Diffraction of Low-Speed Electrons by Single Crystals of Copper and Silver

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Diffraction beams for normal incidence on the (100) faces of copper and silver crystals.—Previous results for a *copper crystal* are checked and extended, by using another crystal of exceptionally pure copper. All of the expected diffraction beams which are x-ray analogues in the two principal azimuths and in the range below 325 volts are found. These beams require values of refractive index greater than unity, but the associated values of inner potential are *not constant.* Another class of weak beams is found characteristic of the copper lattice, but which require a refractive index of approximately unity for the first order beams of the two principal azimuths. These weak beams accompany the main beams on the high voltage side as satellites. Conditions for orders higher than the 1st are more complicated and indicate that the above method of classification is not sufficient. For a *silver crystal* the number of experimental maxima is considerably greater than the number of theoretical beams in the low-voltage range. These maxima cannot be classified as main beams requiring a refractive index greater than unity, and weak satellites requiring unit refractive index as in case of a copper crystal, but whenever two or more experimental maxima are to be associated with a given theoretical beam, they are, in general, grouped as components of fine structure of a single diffraction beam.

Intensity measurements on diffraction beams as a function of angle of incidence.—*For copper,* as the angle of incidence is changed by only a few degrees from normal, large intensity changes of the various diffraction beams are observed. Some beams increase while others decrease in intensity for a given change in angle of incidence. Primary voltage and collector angle are adjusted for each observation. For *silver,* as the angle of incidence is changed from normal the relative intensities of the components associated with a particular beam change rapidly. Some components may disappear and others appear at different voltages, as the incident angle is changed a few degrees. The plane grating formula is approximately satisfied over considerable ranges in the angle of incidence, but there are other ranges for which it is not satisfied. The above variations for various beams do not correspond; neither do those for the beams associated with different orders of reflection from the same set of Bragg planes. Intensity measurements are given for most of the beams in the two principal azimuths below 350 volts for ranges in the angle of incidence, including normal incidence, through which the beams are observable.

Regular reflection of electrons from the (100) set of planes.—For copper, with angle of incidence equal to angle of reflection, curves obtained by measuring collector current as a function of primary voltage show many irregularities. For silver, the curves contain many irregularities which do not correspond to those for a copper crystal under similar conditions. For the same angle of incidence and the same set of reflecting planes, the results are not the same for the plane of reflection in the (100) and the (111) azimuths, respectively.

Diffraction beams due to a surface gas lattice on the (100) faces of copper and silver crystals.—For copper, "additional" beams which were formerly reported have since been found to decrease in intensity after prolonged heat treatment of the copper crystal at temperatures near its melting point. These beams indicate a *simple-cubic, single-spaced* lattice with the same constant as that for the copper lattice. They require values of refractive index greater than unity. When the surface gas lattice becomes thin it changes in structure from a *simple-cubic, single-spaced* lattice to a *face-centered,*

double-spaced lattice. The beams characteristic of the latter structure require *unit* refractive index. Hydrogen also forms in either of the above two lattices on a copper crystal, depending on the pressure of the hydrogen while the lattice is formed. The lattice which is characteristic of the thicker layer is very unstable and soon changes to that of the thinner layer after the pressure is removed. For *silver*, only a few very weak beams due to a surface gas lattice are found below 50 volts after heating the crystal a short time at red heat. They indicate a double-spaced, face-centered structure.

Inner potential. The measured value of the inner potential is neither constant nor a continuous function of the voltage. It is found to change discontinuously, by several volts in some cases, as the angle of incidence is varied. Results for the crystals of copper and silver which have the same lattice structure are found to differ widely. Hence they appear to be a function of the type of atom.

Surface action. Experimental methods of distinguishing between effects due to surface action and those due to a space lattice are discussed.

INTRODUCTION

EXPERIMENTS on electron diffraction by solids may be divided, according to their correlation with simple theory, into two classes. (1) Those with high-speed electrons having energies of several thousand equivalent volts have been performed by various observers[1] with polycrystalline targets. The results are all in accord with those to be expected on the basis of de Broglie's original equation $\lambda = h/mv$. Recently Rupp[2] has extended previous measurements to electron energies as high as 220 k.v. and finds the results in accord with theory when relativity is included. Although Kikuchi[3] obtained unusual results when using mica crystals, they are explained when proper account is taken of the particular conditions which obtain in the mica crystal. G. P. Thomson[4] has recently extended measurements with high-speed electrons to single crystals of copper, silver, and rocksalt. Although the results are much more complicated than one should anticipate, they appear to be accounted for by assuming that the etched surface of the crystal is composed of lumps of dimensions about 10^{-6} cm through which electrons can pass when striking the surface at glancing angles of incidence.* (2) Experiments with low-speed electrons having energies less than a few hundred volts show many deviations from the predictions of simple theory. In the original experiments of Davisson and Germer,[5] using normal incidence on the (111) face of a single nickel crystal, several expected beams were missing while a few unexpected beams were found. When using an arrangement corresponding to Bragg reflection, i.e., angle of incidence other than normal and equal to angle of reflection, many anomalous beams were present.[6] Rupp,[7] with an

[1] See references in "Wave Mechanics of Free Electrons" by G. P. Thomson.

[2] E. Rupp, Ann. d. Physik **10**, 927 (1931).

[3] S. Kikuchi, Proc. Imp. Jap. Acad. **4**, 271, 275, 354, 471 (1928); Jap. Jour. Physics **5**, 83 (1928).

[4] G. P. Thomson, Proc. Roy. Soc. **133A**, 1 (1931).

* Recent experiments of Davisson and Germer (paper at Cambridge meeting of Am. Physical Society, Feb. 1931) with high-speed electrons and single crystals of nickel and tungsten do not show such characteristics.

[5] C. Davisson and L. H. Germer, Phys. Rev. **30**, 705 (1927).

[6] C. Davisson and L. H. Germer, Proc. Nat. Acad. **14**, 619 (1928).

[7] E. Rupp, Ann. d. Physik **5**, 453 (1930); see also H. E. Farnsworth, Phys. Rev. **36**, 1799 (1930).

arrangement similar to the latter, appears to find fewer anomalies but reports several half-order beams. Early experiments by the writer,[8] using normal incidence on a (100) face of a single copper crystal, showed the presence of several "additional" beams which were later[9] greatly reduced in intensity by prolonged heating of the crystal at temperatures near the melting point of copper, and hence are attributed to gas. In these later experiments another weak class of beams (referred to as satellites) was found whose intensity did not decrease with prolonged heating of the crystal. Most of them occur at such voltages as to require a unit refractive index while the intense beams require values of refractive index greater than unity. Boas and Rupp[10] have more recently reported similar beams for tungsten. Previously unpublished results obtained by the writer for a copper crystal using an arrangement corresponding to Bragg reflection also show the presence of many unexpected beams.

It thus seems clear, as has already been emphasized by G. P. Thomson,[4] that high-speed electrons are much more suitable for investigations of crystal structure similar to those made with x-rays.

On the other hand, the very fact that unexpected results are obtained with low-speed electrons shows that certain conditions within the crystal reveal themselves to this method of experiment, but entirely escape detection by high-speed electrons or x-rays. Since low-speed electrons, when impinging on a crystal surface, are affected by fields which have little or no influence on high-speed electrons or x-rays, possibilities at once suggest themselves of obtaining, by the use of low-speed electrons, valuable information which is inaccessible to other methods of investigation. Questions of inner potential and the associated refractive index are immediately involved. The regions in the outermost parts of the atoms that play no part in the scattering of x-rays may here be expected to make significant contributions. Although estimates of the inner potential of ionic crystals have been made from observations with high-speed electrons,[11] it seems reasonable to expect that information regarding possible variations from its mean value can be obtained only with the use of low-speed electrons. A wide range of experimental observations combined with a satisfactory method of interpretation are required to make this information available.

The theory of electron diffraction by a space-lattice has been discussed by Bethe[12] and by Morse.[13] The latter has accounted for the anomalous results of Davisson and Germer for a nickel crystal. v. Laue[14] has estimated the influence of the gradual transition of the field across the boundary of a crystal and found that the surface action may be neglected for electrons of 200 or more volts energy, but that for lower energies the theories of Bethe and

[8] H. E. Farnsworth, Phys. Rev. **34,** 679 (1929).
[9] H. E. Farnsworth, Phys. Rev. **35,** 1131 (1930).
[10] W. Boas and E. Rupp, Ann. d. Physik **7,** 983 (1930).
[11] A. G. Emslie, Nature **123,** 977 (1929). G. P. Thomson, Proc. Roy. Soc. **133A,** 1 (1931).
[12] H. Bethe, Ann. d. Physik **87,** 55 (1928).
[13] P. M. Morse, Phys. Rev. **35,** 1310 (1930).
[14] M. v. Laue, Phys. Rev. **37,** 53 (1931).

Morse require extension. Contributions have also been made by Kronig and Penny,[15] and by Hill.[16] There is, however, nothing in these treatments which would lead one to expect that the results might vary greatly among different substances having identical crystal lattices. The results contained in the present paper show that this is actually the case.

It appears that further progress can only be made by first obtaining experimental data for various crystals under similar conditions. These data should include an accurate measure of the intensities of the various diffraction beams over a considerable range of the variables upon which the values of the intensities depend. That the angle of incidence of the primary beam is one of the most significant of these variables was observed a few years ago by the writer during some of the first experiments with a copper crystal. At that time, while searching for a possible polarization effect due to weak magnetic fields, it was found that large changes of intensities of some of the diffraction beams were produced by a transverse magnetic field of a fraction of a gauss. The primary voltage was adjusted to best value for each field. The observed changes of intensities appeared much larger than those which one might reasonably expect as a result of the small change in the angle of incidence produced by the magnetic field. In order to determine the cause, the apparatus was modified so that the angle of incidence could be varied. It was then found that the large intensity changes were due entirely to the small changes in the angle of incidence. These intensity changes have now been investigated in some detail.

The present paper contains results for a copper crystal which supplement those previously reported.[8,9] Some of the results reported here have been briefly described in a letter to the Editor of the Physical Review[9] some time ago. A more detailed account has been postponed since it appeared that an interpretation of some of them might depend on corresponding results for a crystal of some other metal. That this is the case is shown by unexpected results which have now been obtained for a silver crystal.

Apparatus

The experimental arrangement in use at present is a modification of that which has already been described in detail.[8] Hence it will be sufficient to refer to the original description and to indicate what changes have been made. These changes have been incorporated at different times during the last two and one-half years, so that all of the results reported here have not been obtained with the apparatus in its present form.

The electron gun has been altered to the form shown by AB, Fig. 1. The diaphragmed tube which limits the primary electron beam has been greatly increased in length. This results in a more sharply defined electron beam, and makes possible a more accurate alignment of its direction. In order to keep the total distance between filament and target the same as previously, an alteration in the geometry of the parts near the filament was required. Al-

[15] R. de L. Kronig and W. G. Penny, Proc. Roy. Soc. **130**, 499 (1931).
[16] E. L. Hill, Phys. Rev. **37**, 785 (1931).

though this modified form does not produce as large electron currents as the former one at very low primary energies of the order of a few equivalent volts, its other advantages make it preferable for the present experiments.

The former mounting of the crystal has been replaced by one which permits a rotation of the crystal about an axis lying in the crystal face and perpendicular to one of the principal azimuths, thus permitting a range in the angle of incidence of the primary electron beam from $-15°$ to $+50°$, measured from the normal. The arrangement is shown in Fig. 1. The crystal is first cut in the approximate form of a rectangular parallelepiped of dimensions about $6\times6\times12$ mm, one of the ends being accurately parallel to a (100) set of planes of the crystal. The sides are cut either parallel to (100) or (110) planes, depending on whether the crystal is to be rotated about an axis parallel to the (100) or (110) azimuths, respectively. The method of prepar-

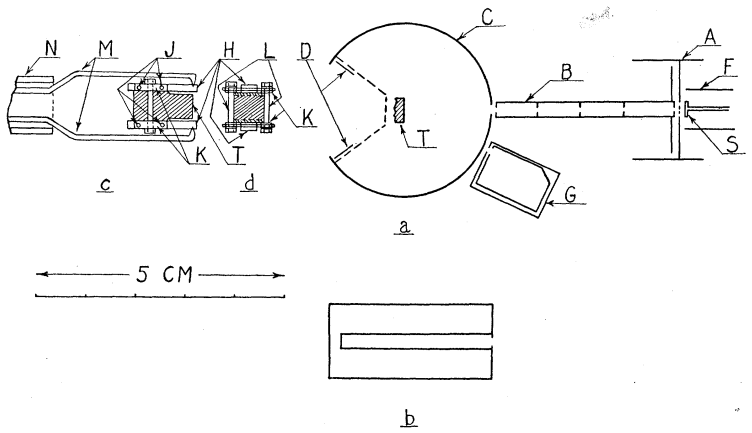

Fig. 1. Apparatus. *a*—top view, *b*—side view of drum, *c*—mounting of crystal, side view, *d*—mounting of crystal, front view.

ing the surfaces has already been described.[8] The etching process varies with the metal of which the crystal is composed. After cutting the crystal to the approximate dimensions given above, one of the cross-sectional dimensions is reduced on the front half of the crystal in order to form a clearance between this half of the crystal and the mounting, as shown in Fig. 1. The mounting consists of two beams of rectangular cross-section H made from molybdenum sheet and clamped rigidly to the back half of the crystal. Four tungsten rods J pass through holes in these beams and also through holes in four other molybdenum beams K arranged as shown. Two other tungsten rods L, threaded on the ends, pass through holes in the beams K. Thin steel nuts on the ends of the threaded tungsten rods hold the mounting in place. The amount of metal contained in the nuts is so small that their magnetic effect at the face of the target is negligible. A tungsten strip (not shown) is held against one side of the crystal near the rear. To outgas the crystal, this strip is bombarded and the crystal thus heated by conduction. This form of mounting was adopted after trying another less satisfactory one. It must ful-

fill the rigid requirement of keeping the crystal in its original adjustment when heated at red-heat temperatures. This mounting makes it unnecessary to drill holes in the crystal, an important consideration for metals which recrystallize rather easily. Small holes (No. 80 drill) near the ends of the beams H admit the points of the tungsten rods M which serve as pivots. These rods pass through a Pyrex glass tube N (parallel to the axis) of 24 cm diameter and 1.2 cm length. At the end nearest the crystal the rods pass through close fitting holes in a molybdenum frame (not shown) fitting inside the tube. At the other end of the tube the rods pass through holes in a steel frame which fits the end of the tube. Set screws prevent the rods from slipping parallel to the tube. The arrangement is such that one of the rods may be moved a small distance parallel to the tube by turning a screw which presses against the end of the rod. This permits a fine adjustment at the time of mounting the crystal. A bar of soft iron which is attached to the steel frame at right angles to the tube axis, serves as a magnetic control by means of which the tube may be rotated about its axis or displaced parallel to it. A molybdenum rod passes along the axis of the tube and may be displaced parallel to it. At the end near the crystal, this rod attaches by means of a tungsten pivot to one end of a movable arm. The other end of the arm is attached by another tungsten pivot to an arm (now shown) fixed to the crystal mounting. At the other end of the tube, the molybdenum rod is connected by suitable coupling to a steel screw which may be turned by another magnetic control. Turning this screw thus rotates the crystal. Loose play is eliminated by a flexible tungsten coiled spring. The Pyrex glass tube is ground accurately round at two points which serve as bearings when an adjustment of azimuth is made. This Pyrex tube slides and rotates in another frame which fits snugly into a part of the main experimental tube.* This frame is the same as that which formerly supported the Faraday cylinder E, Fig. 1 of previous article.[8] The Faraday cylinder E has been removed in the present arrangement. This arrangement makes it possible to withdraw the crystal into a side tube where it may be outgassed by electron bombardment from the rear. An automatic trap door prevents evaporated metal from entering the main part of the tube. All motions are effected by magnetic controls sufficiently removed from the crystal to have no disturbing magnetic effect.

The accuracy of the adjustments depends to a great extent on the accuracy of the mounting of the crystal. The front face of the crystal can be made parallel to a desired plane to within 0.5° by methods previously described.[8] After cutting and etching the crystal to the desired size and shape it is placed in the mounting, care being taken not to scratch the forward half of the crystal by touching with any hard surface. The front half is protected with moist filter paper during the adjustment, care being taken that nothing touches the front face. After clamping the mounting on the crystal as nearly as possible in adjustment, it is placed on a goniometer and viewed with a telescope at several feet distant rather than with one attached to the instru-

* I am indebted to Mr. Newton Underwood for the design of certain parts of this arrangement.

ment. The telescope is mounted with its axis perpendicular to the axis of the goniometer, and a small beam of light nearly coincident with the telescope axis is directed toward the crystal. If the crystal has been properly etched, reflections may be observed from the sides as well as from the front. These make it possible to test the adjustment with the desired accuracy. With silver good reflections were obtained from both (100) and (110) planes on the sides of the crystal. The crystal is so oriented with respect to the goniometer and telescope that it may be rotated about the proper axis to test the alignment of the mounting with respect to the crystal. The straight line connecting the centers of the small holes in the mounting should lie in a desired azimuth and pass through the center of the front face parallel to a particular plane. If the front face were cut and etched exactly parallel to the desired plane then, of course, the line in question should lie in the plane of the face. Also, if this adjustment were exact, the line connecting the centers of the small holes would be parallel to the line of sight when the visible halves of the holes appear lined up in the telescope. (Only one-half of each hole is visible by transmitted light, the other half being shielded by the crystal.) If the front plane is not exactly parallel to the desired plane, the line connecting the visible parts of the holes will not be parallel to the atomic plane in question. To eliminate this possible error, indicator marks were placed in the mounting at the same distance, to within 0.01 mm, from each hole. The line connecting these could be adjusted to the desired position to within 0.5°. The crystal and mounting were cleaned before adjusting and were not subsequently touched with the hands. After placing the crystal with its mounting in position between the two tungsten pivots, one of these is adjusted so that the desired crystal plane is perpendicular to the axis of the Pyrex glass tube which supports the crystal. To check the alignment in the experimental tube, the parts are first assembled with the filament, which acts as the electron source, removed. The alignment is then adjusted until a narrow beam of light, which is sent down the electron gun, is reflected by the crystal face back through the gun into a telescope placed 10 feet from the tube.

Further Experiments with a Copper Crystal

Preparation of crystal

The crystal used for the present experiments was cut from one made of exceptionally pure copper* by slowly lowering the melt through a constant (in time) temperature gradient in a vertical-type, molybdenum-wound, hydrogen furnace. A lowering speed of 1/8 in. per hour was used. From 90 to 100 hours were required for the run including time of bringing the furnace up to temperature. The mold was made from graphite rod of highest purity obtainable from the Acheson Graphite Corporation. A coating of nickel electroplated on the outside of the crucible helped to preserve it. The original crystal was 3/4 in. in diameter and 7 in. long with the lower end tapering to

* I am indebted to Dr. S. Skowronski of the Rantan Copper Works, Perth Amboy, N. J., for the copper which was of greater purity than the standard melting point copper used by the Bureau of Standards.

TABLE I. *Main diffraction beams for the copper lattice; approximately normal incidence.*

Beam and order numbers*	Plane of reflection	Experimental colatitude angle	Experimental voltage	Theoretical voltage	Voltage difference	Corrected intensity / Background intensity	Corrected relative intensity
			(100) Azimuth				
1–1	(210)	63.0°	60.3	72.2	11.9	20.4	100
2–1	(310)	43.0°	115.5	128.4	12.9	3.3	62
3–1	(410)	31.5°	191.5	208.5	17.2	2.3	76
4–1	(510)	25.0°	296.5	312.4	15.9	1.2	54
1–2	(320)	74.0°	200.5	217.0	16.5	2.4	10
2–2	2(210)	56.5°	260.5	288.9	28.4	1.9	11
			(111) Azimuth				
1–1	(311)	67.5°	26.5	38.8	12.3	49.0	84
2–1	(511)	35.8°	69.7	84.2	14.5	6.9	88
3–1	(711)	25.8°	127.5	153.3	24.8	2.5	70
4–1	(911)	17.5°	220.0	245.7	25.7	1.2	61
1–2	(211)	74.0°	99.0	104.0	5.0	5.5	11
2–2	2(311)	54.0°	138.0	155.3	17.3	4.7	45
3–2	(411)	41.2°	203.0	234.0	31.0	1.8	22
4–2	2(511)	31.0°	320.0	337.0	17.0	4.6	69
2–3	(733)	63.5°	242.5	264.5	22.1	3.9	7

* The notation 2–1, e.g., refers to the second beam in the first order. The notation of orders is the same as that originally used by Davisson and Germer. It should be noted that the second-order beams in this notation are not all second-order beams in the Bragg notation. This is seen by comparing with the corresponding values in the second column. The 2–2 beam in the (100) azimuth is, however, a second order reflection from the (210) set of planes. The lowest index numbers are used for the Miller indices in the second column. The corresponding reflections are respectively (420), (620), (820), (10,2,0), (640), (840), (311), (511), (711), (911), (422), (622), (822), (10,2,2), (733).

TABLE Ia. *Corresponding satellites.*

Experimental colatitude angle	Theoretical colatitude angle	Experimental voltage	Theoretical voltage	Voltage difference
	(100) Azimuth			
55.3°	53.1°	72.5	72.2	−0.3
37.5°	36.9°	128.5	128.4	−0.1
30.5°	28.1°	210.5	208.7	−1.8
24.7°	22.7°	310.5	312.4	1.9
	67.4°		217.0	
57.8°	53.1°	277.0	288.9	11.9
	(111) Azimuth			
53.7°	50.5°	37.3	38.8	1.5
29.5°	31.6°	87.0	84.2	−2.8
24.5°	22.3°	146.0	153.3	7.3
17.5°	17.9°	243.0	245.7	2.7
64.5°	70.3°	111.0	104.0	−7.0
50.5°	50.5°	154.5	155.3	0.8
39.0°	38.0°	215.0	234.0	19.0
62.0°	64.4°	260.0	264.6	4.6

a point. Orientation of the crystal was determined by the method previously described.[8] Etching was done sometimes with ammonium persulphate and sometimes electrolytically with the crystal as anode. In the latter case it was found that for low current densities etching occurs only parallel to (111) planes. For higher current densities etching occurs predominantly parallel to (100) planes if the conditions are right.

Number and relative intensities of main diffraction beams for approximately normal incidence

The results obtained with the first copper crystal of unknown purity which was obtained from the General Electric Company are in satisfactory agreement with those obtained with this crystal under the same conditions when one considers a slight difference in the angles of incidence due to error, and the corresponding voltage changes which have been found to result from small changes in the angle of incidence. *All* of the expected diffraction beams in the two principal azimuths and in the range below 325 volts were observed for the second crystal. As before, only full-speed electrons were admitted to the Faraday collector. After further heating of this crystal at temperatures considerably higher than those previously used, a class of "additional" beams occupying the positions required by a *simple cubic* structure had decreased in intensity to a small fraction of their former values and hence are due to a gas lattice on the surface. (This crystal has been heated at various red-heat temperatures, some near the melting point, for 43 hours. During this time recrystallization occurred only to a slight extent in the region where the mounting and crystal came in contact).

Table I contains the relative intensities of the main diffraction beams for approximately normal incidence. These are the maximum deflections obtained for the various beams with optimum values of primary voltage and colatitude angle, and with a constant primary electron current. It might appear advisable to obtain the relative intensity of an electron diffraction beam by the method of integrated reflection used for x-rays. This has not been done because of the experimental difficulties which would be involved. Also, in view of the irregularities which are found, the type of measurements made here appear just as significant. Because the adjustment for normal incidence was in error by approximately 1° (the accurate method of adjustment described above was not used for this crystal), and since the intensities of the beams vary with the angle of incidence, the values of intensity in Table I probably differ somewhat from the correct values for normal incidence.

Beams requiring unit refractive index

In addition to the beams described above there is another class of weak beams a few of which were observed during the investigation with the first copper crystal.[8] Most of the observations on these beams were obtained after the gas beams had been greatly reduced in intensity. The first beams of this class which were observed occur at such primary voltages as to require a unit refractive index, while the "main" beams require a refractive index greater

than unity. A search for other weak beams of this nature revealed a whole series of such beams which accompany the main intense diffraction beams as satellites on the high voltage side. Most of these satellites are so close to the main beams and have such a small relative intensity that they are not completely resolved, and hence were not observed by the usual method of taking colatitude curves for various primary voltages. In these cases their presence was detected by varying the primary voltage in small steps, and measuring the current to the Faraday collector, whose angular position was adjusted for the maximum of the beam at *each* reading, while the total primary current

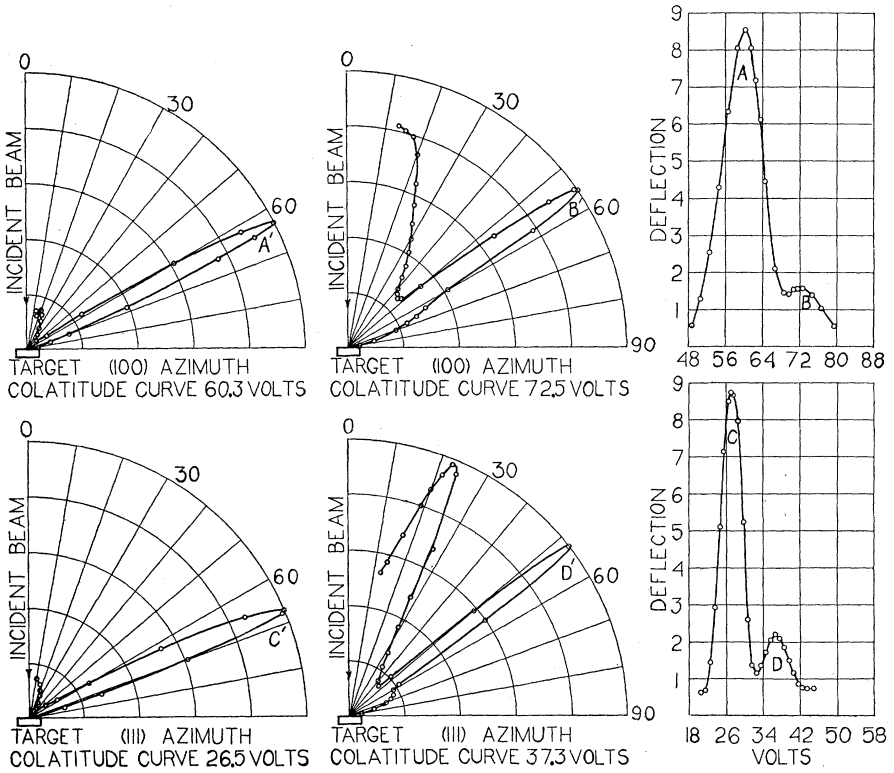

Fig. 2. Curves showing satellites for a copper crystal. The maxima B and D are the satellites of the main beams A and C, respectively. The colatitude curves A', B', C', and D' correspond to the maxima A, B, C, and D, respectively.

was held *constant* for the entire set of observations. The operating conditions of the experimental tube must be kept very constant for such a set of observations. A fine adjustment in the filament circuit controlled the primary current. The results of these observations may be plotted as in Figs. 2 and 3. Curves at the right in Fig. 2 show the deflections corresponding to the beam maximum for various primary voltages. These curves show the growth and decay of particular diffraction beams with weaker beams accompanying them on the high voltage side. The colatitude curves are shown for the voltages

corresponding to the peaks of these curves. The satellite D is seen to be very well resolved and was originally detected as a beam distinct from C. The curve in the upper left of Fig. 3 shows two main beams A and C with the accompanying satellites B and D. A slight indication of another beam at G is due to a weak gas beam. At higher voltages the satellites are very weak and appear as bulges in the curve of the main beam, as shown in the curves at the right of Fig. 3.

The positions of the various beams are given in Table Ia. It is to be noted that in the (100) azimuth the satellites which accompany the 4 first-order beams below 325 volts all occur within 2 volts of the theoretical values for unit refractive index; that of one second-order beam occurs within 11.9 volts;

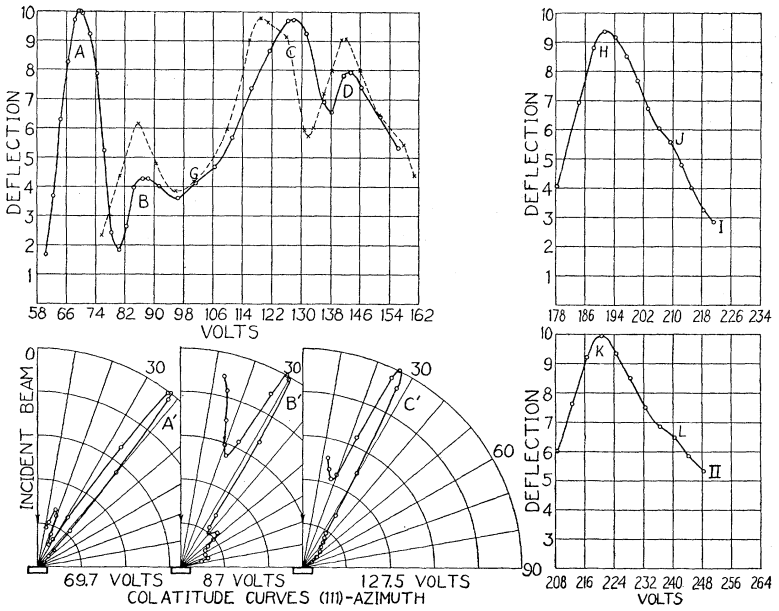

Fig. 3. Curves showing satellites for a copper crystal. The maxima B and D are the satellites of the main beams A and C, respectively. J and L are satellites of H and K, respectively. The colatitude curves A', B', and C' correspond to the maxima A, B, and C, respectively. The dotted curve is for angle of incidence $-2.5°$. Curve I is for the 3rd beam, 1st order, (100) azimuth; curve II for the 4th beam, 1st order, (111) azimuth.

that of the other second-order beam is missing. In the (111) azimuth, the satellites of 3 first-order beams are within 2.8 volts of theoretical values; that of the other first-order beam below 325 volts is within 7.0 volts; those of 2 second-order beams are within 4.6 volts; that of the other second-order beam is within 19.0 volts; that of 1 third-order beam is within 5 volts. The intensities of the satellites of first-order beams are between 10 and 20 percent of those of the main diffraction beams at the lowest voltages, and decrease to an unmeasurable amount at about 325 volts. The satellites are as sharp in voltage and colatitude angle as the main diffraction beams, and are not confined to large colatitude angles. Hence, they are not due to a two-dimensional sur-

face grating effect. At the time these observations were taken it was thought that all of the above beams were to be associated with a unit value for the refractive index. Although the values for several of the beams are off by more than the experimental error, it seemed significant that with only one exception all of the first-order beams fall well within observational error of the required value for unit refractive index. However, since several of the beams classified as satellites of higher order beams for the copper lattice require values of refractive index which differ from unity by more than the experimental error, it appears that this method of classification is not sufficient for these results. It is also entirely inadequate for classification of the results to be described for a silver crystal.

Beams due to a surface gas lattice

There are, however, certain significant facts pertaining to diffraction from a gas lattice which are in accord with the above classification. Some of the stronger gas beams characteristic of the simple cubic lattice were found to have satellites requiring a refractive index of unity. Also, as the stronger gas beams become less intense on outgassing the crystal, their voltage shifts so as to make the corresponding value of the refractive index closer to unity. Furthermore, gas beams characteristic of a *double-spaced, face-centered* lattice appear only when the gas layer is very thin and these require a refractive index close to *unity*.

G. P. Thomson[4] has recently suggested that the "additional" beams which the writer first listed for copper may be due to a layer of compound on the surface which might be formed by moderate heating if the vacuum is not high, and that heating strongly enough to vaporize the copper would probably remove the layer. This does not appear probable to the writer because even the first heating, after which the beams in question were still strong, was sufficient to evaporate considerable copper from the surface. It appears more probable that these particular beams are due to a surface layer of gas of simple-cubic, single-spaced structure having the same lattice constant as copper; that when the gas layer becomes thin after sufficient outgassing, it changes over to a double-spaced, face-centered structure; and that this gas layer is much more difficult to remove by heat treatment than are similar gas layers on nickel or silver.

G. P. Thomson[4] also states that Rupp's half-order beams are undoubtedly to be explained as a penetration of the metal lattice by hydrogen atoms in such a manner as to make alternate planes different without appreciably altering the spacing. My own results for a hydrogen lattice[9] indicate, however, that the gas lattice is on the surface rather than interpenetrating with the metal lattice. As previously pointed out by the writer,[9] hydrogen was found to form in two different lattices depending on the pressure of the hydrogen while the lattice is formed. At small pressures (less than 0.5 mm Hg) a relatively thin, double-spaced, face-centered structure is formed; at higher pressures (2 mm Hg) a thicker, single-spaced, simple-cubic structure takes its place. The beams for the first structure require a refractive index of approxi-

mately *unity* while those of the second structure require one *greater than unity*. The fact that this second structure is extremely unstable and reverts to the first structure during a few minutes seems to confirm the idea of the surface lattice.

From observations on certain diffraction beams from a surface layer of gas atoms assumed to be one atom deep, Germer[17] concluded that the spacing between the layer of gas atoms and the surface layer of nickel atoms is not a whole number multiple of the spacing between the adjacent layers of nickel atoms. He was led to this idea from the marked differences in the intensities of the various beams from the surface gas layer, but his computations on the spacing in question were based only on the positions and wave-lengths of these beams, without taking into account a refractive index. It is clear that

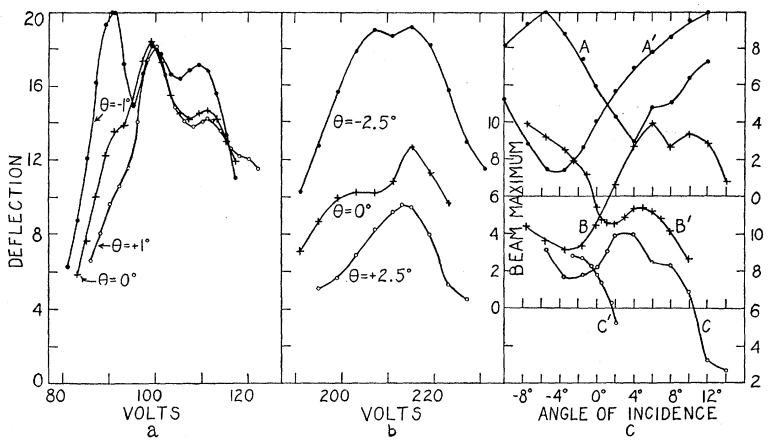

Fig. 4. Curves showing effects of changes in the angle of incidence. *a.*—1st beam including associated components, 2nd order, (111) azimuth for three different angles of incidence. *b.*—3rd beam including associated components, 2nd order, (1$\bar{1}$1) azimuth for three different angles of incidence. *c.*—intensity change with angle of incidence for the following: *A.*—1st beam, 1st order, (111) azimuth; *A'.*—satellite of this beam; *B.*—2nd beam, 1st order, (111) azimuth; *B'.*—satellite of this beam; *C.*—3rd beam, 1st order, (111) azimuth; *C'.*—satellite of this beam.

with a value of the refractive index other than unity, a different spacing would result. The observations described below on the variations in intensities of the main beams due to a metal lattice, and in the associated values of refractive index make Germer's interpretation appear very doubtful.

Intensity measurements as a function of angle of incidence

Only a relatively small number of this type of observations has been obtained for copper, but before getting more it seemed desirable to obtain corresponding observations for another metal such as silver. The curves in Fig. 4c show the variations of intensities of some of the diffraction beams with changes in the angle of incidence. For various angles of incidence (measured from the normal) the primary voltage and Faraday collector angle were ad-

[17] L. H. Germer, Zeits. f. Physik **54**, 408 (1929); Bell Tech. Jour. **8**, 591 (1929).

justed for maximum deflection while the total primary current was held constant. These curves have not been corrected for background scattering. Negative angles indicate that the normal is on the opposite side of the primary electron beam from the Faraday collector. The ordinates are arbitrary units, and those of one curve are not to be compared with those of another. Curves for three main diffraction beams in the first order of the (111) azimuth are shown with those of the corresponding satellites. There appears to be no similarity between the curves for the different beams; neither is there a correspondence between the behavior of a particular beam and its satellite.* Some beams increase in intensity for a given change in angle of incidence while others decrease. It is also to be noted that in some cases the magnitude of the intensity changes by a hundred percent when the angle of incidence is changed by a few degrees.

The curves in Fig. 4a and b, show the growth and decay of the first and third beams of the second order in the (111) azimuth for slightly different angles of incidence. These observations were taken by the same method as that described above for the curves which have similar coordinates in Figs. 2 and 3. In the curve for normal incidence ($\theta = 0$) shown at the left in Fig. 4 there are two peaks or components with an indication of a third at the left. The small peak at 111 volts is tabulated in Table Ia as the satellite of the stronger beam at 99 volts. It is seen, however, that for an angle of incidence $\theta = -1°$, a component at 91 volts is stronger than either of the other two, while at $\theta = +1°$, this component has practically disappeared. Hence, it is clear that the classification of satellites described above is not sufficient for the present case. It may be emphasized that all of these three components occur within a primary voltage range which should contain only one maximum according to simple theory, so that the different components cannot be ascribed to reflection from different sets of atomic planes in the crystal or to half-order reflections from a double spaced gas lattice. The dotted curve in Fig. 3 shows the corresponding curve for the 2nd beam of the 1st order in the (111) azimuth for angle of incidence $-2.5°$. It is to be noted that a new component has appeared at 119 volts although it is so close to the original one that they are not completely resolved.

Regular reflection from the (100) set of planes

By setting the angle of incidence at some value other than normal and adjusting the position of the Faraday collector so that the angle of incidence equals the angle of reflection, we obtain curves corresponding to the Bragg reflection for x-rays. Three such curves are shown in Fig. 5 for the (100) face of the copper crystal with the plane of reflection containing the (111) azimuth. They are obtained by observing the current to the Faraday collector as the primary voltage is changed in small steps, while the primary electron current is held constant for the entire set of observations. The apparatus per-

* These observations were taken previous to those of the type shown in Fig. 4a. Hence it is possible that additional components exist for the beams in Fig. 4c for certain angles of incidence, but were not detected by this method of measurement.

mitted observations for only small angles of incidence when these observations were obtained. However, a comparison of the three curves shows that very striking changes occur in the range of angle of incidence from 8° to 12°. The arrows along the $V^{1/2}$ axis indicate the positions of theoretical beams for different orders computed from simple theory, assuming unit refractive index It is seen that the small changes in the angle of incidence produce only very slight changes in the positions of these arrows. It may be noted in the curve for $\theta = 10°$ that several of the maxima have double peaks and that the left one is relatively much more intense for $\theta = 8°$ while the right one is more intense for $\theta = 12°$; in other cases the changes are more complicated. The num-

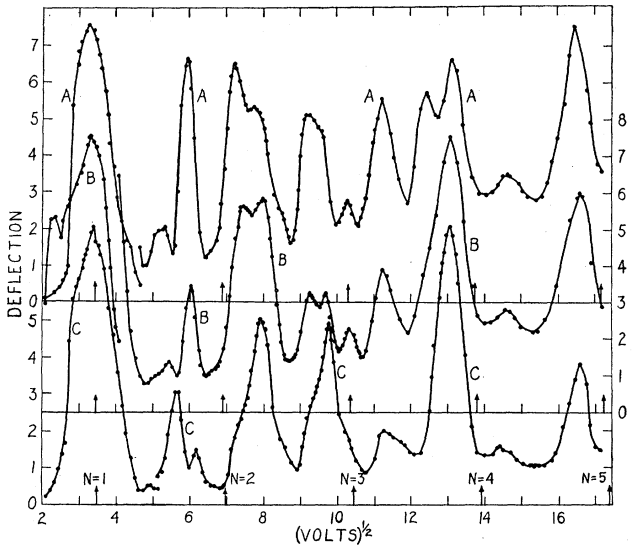

Fig. 5. Regular reflection from the (100) set of planes with the plane of reflection in the (111) azimuth. Curves *A*, *B*, and *C*, are for angles of incidence 8°, 10°, and 12°, respectively. Arrows indicate positions of theoretical beams for different orders, assuming unit refractive index. Discontinuities in the curves indicate changes in the scale of plotting. Vertical scales which overlap are same for all curves. Zero lines are indicated.

ber of experimental maxima is greater than the theoretical number. The irregularities obtained with this type of measurement are undoubtedly to be associated with those obtained by the other type of measurement near normal incidence.

Experiments with Silver Crystals

Preparation of crystal

The crystal was made from pure silver obtained from the U. S. Mint. The original crystal was 3/4 in. in diameter and 7 in. long with the lower end tapering to a point. It was made by the same method as that used for the copper crystal. The crystalline structure is face-centered cubic, the same as copper, with a lattice constant of 4.079A. The dimensions and mounting of the single crystal pieces used in the experimental tube are the same as for the

experiments with copper. Three different pieces of single crystal have been cut and prepared for the experimental investigation. The surface to be studied was in every case cut parallel to a (100) set of planes, but one of the crystals was mounted so that it could be rotated about an axis perpendicular to the (100) azimuth while the other two rotated about an axis perpendicular to the (111) azimuth. Two crystals of the latter type were tested as a check to eliminate the possibility of a faulty crystal and to make sure that the results obtained are really characteristic of silver. Complete observations were taken with only two of them. I am indebted to Dr. B. E. Warren of the Massachusetts Institute of Technology for making an x-ray examination of one of the silver crystals. The crystal was found to have a mosaic dispersion of not more than 1°, and the geometric boundary was found to be parallel to the (100) set of planes to within less than 0.5°. Dilute nitric acid develops the various facets of the crystal which are easily detected by reflected light. In addition to (100) and (111) facets (which are the only strong ones found for copper), (110) facets are almost equally brilliant in reflected light. Etching in strong nitric acid was found to be most suitable for the final preparation of the (100) surface. By using about 55 percent by volume of acid in distilled water, a very smooth mirror-like (100) surface was obtained with no visible reflection from any other planes. Under these conditions the etching is very rapid and only a very short time (a few minutes or less) is required to produce the desired result. The conditions are also very critical. If the solution is slightly too strong, the surface is left very rough and irregular; if it is too weak etching occurs parallel to other planes as well as the plane in question. This method of etching can apparently be applied to planes other than the (100); the necessary condition is that the geometric boundary must be very nearly parallel to the plane in question. Smooth (110) faces were obtained in this way on the sides of one of the crystals.

Silver recrystallizes much more readily than copper under red-heat treatment and consequently it is essential to clamp and bombard the crystal at some distance from the face to be used. In the first trial a silver crystal was mounted at the rear as described above, placed in a preliminary tube, and heated at a dull red heat for eight hours. At the end of this time recrystallization had occurred throughout the whole crystal with the exception of the front end for a distance of about 2 mm. On the other hand it is much easier to outgas silver than copper sufficiently for the present experiments. After giving one of the silver crystals a red-heat treatment of only 10 min. (subsequent to the usual baking of the whole tube), the diffraction beams from the surface gas layer were extremely weak, and the beams characteristic of silver were more intense and sharp than those obtained from a copper crystal after 43 hours of outgassing. The sharpness of the diffraction beams appears to be determined to a greater extent by the etching of the surface than by complete freedom from gas. For example, the diffraction beams from the crystal which had received 8 hours of red-heat treatment were both weaker and broader in colatitude angle than those of another crystal which had received only 10 min. of red-heat treatment. The first crystal had been etched in dilute nitric

acid so that the smooth mirror-like surface was *not* obtained as in the case of the second crystal.

Number of diffraction beams

The curves in the upper part of Fig. 6 show the various beams in the 1st order of the (111) azimuth below 160 volts for normal incidence. These were obtained by the same method as that used for the curves at the right in Fig. 2. The arrows along the voltage axis indicate the positions of theoretical beams. The number of experimental peaks is seen to be much greater than the three theoretical beams in this voltage range. Further, the beams cannot be classi-

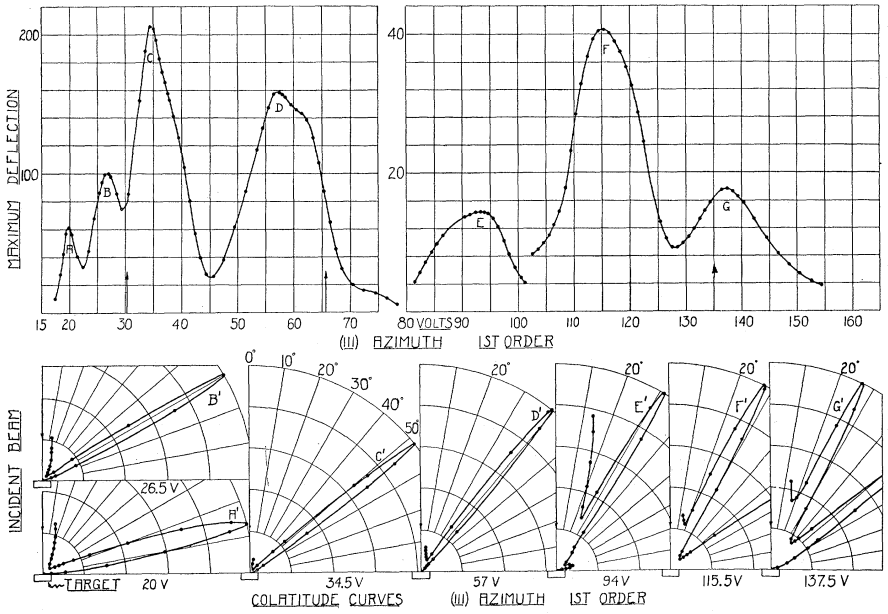

Fig. 6. Curves showing diffraction beams for silver in the 1st order, (111) azimuth below 160 volts for approximately normal incidence. Colatitude curves correspond to maxima in the upper curves which have the same letters.

fied as main diffraction beams requiring a refractive index greater than unity accompanied by weak satellites requiring a refractive index of unity, as was the case for many of the beams for copper. There are three well defined components, with indication of a fourth at 40 volts, in the region of the first theoretical beam at 30 volts; two components in the region of the second theoretical beam; and three components in the region of the third. The colatitude curves at the lower part of Fig. 6 indicate the sharpness of the beams in colatitude and the small amount of background scattering. None of these beams is due to a gas lattice since the half-order gas beams were very weak compared to any of the first order beams shown above.

Table II shows the positions and relative intensities of the diffraction beams for normal incidence. When several experimental components correspond to a single theoretical beam, only the most intense experimental com-

ponent is given in the table. The other components may be obtained from curves to be described below. The *uncorrected* values of intensity are given so that comparison may be made with the curves in Figs. 9 and 10 below. Values of background intensity for normal incidence were not obtained for all of the beams. In general, the ratio of beam intensity to background intensity is much greater for silver than for copper.

TABLE II. *Main* diffraction beams for the silver lattice; normal incidence.*

Beam and order numbers	Plane of reflection	Experimental voltage	Theoretical voltage $V=150/\lambda^2$	Voltage difference	Corrected intensity / Background intensity	Uncorrected approximate relative intensity
			(100) Azimuth			
1–1	(210)	46.1	56.3	10.2	300	100
2–1	(310)	93.5	100.2	6.7	1.7	5
3–1	(410)	141.0	162.8	21.8	7.8	21
4–1	(510)	229.5	243.8	14.3	3.3	7
5–1	(610)	335.5	343.0	7.5		6
1–2	(320)	152.5	169.3	16.8		4
2–2	2(210)	206.5	225.4	18.9		19
3–2	(520)	280.5	303.3	22.8		7
			(111) Azimuth			
1–1	(311)	34.0	30.3	−3.7	150	70
2–1	(511)	56.0	65.7	9.7	75	78
3–1	(711)	115.0	119.6	4.6	8	16
4–1	(911)	168.3	191.7	23.4		4
1–2	(211)	77.5	81.1	3.6	36	9
2–2	2(311)	112.5	121.2	8.7	36	16
3–2	(411)	158.5	182.6	24.1	36	9
4–2	2(511)	250.5	262.9	12.4		9
2–3	(733)	192.5	206.5	14.0	30	6
3–3	3(311)	252.5	272.7	20.2		7

* Only the values for the most intense component of each beam are given. See note below Table I for notation.

Gas beams for silver

Only a few very weak beams due to a surface gas lattice were found below 50 volts. They fall on the one-half order lines in both the (100) and (111) azimuths so as to indicate a double-spaced, face-centered, structure. Because of their extreme weakness compared to the other beams (less than 2 percent of the most intense beam), their influence must be negligible.

Intensity measurements as a function of angle of incidence

Because of the many irregularities in the diffraction beams, no curves of the type of those at the right in Fig. 4 were obtained. A more complete record is obtained by curves similar to those at the left in Fig. 4 or those in Fig. 6 for various angles of incidence. The curves in Figs. 7 and 8 show some of the changes which occur for beams in the (100) azimuth with changes in angle of incidence. These curves all illustrate the fact that any particular diffraction beam consists of several components whose relative intensities change rapidly with change in angle of incidence. The curves in Fig. 8 show the changes which occur in a single diffraction beam over a considerable range in

angle of incidence. Starting at the upper left and proceeding from top to bottom in each successive column we trace the changes which occur as the angle

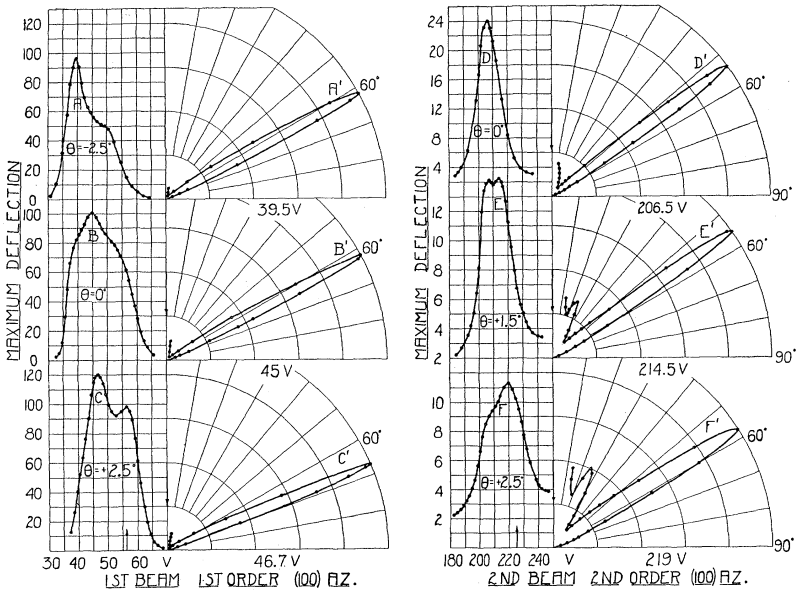

Fig. 7. Curves showing effects of changes in the angle of incidence. (The values of θ for the curves of the 1st beam—1st order should be corrected by subtracting 0.5° from each of the values given.)

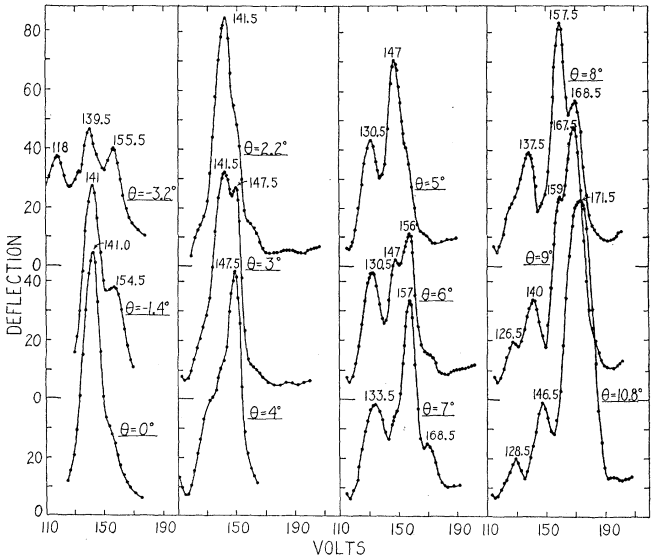

Fig. 8. Curves for the 3rd beam, 1st order, (100) azimuth for several angles of incidence. Corrected voltages for the various maxima are given on the curves.

of incidence is varied from negative values to positive values. In some cases components appear on the high voltage side and increase in intensity while

those on the low voltage side disappear. This, however, is not a general rule. It is a striking feature that for many of the components the voltage corresponding to the peak deflection remains practically constant over the whole range of angles θ at which the component is observable. This means, of course, that for each of these components the associated wave-length is independent of the angle of incidence within certain limits. Since, however, the *plane* grating formula *is satisfied* over a considerable range in the angle of incidence, (see also next section) it is evident that for this case the colatitude angle of the beam does not change by twice the change in the angle of incidence, but by an amount such as to keep the wave-length of the maximum constant. This is clearly not in accord with the simple theory according to which one

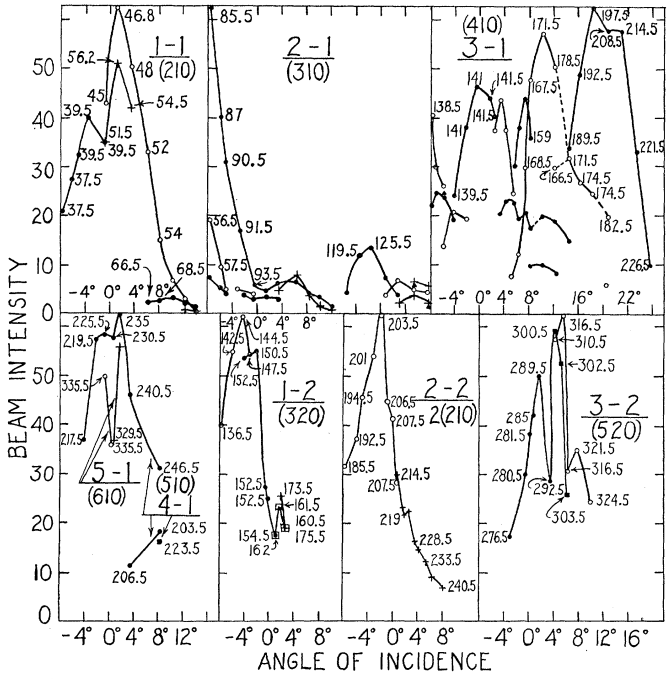

Fig. 9. Curves showing relative intensities of beam components as a function of angle of incidence for the (100) azimuth (uncorrected for background scattering). Plane of reflection is in the (100) azimuth. Designation of beam 3–2 signifies third beam in the second order as per notation in Table I. Values of corrected voltages are given for several of the points.

should expect only one component for each angle of incidence, with the maximum shifting in voltage, as θ is changed, so as to satisfy the Bragg reflection formula; and also the condition that the change in the colatitude angle of the beam shall be twice the change in the angle of incidence.

Observations similar to those of Fig. 8 have been obtained for most of the diffraction beams in the (100) and (111) azimuths in the voltage range below 350 volts and for angles of incidence in the range from $-10°$ to $+25°$ at which the beams have a measurable intensity. In order to indicate the variations in intensity of the large number of beams, each having several com-

ponents, the results have been plotted as in Figs. 9 and 10. Each of the plotted points of these curves represents a peak in the type of curves shown in Fig. 8, that is, any one of the curves in Figs. 9 and 10 shows the variation of intensity of a particular component of a diffraction beam as a function of the angle of incidence of the primary beam. Corresponding to each plotted point there is a particular colatitude angle and primary voltage, the values of which are given in Figs. 9 and 10 for some of the points. In case two components of the same beam have equal intensities at the same angle of incidence, even though their optimum voltages are different, their points on the plots of Figs. 9 and 10 will coincide. Referring, for example, to the first beam in the first order of

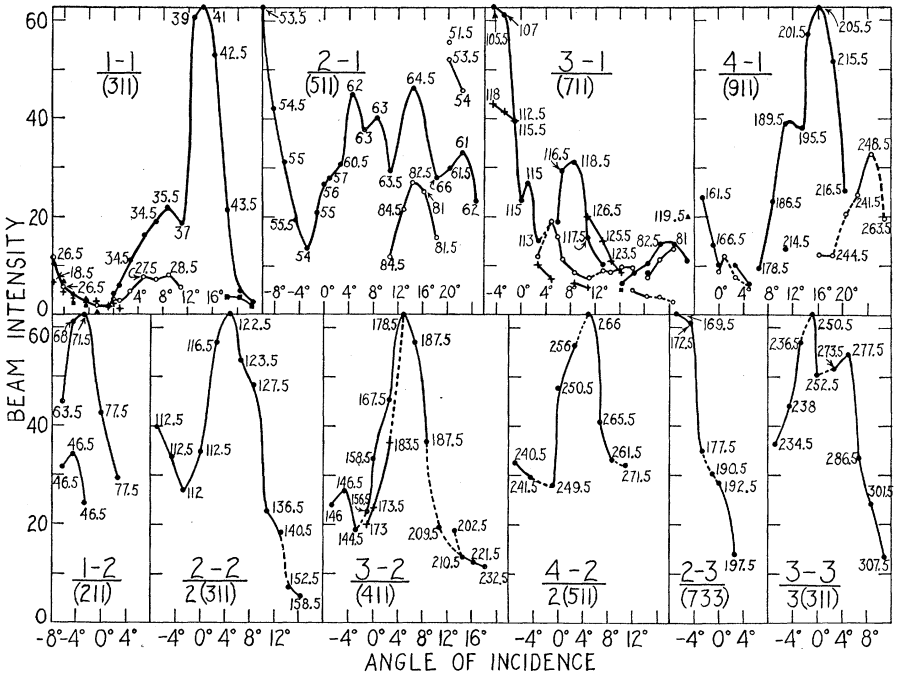

Fig. 10. Curves showing relative intensities of beam components as a function of angle of incidence for the (111) azimuth (uncorrected for background scattering). Plane of reflection is in the (111) azimuth. Notation is the same as in Fig. 9.

the (100) azimuth, Fig. 9, we see that for $\theta = -8°$ there is only one component of this beam. As θ becomes more nearly zero, the intensity of this component increases and then decreases and is not observed for positive angles of incidence. At $\theta = -0.5°$ there are two components of equal intensity and one of greater intensity, all of which appear at different voltages (see curve B of Fig. 7). As θ is increased, two of these components increase in intensity and then decrease, one of them continuing to $\theta = 14°$. Two weaker components also appear at the larger angles of incidence.

The curves in Figs. 9 and 10 have not been corrected for background scattering or for the overlapping of different components in the voltage range. The latter condition probably introduces considerable change in the rela-

tive intensities but corrections are uncertain and since the changes of intensities of the various components are so great, the general features of the curves in Figs. 9 and 10 are not seriously affected by the above uncertainties. Although great accuracy is not claimed for the exact shape of the curves for the weaker components of any one beam, their number indicates the complexity of the phenomenon. In some cases there is uncertainty as to the course of a curve between plotted points. In these cases the most probable course is indicated by a dotted line. This uncertainty is due partly to the fact that more experimental observations are needed in these regions and partly to the lack of resolution of the components in question. In some cases two components appear to merge into one.

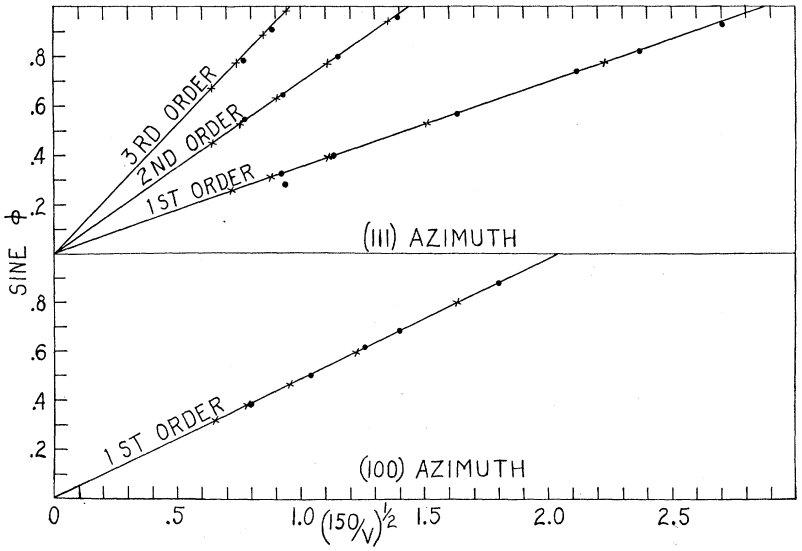

Fig. 11. Plot of sin ϕ against $\lambda=(150/V)^{\frac{1}{2}}$, ϕ = colatitude angle for normal incidence. Solid circles denote experimental maxima. Crosses denote theoretical beams.

The intensities of the components of one beam are not to be compared with those of another beam directly from the plots in Figs. 9 and 10 since the maximum points of the various beams have obviously been made the same. However, a comparison may be made with the use of Table II which gives the approximate relative intensities of the *most intense* components of the various diffraction beams for normal incidence of the primary beam. The relative intensities change somewhat with the vacuum conditions so that they must be considered as approximate. Although each beam is characterized by very great and unique intensity changes with change in angle of incidence, special comment may be made about the 2nd beam of the 1st order in the (100) azimuth. At normal incidence the intensities of the components of this beam are so weak as to be scarcely observable, while for $\theta=-8°$ the intensity of one component is at least one-half of the maximum value which the 1st beam ever attains.

Test of plane grating formula

Fig. 11 shows a plot of sin ϕ against $\lambda = (150/V)^{1/2}$ for normal incidence. The solid lines were plotted from the plane-grating formula using a grating spacing a = 4.079A taken from International Critical Tables. The solid circles were obtained from the experimental values corresponding to the different components of the electron diffraction beams. The crosses represent positions of theoretical beams. The fact that the points lie so closely on the lines furnishes an excellent check of the plane-grating formula and at the same time shows that the angle of incidence is zero within the error of measurement.* The 3rd order beams are slightly displaced due to the fact that they emerge from the crystal at large colatitude angles. These observations were obtained for the third silver crystal after improvements in apparatus had been made. For angles of incidence other than zero the plane grating formula $\lambda = D/n$ (sin θ_2-sin θ_1) is found to apply approximately to the various beam components over certain ranges of the incident angle, but for other ranges the formula fails to hold. In general, it appears that the formula does not hold for incident angles which differ from zero by more than several degrees or for beams whose intensities are very weak for the incident angle in question, although there are exceptions to this statement. Table III shows values for two typical beams selected at random. The calculated values of θ_2 were obtained by solving the above plane grating formula for θ_2, in which $\lambda = (150/V)^{1/2}$. It is seen that the observed and calculated values of θ_2 are in fair agreement except in the case of the 2nd beam for angles of incidence greater than about 5°, where the two values differ by as much as 5 or 6 degrees. Referring to Fig. 10, we see that this beam is most intense for $\theta = 5°$.

TABLE III. *Test of plane grating formula.*

V in volts observed	θ_1 observed	θ_2 observed	θ_2 calculated	V in volts observed	θ_1 observed	θ_2 observed	θ_2 calculated
	1st beam, 1st order, (100) Azimuth				*2nd beam, 2nd order, (111) Azimuth*		
37.5	−7.7°	58.7°	57.8°	112.5	− 6.2°	43.2°	43.8°
37.5	−5.8°	60.8°	61.6°	112.5	− 4.4°	45.4°	46.3°
39.5	−5.0°	61.0°	60.3°	112.0	− 2.6°	48.1°	49.2°
39.5	−3.0°	64.5°	64.6°	112.5	0°	53.0°	53.1°
45.0	−0.5°	62.0°	62.4°	116.5	+ 2.8°	55.7°	56.7°
46.8	+1.7°	65.7°	65.4°	122.5	+ 5.0°	56.5°	58.9°
56.2	+1.7°	57.1°	56.2°	123.5	+ 6.8°	59.7°	62.1°
48.0	+3.5°	69.3°	68.1°	127.5	+ 8.8°	61.7°	65.0°
54.5	+3.5°	62.0°	61.0°	136.5	+10.9°	62.6°	66.5°
52	+6.4°	69.7°	70.8°	140.5	+13.0°	64.5°	70.2°
66.5	+6.4°	59.4°	57.9°	152.5	+14.6°	66.9°	70.5°
54.0	+8.3°	73.6°	73.9°	158.5	+16.4°	68.6°	73.3°
68.5	+8.3°	61.7°	60.4°				

* It may be noted that there are 2 experimental components to be associated with the 4th beam in the 1st order of the (111) azimuth. One of these components falls exactly on the line but the other does not. For an angle of incidence $\theta = -1°$, only the component which *does not* fall on the line is present, while for $\theta = +1°$, only the component which *does* fall on the line is present. (See Fig. 10).

Regular reflection from the (100) set of planes

Figs. 12 and 13 show curves for silver which were obtained by the same method as that used to obtain similar curves for copper. The two curves in Fig. 12 were both obtained for the same angle of incidence of 8.5° but for the upper one the plane of reflection contains the (100) azimuth while for the lower one the plane of reflection contains the (111) azimuth. In Fig. 13 are shown two corresponding curves each for 20° angle of incidence and a third for 40° angle of incidence in the (100) azimuth. Many other curves were obtained for other angles of incidence between 7° and 40°. From an inspection of the curves it appears that for the same angle of incidence the results for the (100) and (111) azimuths are quite different, but the difference appears to be greater for the larger angles of incidence than for the smaller ones. The

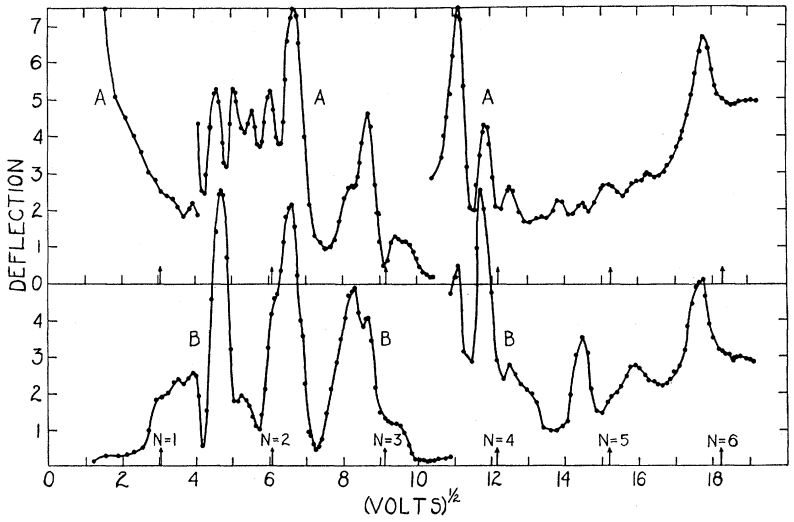

Fig. 12. Regular reflection from the (100) set of planes. Both curves are for angle of incidence 8.5°. For curve *A* the plane of reflection is in the (100) azimuth. For curve *B* the plane of reflection is in the (111) azimuth. Arrows indicate positions of theoretical beams for different orders, assuming unit refractive index. Discontinuities in the curves indicate changes in the scale of plotting.

results in a particular azimuth also appear to be more complicated for the larger angles of incidence than for the smaller ones. Several of the curves have been checked to establish the reality of the numerous maxima and minima. For example, the upper curve in Fig. 13 was obtained at two times differing by about one month and after different previous heat treatments of the crystal. The two curves were, however, exactly alike in all details except for very slight changes in relative intensities of some of the peaks. Although the angles of reflection at which the beams attain maximum intensity are, in general, equal to the corresponding angles of incidence, within experimental error, several cases have been noted for which the deviations from the expected values (3° in some cases) for certain beams are too large to be attributed to experimental error. These deviations have not been investigated in detail, but

they are probably to be associated with the deviations from the plane grating formula mentioned in the previous section.

Discussion of the Results

A comparison of the results for copper with those for silver

For normal incidence the deviations from the predictions of simple theory are more noticeable in the results for a silver crystal than in those for a copper crystal. Referring to the relative intensities of the corresponding beams in Tables I and II, we see that those for silver vary through wider ranges and appear more unsystematic than those for copper. The number of experimental components to be associated with a single theoretical beam is in general also greater for silver than for copper.

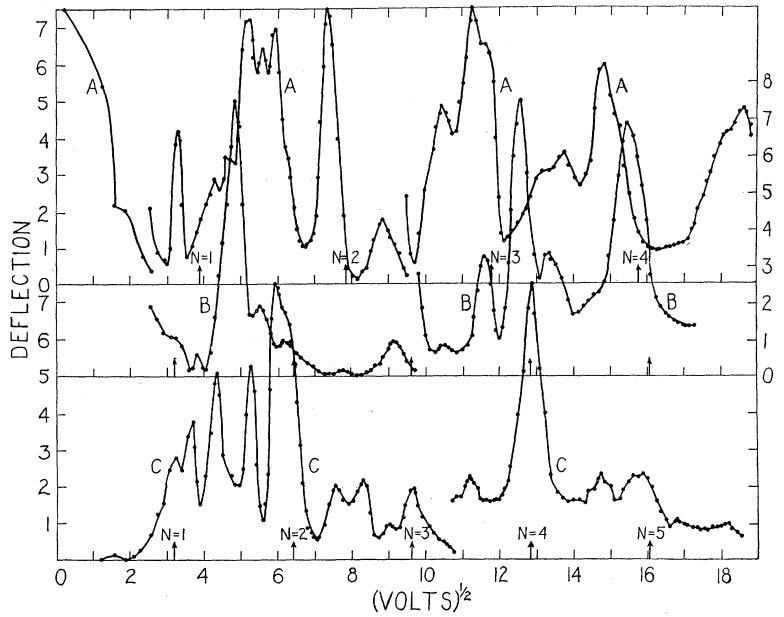

Fig. 13. Regular reflection from the (100) set of planes. Curves A and B are for angles of incidence of 40° and 20°, respectively, with the plane of reflection in the (100) azimuth. Curve C is for angle of incidence 20° with the plane of reflection in the (111) azimuth. Other notation is the same as for Fig. 12.

Although a detailed comparison of the variations of intensities of the main diffraction beams due to changes in angle of incidence for silver with those for copper cannot be made at present because of insufficient observations for the copper crystal, a qualitative comparison for certain corresponding beams is possible. Referring to Fig. 4c we note the variations of the 1st, 2nd, and 3rd main beams in the 1st order (111) azimuth for copper as given by the curves A, B, and C, respectively. Comparing these with the corresponding curves, 1–1, 2–1, 3–1 in Fig. 10 for the strongest components of the same beams for silver, we observe no particular correspondence. For regular reflec-

tion from the (100) face at angles of incidence other than normal under similar conditions the results for the two crystals do not correspond.

It is thus clear that although there are deviations from the simple theory in the case of both crystals, these deviations are widely different for the two crystals. Since both crystals have the same lattice structure and since the surface of the crystal was in each case parallel to the (100) face, it would seem that the difference must be due to differences in conditions brought about by the two different kinds of atoms.*

Inner potential and refractive index

From my first experiments with a copper crystal,[8] it appeared that the inner potential could be represented by a smooth curve which approaches a constant value for the higher primary voltages, but which decreases with decreasing primary voltage below about 150 volts. Although some of the experimental points deviated considerably from this line, the differences were attributed to experimental error. The results for copper and silver reported here show that the concept of a constant inner potential or even of one that varies smoothly in the manner indicated above is not in accord with the results obtained by such experiments on electron diffraction. One need only consider curves such as shown in Figs. 7 and 8. If the voltage corresponding to the maximum of a diffraction beam is obtained for normal incidence, the inner potential is given at once by the difference between this voltage and that of the corresponding theoretical beam. If now the angle of incidence is changed only a small amount, the beam maximum may occur at a voltage differing by several volts from the first value, while the change in angle is too small to appreciably change the corresponding theoretical voltage. As a result, the inner potential as determined from the second observation will differ widely from that of the first. Hence a small change in the angle of incidence results in a greatly different measured value of the inner potential.

The fact that the results for the case of regular reflection depend on the azimuth of the crystal which lies in the plane of reflection, as shown in Fig. 12, clearly indicates that the usual concept of a refractive index does not apply in this case, for the distance between adjacent reflecting planes is the same in the two cases.

Intensities of diffraction beams

The extraordinary dependence of the intensities of the diffraction beams on the angle of incidence of the primary beam leads one to make a comparison with x-ray measurements. It is well known that the intensities of x-ray reflections are interpreted in terms of the electron distribution in the atoms. Measurements with x-rays indicate spherical symmetry of the individual atoms in the crystal lattice, but, as recently emphasized by James and Brind-

* The only other difference is that of the lattice constant. This, of course, causes the diffraction beams to appear at different electron speeds or equivalent wave-lengths, the influence of which on the present results is not exactly known. This uncertainty can be eliminated by comparing observations on silver and gold, which have practically the same lattice constant.

ley,[18] the scattering of x-rays "at any appreciable angle is due mainly to the inner electrons of the atoms, for which the departure from spherical symmetry due to the packing of the atoms in the crystal is small, and the scattering powers of atoms in simple crystals in general depend only on the angle through which the radiation has been scattered, and not on the direction in which it has passed through the crystal." They further emphasize that "in any real crystal structure, the arrangement of the outer electrons of the atoms must be to some extent distorted from spherical symmetry, and this procedure of assigning a definite scattering power to each atom, and assuming it to remain the same for a given type of atom from crystal to crystal, can only be an approximation."

In the results reported here one might expect a similarity to exist between the characteristics of the diffraction beams corresponding to different orders of reflection from the *same set* of atomic planes.* An examination of the results given above shows four such cases for consideration. The curves 1–1 and 2–2 in Fig. 9 correspond to 1st and 2nd order reflection from the (210) set of planes. Similarly the curves 2–2, 4–2, and 3–3 in Fig. 10 correspond to 2nd order reflections from (311) and (511) planes and 3rd order reflection from (311) planes, respectively. It cannot be said that the curves for different order reflections from the same set of planes correspond in any of these cases. However, it should be emphasized that these different order reflections correspond to considerably different primary voltages so that if the effect in question is a function of the associated wave-length of the incident electrons as well as the direction, we are here unable to separate the two.

Mark and Wierl[19] have already determined the atom form factors for Al, Ag, and Au in the polycrystalline state with the use of high-speed electrons, and have shown that the atom form factor F^* as determined with high-speed electrons is related to the F determined with x-rays by the relation $F^* = (Z-F)/\sin^2\theta$ (Z = atomic number, 2θ = the scattering angle) as is to be expected from a consideration of the different conditions which govern the scattering of x-rays and electrons. Comparison is made with the x-ray F curve for aluminum obtained by James, Bridley and Wood[20] which is in good accord with the theoretical one obtained from the charge distribution determined by the method of Hartree. The above method cannot be used with very low-speed electrons, and uncertainties would arise in attempting to use single crystals since values of extinction and absorption coefficients are required for the crystal in question, and these would be difficult to determine for low-speed electrons.

During discussions of these experiments with various physicists the following questions have been raised. (1) Can the components of fine structure be accounted for by a mosaic structure of the crystal? If one considers two or more sets of lattices making small angles with one another, then, of course,

[18] R. W. James and G. W. Brindley, Phil. Mag. **12,** 81 (1931).

* I am indebted to Dr. J. C. Slater for this suggestion.

[19] H. Mark and R. Wierl, Die Naturwiss **18,** 778 (1930); Zeits. f. Physik **60,** 741 (1930).

[20] R. W. James, G. W. Brindley and R. G. Wood, Proc. Roy. Soc. **125A,** 401 (1929).

the conditions for constructive interference for the different lattices would require different wave lengths for a given primary beam which would result in an apparent fine structure. However, an examination of observations over the ranges of variables used shows that such an hypothesis is insufficient. Furthermore this possibility is excluded by the fact that the results have been checked for more than one specimen of a particular crystal. (2) Can the components be a type of secondary maxima such as are observed in the optical case with a grating having a small number of rulings? Although there appears to be a similarity in the two cases, an examination shows that there is no close correspondence. It is difficult to see how the relative intensity changes may be accounted for on this view. Also, the secondary maxima are decreased in intensity as the number of lines in the grating is increased. A consideration of the sharpness in colatitude angle for the beams from copper and silver crystals indicates that the number of rows of atoms in the elementary crystal gratings is greater in the case of silver, while the components of fine structure are also more pronounced for silver.

Surface action

Before considering further a possible interpretation of these results on diffraction of low-speed electrons it is essential to determine the influence of the surface action due to the gradual transition of the field across the boundary of the crystal as considered by v. Laue.[14] Is it possible, for example, that the observations in question are due entirely to this surface action, or are they fundamentally characteristic of a space-lattice with perhaps a minor alteration resulting from the surface action? As already mentioned, v. Laue's own deductions lead to the conclusion that this surface influence may be neglected for electrons having energies greater than 200 volts. The desirability of obtaining experimental evidence on this point is immediately apparent. Fortunately there appear to be several methods of approach to this problem. (1) A comparison of the results for primary electron energies above and below 200 volts. This shows that although the results in the lower voltage region are in general more complicated in regard to the number of components of a particular beam, the general characteristics of this fine structure together with the great dependence of intensity on angle of incidence is certainly present at the highest energies studied at 325 volts. An extension to still higher energies is desirable. (2) A comparison of the results obtained when different thicknesses of the surface gas lattice are present. It has been shown that for a (100) surface of a copper crystal, the gas forms in either a single-spaced, simple-cubic or a doubled-spaced, face-centered structure, depending on the thickness of the gas layer. We have here a transition, not from a copper lattice to vacuum, but from a copper lattice to a gas lattice. The characteristic beams for the copper lattice can then be influenced only by *inter-surface* action which may arise from the transition from a copper to a gas lattice, and only the beams due to the gas lattice can be affected by a pure surface action. The first of these should certainly be expected to change when the gas layer becomes thinner and shifts from one to the other of its characteristic structures.

No evidence of a change in the characteristics of the beams for a copper lattice have been observed when the above change occurs. This point must, however, be investigated in more detail. From intensity measurements it appears that the thicker gas lattice on a copper crystal must in some cases be at least several atoms deep, even when a strong diffraction beam for the copper lattice at 26.5 volts can be observed. Hence, these low-speed electrons must pass through *several layers* of gas atoms without excessive absorption. (3) Comparison of results obtained when atoms of one metal are deposited by evaporation on a single crystal of another metal. From our information about surface gas lattices it would appear that a surface metal lattice could be formed. The characteristics of the underlying metal could then be influenced by only an *inter-surface* action arising from the transition from one metal to another. This presumably should be less than that due to a metal-gas junction. (4) Investigation of a silver crystal with the surface parallel to a (110) set of planes. With this arrangement diffraction beams can be obtained which correspond to Bragg reflection from one set of planes that is the same as for the case where the crystal surface is parallel to a (100) set of planes, the difference being that the incident and emergent beams of electrons pass through a (110) boundary plane in one case and a (100) boundary plane in the other. Any difference must then be due to the influence of the boundary plane. A silver crystal is suitable since (110) etched planes can be obtained.

The available evidence at the present time thus indicates that the results are characteristic of a space lattice and that the surface action is at most a relatively minor consideration.

In addition to the experiments suggested above it appears desirable to obtain results for a gold crystal since the lattice constants of gold and silver are so nearly the same. Hence the positions of the theoretical beams are almost identical so that possible differences due to different electron energies of corresponding beams are eliminated, and any differences must result from the different types of atoms.

Experiments with a gold crystal are now well under way, and the suggested experiments on surface action are to be carried out in the immediate future.

The recent tendency in the field of electron diffraction seems to be to avoid experiments with low-speed electrons because of undesirable surface effects and other characteristics not easily accounted for. However, it would seem that a more thorough investigation of these phenomena should lead to significant contributions to our understanding of the metallic state.

I am indebted to friends of the University for continued support of these experiments. Messrs. Newton Underwood, F. E. White, and K. R. Page have greatly aided at different times during the course of the work, and Mr. Morgan Williams assumed responsibility in the production of the single metal crystals.