

Diffraction of Low-Speed Electrons by a Tungsten Single Crystal

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The (1-1-2) and (1-0-0) planes of a tungsten crystal were bombarded at normal incidence with primary electrons and the intensity of the full-velocity secondary beams measured as a function of azimuth, co-latitude (θ), and primary voltage. A new magnetic deflection method of analyzing the secondaries permitted observations at co-latitudes down to zero. The crystal was outgassed 1550 hours at temperatures up to 1600°C at pressures of 10^{-7} mm of Hg or less. Strong sharp beams were observed in the AA' azimuth (Fig. 1) of the (1-1-2) plane at all wavelengths which were used, and were found to be governed in every case by the volume equation $n_2\lambda = d/6^{\frac{1}{2}} + 2(d/6^{\frac{1}{2}})\sin(30^\circ - \theta)$ and in no case by the surface equation. This is the first time that such a pronounced deviation from the usual theory has been observed. The final average experimental value for W_a was 5.52 volts which, combined with photoelectric and thermionic data yields a value for W_i of about 1 volt. The values obtained for W_a were unusually consistent. A few beams of the usual type obeying both interference equations were observed in the B and C

azimuths of the (1-1-2) plane and also in an azimuth 30° from B . They were all quite broad, however, and consequently no attempt was made to estimate W_a from them. Beams were found in the case of the (1-0-0) plane which could be detected for various wave-lengths within the immediate neighborhood of their predicted location and which showed a tendency to vary in latitude in obedience with the volume equation, but became too weak to observe if the wave-length chosen was very far from the predicted value. Slight variations in the angle of incidence were found to have a very great effect on the observations. Some of those portions of the observations which differ from typical results obtained in similar investigations with other metals can be correlated qualitatively with the peculiarities of the tungsten crystal lattice. It seems likely that the explanation of the peculiarly governed beams observed in the AA' azimuth of the (1-1-2) plane and of Kikuchi's "N-pattern" for mica is somehow contained in the relation of atomic plane population to interplanar distance.

I. INTRODUCTION

THE present work was undertaken partly for the purpose of trying out a new type of apparatus¹ to see how it would perform in actual service, and partly to see whether a change from the low melting point face-centered cubic crystals which have so far been the usual subject of low-speed single crystal work to a high melting point body-centered cubic crystal would produce any noteworthy difference in the results. Having decided upon a new type of apparatus and a different type of crystal, conventional procedure was further violated by selecting as the first plane for study the (1-1-2) plane which has several unique characteristics as pointed out in section IV. The (1-0-0) plane was studied subsequently. The apparatus is unusual in two respects. (1) It enables one to analyze diffracted electron beams emitted at angles with the normal as small as one pleases, down to zero, even though the primaries are incident normally. (2) It eliminates the

necessity of allowing for contact potentials between the filament and other parts of the electron gun when determining the velocity of the incident primary electrons.

II. THE CRYSTAL

The crystal was cut from a bar of tungsten about 20 mm long by 7 mm wide by 5 mm thick for which we are indebted to Professor P. I. Wold of Union College. The material reached Professor Wold rather indirectly from Germany, and formed part of a larger bar with which he proposes to carry out Hall-effect measurements.

The bar contained perhaps a dozen crystals ranging in size from about $1 \times 3 \times 1$ mm up to a large one which was approximately $7 \times 7 \times 4$ mm. A section of the bar containing this crystal along with two or three other much smaller ones was carefully sawed out using a thin sheet of copper armored with carborundum powder. The bar was moved back and forth along the edge and held in the fingers so as not to damage it by clamps.

The positions of the various atomic planes

¹ Sproull, R. S. I. 4, 193 (1933).

were determined before the crystal was sawed from the bar, taking advantage of the well-known fact that chemicals which attack a metal crystal dissolve away the surface in such a way as to expose facets which coincide with various of the more prominent atomic planes. The bar was dropped into a boiling 3 percent solution of H_2O_2 and etched for about five minutes and then mounted on a goniometer. The angular positions of the reflected beams of light from an incident beam of parallel rays were determined with respect to one edge of the bar and the normal to the surface. By locating a dozen or so of these beams, it is possible to determine from which plane each individual beam is reflected, and thus to determine accurately the orientation of the unit atomic cubes in the bar. It was found that the large 7×7 mm face of the bar lacked only $6^\circ 40'$ of coinciding with the (1-1-2) plane. The (1-1-2) plane is an important one in a body-centered cubic, and is the plane which tends to develop most prominently in tungsten when it is etched, according to Smithels.² From this, we suspected that it might also tend to become more prominent under the action of outgassing in a vacuum.

Next, the crystal was sawed from the bar. A steel wedge about an inch square with its faces at an angle of $6^\circ 40'$ with each other was machined, and a hole about 1 cm in diameter was bored through it. The wedge was then bolted to a steel plate an inch square, the bolt heads being countersunk so as to leave the upper face of the wedge clear. The upper and lower faces of the tungsten segment containing the crystal were parallel. Consequently, when it was placed in the hole in the wedge with its bottom face resting on the steel plate, and then turned to the proper azimuth, the part which protruded above the upper face of the wedge was just the part which should be removed in order to expose a (1-1-2) plane. Wood's metal was poured around the crystal, and when it froze, the crystal was ready for grinding. It was ground with fine carborundum powder and water on plate glass until flush with the upper face of the wedge. It was then polished to mirror brilliance on a high-speed linen wheel with emery flour. After removal from the wedge,

² See Smithels' book *Tungsten*, Chapman and Hall, London.

the crystal was re-etched and mounted in an x-ray camera, and from the positions of the Bragg x-ray lines it was determined that the (1-1-2) plane really coincided with the geometrical surface within less than a degree.

For the electron diffraction experiments, the crystal was inserted in a molybdenum socket having jaws which were too small to be struck by any appreciable number of primary electrons, the socket being rigidly fastened to a long heavy quartz tube mounted in bearings so that the azimuth could be varied by rotating the quartz tube. The tube was rotated and the molybdenum socket bent until no perceptible wobble of the (1-1-2) face remained. In this manner the (1-1-2) face was aligned with its normal within 10 or 20 minutes of the axis of the quartz tube, for when the error was 1° , the wobble was very noticeable. The quartz tube was then aligned with its axis parallel to the direction of motion of the primary electrons striking the crystal, this adjustment being made by heating and bending the outer Pyrex walls of the experimental tube, and being accurate to $\frac{1}{2}^\circ$.

III. OUTGASSING TREATMENT AND REPRODUCIBILITY OF RESULTS

A vacuum of 10^{-7} mm of mercury or better was maintained throughout the work, and the crystal was outgassed continuously except when a set of readings was being taken, the temperature at the start being about 1000°C , and being increased gradually to about 1600°C after 1550 hours at the close of the experiments. After the first 100 hours of outgassing, the contact potential between the tungsten crystal and the surrounding molybdenum chamber became constant and remained 2 volts during the rest of the work. This early attainment of stability is in agreement with the observations of Dowling³ and Glasoe.⁴ After the first 300 hours of outgassing, it was found that diffraction data could be duplicated almost exactly if a given set of observations were repeated, even after a lapse of several weeks.

Langmuir has found that a monatomic layer of oxygen clings to tungsten surfaces even at very high temperatures, half of it being driven off in 15

³ Dowling, Phys. Rev. 25, 812 (1925).

⁴ Glasoe, Phys. Rev. 38, 1490 (1931).

seconds at 1800°C. Boas and Rupp⁵ in their work with polycrystalline tungsten found "additional beams" fitting the usual diffraction theory if one postulates a lattice spacing of 4.46Å which they attributed to this oxygen layer. Such beams were not found in the present work, which might indicate that the oxygen layer and other impurities were drawn off as positive ions by the electric field while the crystal was being bombarded at 2000 volts although they might not have been removed by simply heating the crystal to the same, or even a higher temperature.

IV. PECULIARITIES OF THE (1-1-2) PLANE

According to Davey,⁶ the length of an edge of the unit cube in tungsten is $d = 3.155\text{Å}$. Fig. 1 is a plan of the (1-1-2) plane. If the circles be taken as atoms at the corners of the unit cubes, the squares will represent "body-centered atoms," and *vice versa*. Those numbered 1 are in the surface layer; those numbered 2 are in the first layer beneath the surface, those numbered 3 in the second, etc. It is to be noted that there is line symmetry about the line BC in Fig. 1, but not

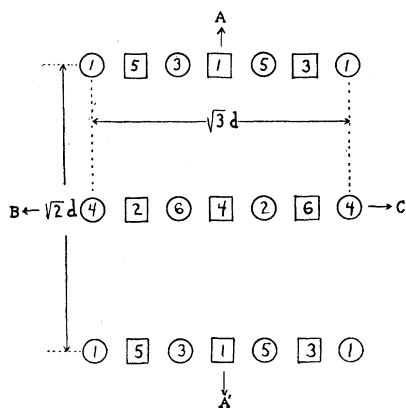


FIG. 1. The tungsten lattice viewed along the perpendicular to the (1-1-2) planes.

about the line AA' . Hence electron beams in the azimuths marked A and A' should be alike, but beams in the B azimuth should be different from those in the C azimuth. Atoms in the sixth layer beneath the surface lie directly beneath surface atoms, contrasting with the situation in the

(1-0-0) plane, where atoms directly beneath the surface atoms are found in the second layer beneath the surface, and in the case of the (1-1-1) plane, the third, these planes being cited for comparison because they are the ones other experimenters have chosen for study. The atoms in the (1-1-2) planes are staggered to an unusual extent with respect to the normal to the planes, and the perpendicular distance between the (1-1-2) planes is only $d/6^{1/2}$ or 1.29Å, very much shorter than the corresponding distance for the crystal faces usually bombarded by other experimenters with single crystals. Another unusual feature of the (1-1-2) plane is that the distance measured in the AA' azimuth between rows of atoms parallel to the BC azimuth is $4\frac{1}{2}\text{Å}$, much longer than the "grating spacings" that have been used in most of the single crystal electron diffraction experiments. Consequently, the ratio of the grating spacing to the interplanar distance is extraordinarily high in this azimuth. Another fact possibly of significance is that the rows of atoms parallel to the BC azimuth happen to be the most densely packed rows in the crystal. That is, the atoms in these rows (which are the diagonals of the lattice cubes) are $3\frac{1}{2}d/2$ apart, and this is the distance of closest approach for tungsten. These peculiarities are described at length because they may help to account for the unusual behavior of the secondary beams diffracted in the AA' azimuth.

V. THEORY

Throughout the paper, we are dealing exclusively with the "full velocity secondaries," that is, those electrons which have undergone elastic collision with atoms of the crystal and have recoiled with a velocity equal to that of the incident primary electrons.

In Fig. 1, imagine a plane perpendicular to the paper (i.e., perpendicular to the (1-1-2) plane) and lying in the azimuth marked AA' . The arrangement of the atoms in this section is represented in the inset of Fig. 2. By examining this inset it is easy to see that phase waves of length λ incident normally upon the crystal and diffracted by the atoms Z and X at a co-latitude θ as shown will be in phase after diffraction provided

$$n_1\lambda = 2\frac{1}{2}d \sin \theta, \quad (1)$$

⁵ Boas and Rupp, *Ann. d. Physik* [5], 7, 983 (1930).

⁶ Davey, *Phys. Rev.* 26, 736 (1925).

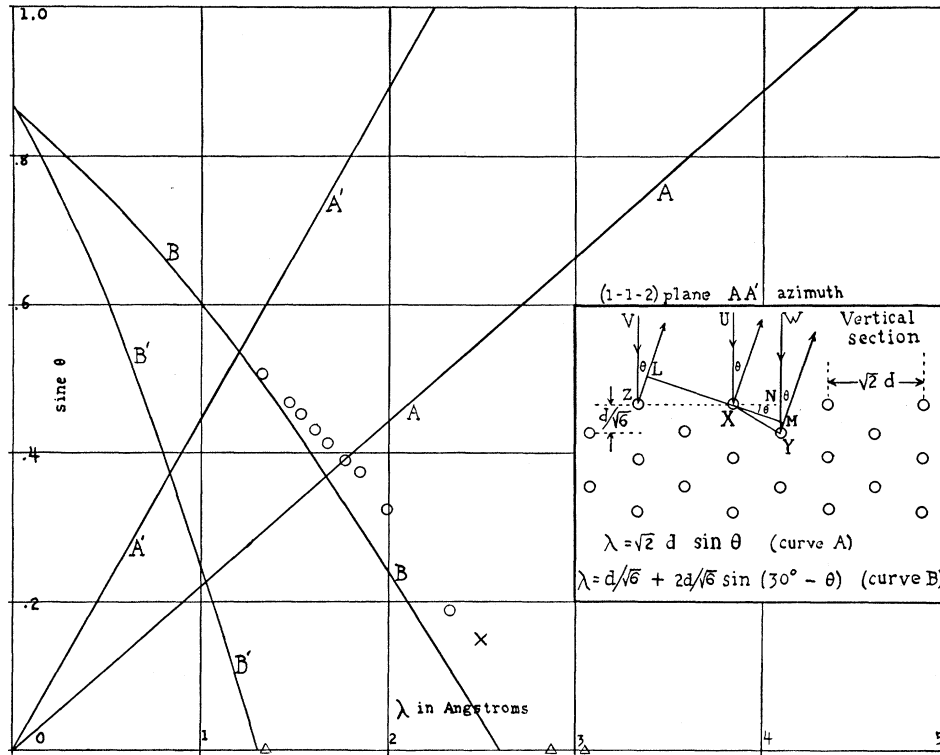


FIG. 2. Graphs of the interference equations for the (1-1-2) plane in the azimuths *A* or *A'* of Fig. 1. Inset is a vertical section of the (1-1-2) planes in the *AA'* azimuth.

where n_1 is any integer and d is the edge of a unit cube = 3.155 Å. This is the condition for constructive interference between all the atoms of any one layer, by an obvious generalization.

If, in addition, we are to have constructive interference between the rays diffracted from all the layers, the waves diffracted from such atoms as *X* and *Y* must be in phase. That is, $NY + YM$ must be an integral number of wave-lengths, n_2 , whence we have

$$n_2 \lambda = d/6^{\frac{1}{2}} + 2(d/6^{\frac{1}{2}}) \sin(30^\circ - \theta) \quad (2)$$

as the second interference condition. Beams are usually expected only when λ and θ have such values as to satisfy both (1) and (2) simultaneously. Eq. (1) is often called the "surface condition" and (2) the "volume condition" of interference. Following usual practice, these two equations are graphed (main part of Fig. 2) with $\sin \theta$ as ordinates and λ as abscissae, the intersections of the two sets of curves predicting the co-latitude θ and the wave-length λ (and hence the primary voltage V , since $\lambda = h/mv = (150/V)^{\frac{1}{2}}$)

at which the beams should occur. The straight lines represent the surface condition for $n_1 = 1, 2$, etc., and the curved lines represent the volume condition for $n_2 = 1, 2$, etc.

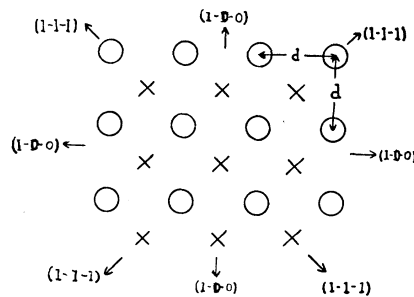


FIG. 3. The tungsten lattice viewed along the perpendicular to the (1-0-0) planes.

If we do the same thing for the (1-0-0) plane in the azimuths marked (1-0-0) (Fig. 3), we obtain the surface condition

$$n_1 \lambda = d \sin \theta$$

and the volume condition

$$n_2\lambda = \frac{1}{2}d + d/2^{\frac{1}{2}} \sin (45^\circ - \theta)$$

illustrated and plotted in Fig. 4.

Corresponding equations for some of the other cases studied are: (1-1-2) plane, B azimuth

$$n_1\lambda = 3^{\frac{1}{2}}d/2 \sin \theta, \quad (\text{surface})$$

$$n_2\lambda = (2/3)^{\frac{1}{2}}d + 3^{\frac{1}{2}}d/2 \sin (70^\circ 30' - \theta); \quad (\text{volume})$$

(1-1-2) plane, C azimuth

$$n_1\lambda = 3^{\frac{1}{2}}d/2 \sin \theta, \quad (\text{surface})$$

$$n_2\lambda = d/6^{\frac{1}{2}} + \frac{1}{2}d \sin (54^\circ 45' - \theta). \quad (\text{volume})$$

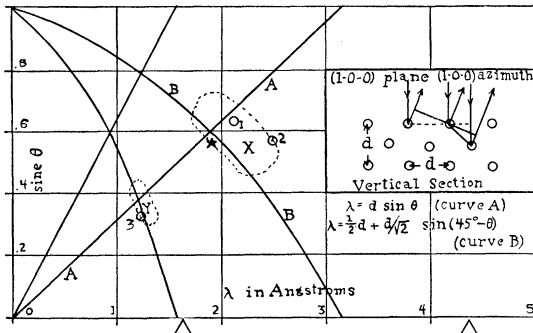


FIG. 4. Graphs of the interference equations for the (1-0-0) plane in the (1-0-0) azimuths of Fig. 3. Inset is a vertical section of the (1-0-0) planes in the (1-0-0) azimuth.

These sets of equations differ because there is not line symmetry about the line AA' (see Section IV). For the case of diffraction in the azimuths marked X due to the rows of atoms indicated by the dotted lines in Fig. 5, one obtains

$$n_1\lambda = (6/11)^{\frac{1}{2}}d \sin \theta \quad (\text{surface})$$

and

$$n_2\lambda = d/6^{\frac{1}{2}} + (2/11)^{\frac{1}{2}}d \sin (73^\circ 10' - \theta); \quad (\text{volume})$$

(1-0-0) plane, (1-1-1) azimuths (see Fig. 3)

$$n_1\lambda = 2^{\frac{1}{2}}d \sin \theta, \quad (\text{surface})$$

$$n_2\lambda = \frac{1}{2}d + 3^{\frac{1}{2}}d/2 \sin (35^\circ 16' - \theta). \quad (\text{volume})$$

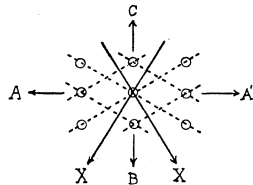


FIG. 5. Plan of the (1-1-2) plane similar to Fig. 1, but showing only one layer.

In the present apparatus, the collector can be moved into such a position as to catch secondary electrons leaving the crystal at normal exodence, so that the case $\theta=0$ can be studied. One should note that this represents the zeroth order of surface interference, that is, $n_1=0$ for all the surface equations, which degenerate to $0=0$. In Figs. 2 and 4 this means that the surface equation is represented merely by the λ axis which should therefore be regarded as one of the system of straight lines in the graphs. At $\theta=0$, therefore, one should expect to find maxima in the collector current at certain specific values of λ (and hence V) determined by the intersections of the curved lines with the λ axis. When $\theta=0$, all of the volume equations for the various azimuths of any one plane become identical, as one would expect.

VI. THE OBSERVED BEAMS

Each set of observed beams will be described upon the basis of the following aspects:

A, *Intensity* of the beams compared to the background of random scattering upon which they are superimposed.

B, *Sharpness in co-latitude*. That is, maintaining the bombarding potential constant at the value at which a typical beam of the set is fully developed, does the electron current at various colatitudes in the neighborhood of the maximum decrease rapidly or slowly for a given azimuth?

C, *Sharpness in azimuth*. Maintaining the bombarding potential constant at the value at which a typical beam of the set is fully developed, does the electron current at various azimuths in the neighborhood of the one being studied decrease rapidly or slowly for a given co-latitude?

D, *Rate of growth and decay*. If one explores a typical beam of the set by varying the co-latitude with constant azimuth, not only at the critical bombarding potential at which the beam is fully developed, but also at various other values of V in the neighborhood, does the beam fade out or "decay" rapidly as V recedes from this critical value?

E, *Mode of growth and decay*. If one maintains the bombarding potential at a constant value differing slightly from the critical value at which a typical beam of the set is fully developed, is the location of the beam in co-latitude such as to

agree closely with the *surface* interference condition or with the *volume* interference condition, or with neither? (A beam should be fully developed in a given azimuth only when both θ and V are chosen so as to simultaneously satisfy both conditions; when V is varied slightly, *both* conditions can not be satisfied.)

1. Sets of beams in the B and C azimuths of the (1-1-2) plane. (Fig. 1)

A, Very weak and difficult to detect. B, Moderately sharp in co-latitude. C, Moderately sharp in azimuth. D, Very rapid decay. E, Mode of decay indeterminate, because decay is too rapid.

2. The sets of beams in the azimuths of the (1-1-2) plane marked X in Fig. 5

Exactly similar to the sets just described.

3. Beams in the (1-1-1) azimuths of the (1-0-0) plane (Fig. 3)

A, Weak. B, Very broad in co-latitude. C, Broad in azimuth. D, Fairly rapid decay. E, Tendency to satisfy the volume condition rather than the surface condition.

4. Beams in the (1-0-0) azimuths of the (1-0-0) plane (Fig. 3)

A, Rather weak. B, Very broad in co-latitude. The $n_1=1=n_2$ beam is shown plotted in co-latitude (θ) in Fig. 6A where the radii represent collector current for the various values of θ . The arrow indicates the peak which is approximately at its maximum development at this voltage. The $n_1=1; n_2=2$ beam is shown similarly in Fig. 6C. C, Broad in azimuth. The $n_1=1=n_2$ beam is shown plotted in azimuth in Fig. 7, the radii again representing collector current. D, Unusually slow growth and decay. The $n_1=1=n_2$

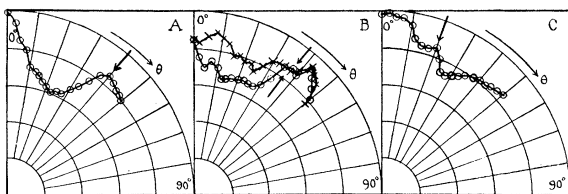


FIG. 6. Co-latitude curves for the (1-0-0) plane. A, The $n_1=1=n_2$ beam at full development. B, Two curves showing the same beam at a bombarding potential 10 volts less than A.C. The $n_1=1; n_2=2$ beam.

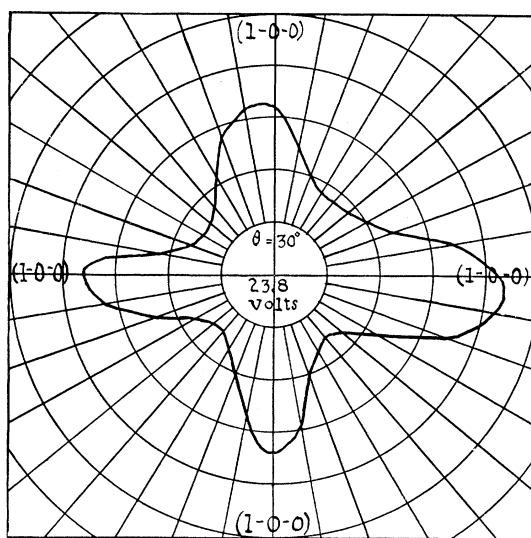


FIG. 7. An azimuth curve of the $n_1=1=n_2$ beam for the (1-0-0) plane taken at a co-latitude of 30° ; bombarding potential $V=23.8$ volts.

beam could be detected at any value of V between 25 and 50 volts. Fig. 6B shows co-latitude curves taken at a value of V ten volts less than that at which the beam is fully developed, the peaks being indicated by the arrows. These curves were both taken in (1-0-0) azimuths, but are 90° apart in azimuth (see Fig. 3) and were taken about two weeks apart. The curves of Figs. 6A, B, C were all corrected for change of solid angle subtended by the collector opening as discussed in the article in R. S. I.¹ E, Close agreement with the volume condition.

5. Beams in the A and A' azimuths of the (1-1-2) plane (Fig. 1)

A, Very strong. B, Exceedingly sharp in co-latitude; see Fig. 8. C, Very sharp in azimuth; see Fig. 9, note curve marked 22° (co-latitude). D, No decay whatever; the various co-latitude curves of Fig. 8 were taken at the various voltages indicated, and it is seen that the beam is equally well developed at every voltage which was tried. Only the central portion of each peak was plotted because it was desired to record the whole set in one afternoon under exactly the same conditions. These peaks are so narrow that it was not necessary to make correction for change of solid angle subtended by the collector opening. E, After allowance for refraction (to be

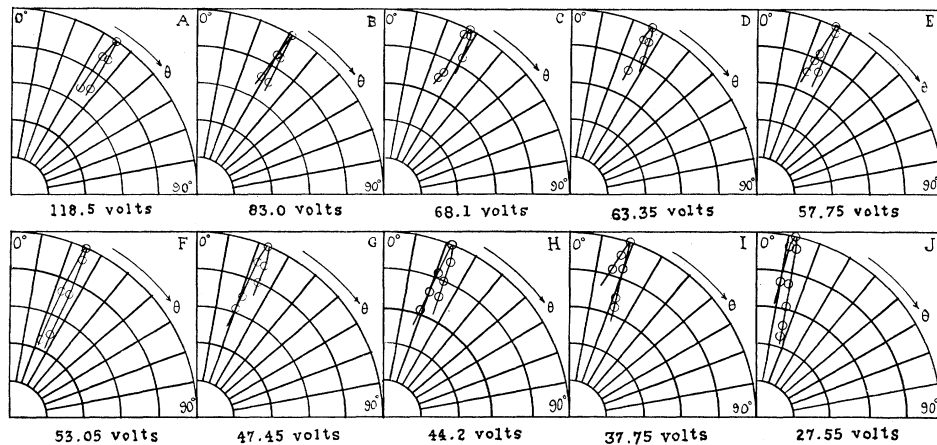


FIG. 8. Co-latitude curves showing the unusual series of $n_2=1$ maxima found in the AA' azimuth of the (1-1-2) plane at ten different values of V as indicated.

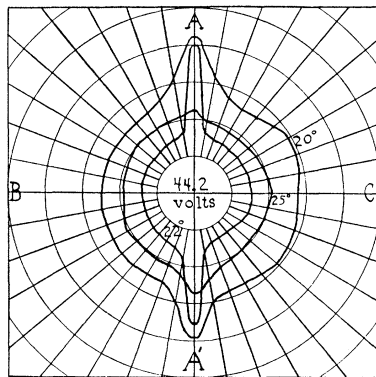


FIG. 9. Azimuth curves of the $n_2=1$ maxima in the AA' azimuth of the (1-1-2) plane at a bombarding potential of 44.2 volts at co-latitudes of 20, 22 and 25 degrees as indicated

discussed in Section VIII), the positions of the beams agree almost perfectly with the volume condition (2), and since there is no voltage of maximum development, it seems that these beams are governed exclusively by Eq. (2) and not at all by Eq. (1).

VII. CORRELATION OF THE OBSERVED BEAMS WITH THE THEORY

The sets of beams described in the preceding section were enumerated in order of their agreement with the theory of Section V. The first beams described behaved most nearly in accord with the theory, while the ones described last departed markedly from it. The behavior of the beams observed in the (1-0-0) azimuth of the

(1-0-0) plane at voltages in the vicinity of the critical value of full development can be illustrated graphically in Fig. 4 by saying that they could be observed throughout the regions X and Y indicated by the dotted lines near the intersections of the curves. The tendency to obey the volume condition rather than the surface condition is indicated by the fact that these regions lie along the curved (volume) graphs and not along the straight (surface) graphs. Other experimenters⁷ studying the process of growth and decay of the electron beams have found a tendency to obey the surface condition more closely than the volume condition. The circles numbered 1, 2 and 3 in Fig. 4 mark the values of θ and λ at which the curves of Fig. 6A, B and C were taken respectively.

The beams found in the AA' azimuth of the (1-1-2) plane and shown in Figs. 8, A-J are located at values of θ and λ indicated by the circles in Fig. 2, where one sees immediately that they are falling along the $n_2=1$ volume curve.⁸ They do not fall exactly on the curve because we have so far neglected to correct for refraction. This correction will be made in the next section.

⁷ See Davisson and Germer, Phys. Rev. 30, last paragraph, p. 734 (1927) or Farnsworth, Phys. Rev. 34, top of p. 693 (1929).

⁸ The striking behavior of these beams as regards growth and decay can be illustrated graphically by comparing Fig. 2 with Fig. 3 obtained by Farnsworth for copper, Phys. Rev. 34, p. 685 (1929), or comparing Fig. 8 with Fig. 10 obtained by Davisson and Germer for nickel, Phys. Rev. 30, 716 (1927).

The cross in Fig. 2 indicates a beam found after only 28 hours of outgassing which evidently falls in line with the circled beams which were discovered later after 440 hours of outgassing at about 1200°C. The beams were followed right up to $\theta=0$.

VIII. CORRECTION FOR REFRACTION AND CALCULATION OF THE SURFACE WORK FUNCTIONS W_a AND W_i

A. Normal exodence

In the case of the experiments at $\theta=0$, one does not need to make any correction for bending at the surface. The only effect of refraction is to make the length of the phase waves within the crystal less than it is outside. Therefore one can merely subtract the experimental value of the bombarding potential V at which a maximum occurs from that at which it is predicted and say that the difference represents the surface work function W_a . If one sets $\theta=0$ in Eq. (2) and solves for λ and then for V using $\lambda = (150/V)^{1/2}$, it turns out that maxima in the collector current should be expected at $\theta=0$ for the (1-1-2) plane for the values of V given in the second column of Table I, corresponding to the choices of n_2 in the first column. Proceeding similarly for the (1-0-0)

TABLE I. (1-1-2) plane.

n_2	$V_{\text{calc.}}$ (volts)	$V_{\text{obs.}}$ (volts)	$W_a (= V_{\text{calc.}} - V_{\text{obs.}})$ (volts)
1	22.5	16.0 (218 hrs. outgassing)	6.5
2	90.0	84.6 (259 hrs. outgassing)	5.4
1	22.5	19.25 (383 hrs. outgassing)	3.25
2	90.0	84.6 (383 hrs. outgassing)	5.4

TABLE II. (1-0-0) plane.

n_2	$V_{\text{calc.}}$ (volts)	$V_{\text{obs.}}$ (volts)	$W_a (= V_{\text{calc.}} - V_{\text{obs.}})$ (volts)
1	15.1	7.9	7.2
2	60.2	56.8	3.4

plane, we obtain Table II. The average of the six values of W_a in Tables I and II is 5.19 volts. The variation in the six values may be due to small variations in the angle of incidence as pointed out by Farnsworth.⁹ The 7.9 volt maximum of Table

⁹ Farnsworth, Phys. Rev. 40, 684 (1932).

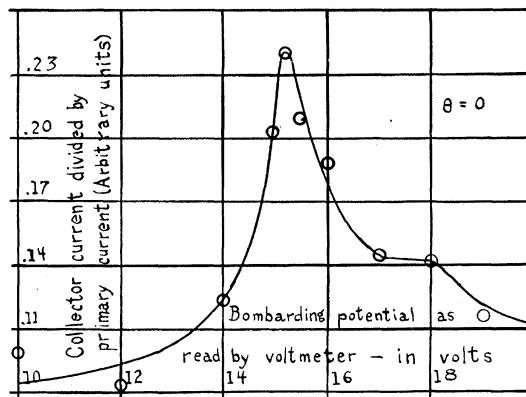


FIG. 10. The $n_1=0; n_2=1$ (normal exodence) maximum in the (1-0-0) azimuth of the (1-0-0) plane.¹⁰

II is shown plotted¹⁰ in Fig. 10 which shows some indication of an accompanying satellite of the type found for copper and silver by Farnsworth.⁹ The positions of these $\theta=0$ maxima are indicated in Figs. 2 and 4 by triangles.

B. Oblique exodence

The extreme sharpness and great intensity of the beams found in the A and A' azimuths of the (1-1-2) plane made it seem advisable to base the estimates of W_a exclusively on these beams, for all of the other beams were so broad in comparison that estimates of comparable accuracy would be impossible. In Fig. 2, it is supposed that the points lie near the volume curves instead of on them because no correction has been made for refraction. If the curves are now corrected for refraction until they are shifted over to coincide with the points, one can estimate from the amount of the correction necessary what must have been the value of the surface work function W_a to which the refraction is due. We now proceed to do this.

¹⁰ In Fig. 10, the abscissae give the apparent bombarding potential as read by a voltmeter (connected from filament to grid) and it is seen that the voltage of the maximum read in this way is about 15½, although the true bombarding potential was 7.9 volts as marked, the discrepancy being due to contact potentials in the electron gun. These contact potentials which are not only large, but quite variable from day to day are of no importance in the present work, but Fig. 10 was plotted so as to emphasize them because they must be considered in using apparatus of the usual type, and their wide fluctuation may account for the irregular variations of W_a reported by some observers.

It must be remembered that due to refraction, the length of the phase waves within the crystal is not λ , but λ' , and that the angle θ at which the beams are observed is not identical with the angle θ' at which the diffraction is really occurring. Consequently, Eq. (2) should be corrected by replacing λ by λ' and θ by θ' using the relation

$$\lambda/\lambda' = \mu = \sin \theta / \sin \theta' \quad (3)$$

μ being the index of refraction given by $\mu = (1 + W_a/V)^{1/2}$ where W_a is the surface work function. If Eq. (2) is thus corrected, and if at the same time one substitutes for d its value (3.155A), one obtains for the first order equation ($n_2=1$)

$$\lambda' = 1.29(1 + 2 \sin(30^\circ - \theta')) \quad (4)$$

or substituting for λ' and θ' their values in terms of λ , θ , and μ from Eq. (3), one obtains

$$\frac{\lambda}{\mu} = 1.29 \left(1 + \left(1 - \frac{\sin^2 \theta}{\mu^2} \right)^{1/2} - 1.732 \frac{\sin \theta}{\mu} \right). \quad (5)$$

Solving this equation for μ , one obtains

$$\mu = \frac{(\lambda/1.29)^2 + 2.685\lambda \sin \theta + 4 \sin^2 \theta}{2(\lambda/1.29 + 1.732 \sin \theta)}. \quad (6)$$

In Table III, the first column gives the colatitude at which the beam occurred as read from Fig. 8. The second column gives the primary voltage V at which the beam was

TABLE III. $A-A'$ azimuth (1-1-2) plane.

θ (degrees)	V (volts)	λ (Angstroms)	μ	W_a (volts)
0	17.62	2.918	1.1324	5.0
12	27.55	2.334	1.0949	5.5
19	37.75	1.994	1.0773	6.1
22	44.2	1.843	1.0743	6.8
23	47.45	1.779	1.0659	6.5
24½	53.05	1.682	1.0544	5.9
25½	57.75	1.612	1.0448	5.3
27	63.35	1.539	1.0421	5.4
28	68.1	1.485	1.0396	5.5
31	83.0	1.535	1.0318	5.5
35	118.5	1.125	1.0198	4.7
Mean: 5.65				

actually observed, this being computed from the magnetic field as explained in the article in R. S. I.¹ The wave-length λ corresponding to this primary voltage as computed from the equation $\lambda = (150/V)^{1/2}$ is given in the third column.

Substituting the values of θ and λ from columns 1 and 3 into Eq. (6), one computes the values of μ given in the fourth column. Then using the equation $\mu = (1 + W_a/V)^{1/2}$ one computes the values of W_a recorded in the fifth column. These values are seen to be fairly consistent and their average is 5.65 volts. If one includes in the average the values for W_a given in Tables I and II, one obtains a final average for W_a of 5.52 volts, which the writer regards as his best experimental value.

IX. EFFECT OF VARIATION OF ANGLE OF INCIDENCE

In a recent paper,⁹ Farnsworth emphasizes the importance of slight variations in the angle of incidence. An azimuth curve was taken with the normal to the (1-0-0) plane inclined at an angle of 2 or 3 degrees to the direction of motion of the incident primary electrons at an angle θ and voltage indicated by the star in Fig. 4. The curve obtained is the solid one in Fig. 11. The tube was

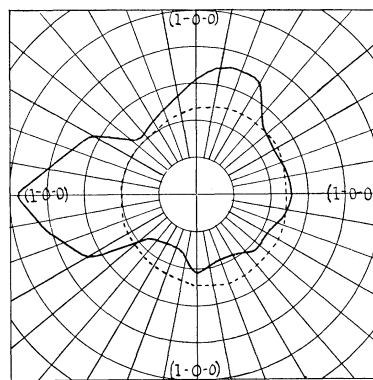


FIG. 11. Azimuth curves showing the effect of slight variations in the angle of incidence.

then cut down, the crystal re-aligned, followed by reassembly of the tube, the usual two weeks of baking, and 100 more hours outgassing of the crystal. The azimuth curve was then repeated at the same latitude and voltage, the result being shown by the dotted curve in Fig. 11. The solid curve exhibits peaks very strongly in the (1-0-0) azimuth at 90° and 180°, and weakly at 270° and 0°, but the dotted curve exhibits no peaks at all. The importance of small variations in the angle of incidence is thus again demonstrated.

X. SUBSEQUENT EXAMINATION OF THE CRYSTAL

Microscopic examination of the crystal after the work was completed revealed slight pitting of the surface by the bombardment, but the crystal facets flashed up in unison over the entire face even more brightly than they had just after the original etching, indicating that if any recrystallization had occurred, it was ultra-microscopic.

XI. DISCUSSION

A. General

In the following discussion, the observed peculiarities of electron diffraction in tungsten are enumerated, followed in each case by a brief attempt to partly correlate them with the known structure of the tungsten lattice.

(1) Except in the case of the AA' azimuth of the (1-1-2) plane, the beams on the whole are less intense, less sharp in co-latitude and azimuth, and have a slower rate of growth and decay (these expressions were explained in Section VI) than those observed by others for nickel, copper, silver, etc.

The (1-0-0) and (1-1-2) planes of tungsten are somewhat less densely populated than the planes examined in these other metals. For example, the populations of the tungsten (1-1-2) and (1-0-0) planes, the (1-1-1) plane of nickel, and the (1-0-0) planes of silver and copper are approximately in the ratio 81 : 99 : 106 : 121 : 155 respectively. This circumstance might enable the primary electrons to penetrate more deeply into the crystal, and the secondaries originating deep within the metal might suffer a second diffraction or undergo irregular scattering on their way back to the surface. Such successive diffraction might help to account for the generally lessened sharpness and rate of growth and decay and for the increased diffusely scattered background.

(2) In general, the volume interference condition seems to play a more important rôle in tungsten than in other metals. This also could be explained on the basis of deeper penetration, which would tend to increase the intensity of the volume maxima and also to increase their sharpness due to improved resolving power.

(3) A unique behavior is observed in the case of the beams diffracted in the AA' azimuth when

the primary beam is incident normally upon the (1-1-2) plane. Here the beams were sharper in co-latitude and azimuth than are usually observed for other materials, and were found at every voltage tried, always at a value of θ agreeing with the volume Eq. (2). In this azimuth of this plane, the surface interference Eq. (1) has negligible effect, or none at all.

The sparse population of the (1-1-2) planes coupled with their small interplanar distance and the unusual staggering of the atoms about the normal pointed out in Section IV might allow penetration of an unusual number of planes by the primaries. From Fig. 1, one can see that the secondaries diffracted at oblique exodence in the B or C azimuths will encounter many obstructing atoms in their journey back to the surface with the results already mentioned in Part 1 of the discussion, but secondaries diffracted at oblique exodence in the A or A' azimuth will find a comparatively free path back to the surface if θ is less than about 35° . This makes the extreme sharpness, great intensity, and the accentuation of the volume interference somewhat more plausible, but fails to account for the absence of destructive interference when Eq. (1) is not satisfied.

The unique behavior is observed with a sparsely populated closely spaced set of planes. The opposite extreme in behavior was observed by Kikuchi with the opposite extreme in structure, though with primary velocities from 10,000 to 85,000 electron-volts. Bombarding films of mica about 10^{-5} cm thick normally to the cleavage planes which are spaced at the relatively great distance of $10A^{11}$ and recording the transmitted secondaries by a photographic plate behind the film, he obtained¹² a so-called "N-pattern" which fits perfectly the surface interference condition applied to the cleavage plane, while the volume condition had no influence which could be even detected. The same phenomenon was noted in mica with x-rays by W. Linnik.¹³

It seems worth noting that while with tungsten the breakdown of the *surface* condition for

¹¹ Siegbahn, Phys. Rev. 8, 320 (1916).

¹² Kikuchi, Proc. Imp. Jap. Acad. 4, 271, 275, 354, 471 (1928); Japanese Journal of Physics 5, 83 (1928).

¹³ Linnik, Nature 123, 604 (1929).

constructive interference is associated with incidence on relatively empty but closely spaced planes, Kikuchi's observed breakdown of the *volume* condition for constructive interference is associated with relatively full planes which are widely spaced. This suggests that the explanation of both anomalies is somehow contained in the relation of population to interplanar distance.

This problem has already aroused the interest of others. W. L. Bragg¹⁴ suggested that the phenomenon could be "readily explained by the familiar laws of diffraction by a three dimensional grating, assuming a slight random warping of the mica planes," and performed an experiment to demonstrate this possibility. It seems doubtful whether the present results can be explained on the basis of an opposite type of deformation of the tungsten crystal.

The sharpness of the beams in the AA' azimuth of the (1-1-2) plane enables one to compute that the phase waves assumed to be associated with the electrons have an effective lateral extent at right angles to the direction of propagation of at least 30Å if one is permitted to apply the usual formulae for resolving power to the phase waves. A similar conclusion was reached by G. P. Thomson.¹⁵

B. Values for W_a

According to Sommerfeld's theory of metals,¹⁶ we have

$$\phi = W_a - W_i \quad (7)$$

where ϕ is the usual photoelectric or thermionic work function (4.55 volts for tungsten), W_a is the height of the potential wall at the metal surface, and W_i is the maximum internal energy of the free electrons in the metal. Therefore, if we take the final value of 5.52 volts for W_a yielded by the present experiments, we get W_i = about 1 volt, whereas an application of Sommerfeld's theory to tungsten yields a theoretical value of 5.7 volts.

The only other determination of W_a for tungsten is that of Boas and Rupp⁵ who obtained values of 0 and 10 volts for polycrystalline material. As regards consistency, the present results are considerably more satisfactory than those recently given by Farnsworth⁹ for a single copper crystal in which case the values of W_a range from 5 to 31 volts. The fact that higher outgassing temperatures could be used with tungsten may account for the more consistent values obtained, and this consistency leads one to attach some possible importance to the difference between the resulting value of W_i and that computed from the Sommerfeld theory. This difference may be due to the limitations of the Sommerfeld theory resulting from the fact that the variations in potential inside the crystal due to the atoms is not considered; or perhaps one is not justified in treating the diffraction from the crystal planes in such a highly idealized way, as though the problem were quite analogous to diffraction of light in optics; or it may be that unsuspected systematic experimental errors are responsible.

In conclusion, the writer wishes to express his sincere appreciation of the invaluable help so willingly offered by Professor C. E. Mendenhall, who directed the work.

¹⁴ Bragg, *Nature* **124**, 125 (1929).

¹⁵ See Thomson's book, *Wave Mechanics of Free Electrons*, p. 72.

¹⁶ Sommerfeld, *Zeits. f. Physik* **47**, 31 (1928).