicular to a (111) surface of a nickel crystal. In making the computation, use was made of the intensity-voltage relation which was assumed to be determined entirely by the

[1] Davisson and Germer, Phys. Rev. **30**, 705 (1927).