An Application of Electron Diffraction to the Study of Gas Adsorption

By L. H. GERMER [1]

Under appropriate experimental conditions, electron scattering by a single crystal of nickel can give rise to diffraction patterns of four quite distinct types. We attribute one of these patterns to the space lattice of the nickel crystal, one to the topmost layer of nickel atoms, one to a monatomic layer of adsorbed gas atoms, and one to a thick layer of gas atoms. From these phenomena some conclusions concerning gas adsorption have been drawn. We have at hand a new and important method of crystal analysis.

IN the paper by Dr. C. J. Davisson and myself entitled "Diffraction of Electrons by a Crystal of Nickel," [2] we published a variety of information concerning the gaseous contamination of the surface of our diffracting crystal. This information was obtained from a study of the modifications produced by adsorbed gas in the electron diffraction pattern. We have subsequently succeeded in obtaining some additional facts concerning adsorbed gas from a further study of our original data. Along with the presentation of these new facts, I am taking this opportunity to publish in greater detail the data upon which our original conclusions were based.

In our Physical Review paper we showed that the interaction of a beam of electrons with a single crystal of nickel gives rise to phenomena which, in their most essential characteristics, are similar to the diffraction phenomena which would be observed if the beam of electrons of adjustable speed were replaced by a beam of X-rays of adjustable wave-length. The diffraction patterns produced by electron scattering are, however, substantially more complicated than would be the corresponding X-ray diffraction pattern. We showed that electron scattering can give rise to diffraction phenomena of four quite distinct types. The diffraction patterns of two of these types arise from the nickel atoms in the crystal lattice, while the diffraction patterns of the other two types have their origins in the layer of gas adsorbed upon the surface. The relative intensities of the diffraction patterns of these four types are determined by the amount of gaseous contamination on the surface of the crystal, and also by the temperature of the surface.

The first publication of our discovery of electron diffraction was contained in a note in "Nature." [3] At the time of this first paper we had already discovered two of these types of electron diffraction, and had distinguished sharply between them. The first type, which we later

[1] Translation from "Zeitschrift für Physik," April 12, 1929, pp. 408–421.
[2] C. J. Davisson and L. H. Germer, *Phys. Rev.*, 30, 705 (1927).
[3] C. J. Davisson and L. H. Germer, *Nature*, 119, 558 (1927).

found to be predominant under all conditions, was the normal diffraction from the space lattice of the nickel crystal. The diffraction pattern of this type is analogous to a Laue X-ray pattern produced by the interaction of a beam of heterogeneous X-rays with a single crystal. The second type of diffraction pattern consisted of a curious but very simple assemblage of twelve electron diffraction beams which, at the time of their discovery, we designated "anomalous beams."

At the time of publication of the note in "Nature" the nickel crystal, with which we were experimenting, had not been heated after the bulb containing it was sealed from the pumps. Subsequently the crystal was heated many times by electron bombardment. The effect of these heatings was to destroy the diffraction pattern of the second type, made up of the so-called anomalous beams, and to intensify greatly the first type of diffraction pattern. Simultaneously patterns of two entirely new types appeared for the first time. These new diffraction patterns were comparatively short-lived. Both of them disappeared completely within a few hours after heating the crystal. After its initial increase in intensity, following such a heating, the diffraction pattern of the first type also became weaker with the passage of time, but at a rate very much less rapid than the rate at which these new patterns changed. After the lapse of some days the diffraction pattern of the second type was again found. At first the beams of this pattern could barely be detected, but they became progressively stronger as the diffraction pattern of the first type became weaker.

Experiments more or less similar to the experiment just described were performed many times. After the initial heating of the crystal the rapidity of occurrence of the changes in the diffraction patterns varied greatly, from one experiment to another. These changes occurred very slowly when the experimental conditions were such as to warrant the belief that the vacuum in the experimental tube was unusually high. The changes took place much more rapidly when the vacuum was known to be comparatively poor. We concluded that the changes in the diffraction patterns which were observed following a heat treatment of the crystal were caused by gas being gradually adsorbed upon its surface. The two new types of diffraction pattern must arise from a clean or nearly clean surface, and their complete disappearance seemed conclusive evidence that the surface had become covered by at least one layer of gas atoms.[4] The diffraction pattern of the first type was weakened only slightly at the time of their disap-

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[4] We have not obtained any information regarding the nature of the adsorbed gas. In referring to this gas the word "atom" has been used to mean either atom or molecule.

pearance, and we therefore concluded that at the time when this pattern was itself greatly weakened the surface of the crystal was covered by *many layers* of gas atoms. Furthermore, we were able to conclude that the diffraction pattern of the second type had its origin in the film of adsorbed gas, and that *many layers* of gas were necessary for its formation.

In Figs. 1–4 are exhibited polar plots of typical electron diffraction beams belonging to the diffraction pattern of the first type. The curves of these figures show the effect of gaseous contamination of the crystal

{422} REFLECTION
CONTAMINATED SURFACE
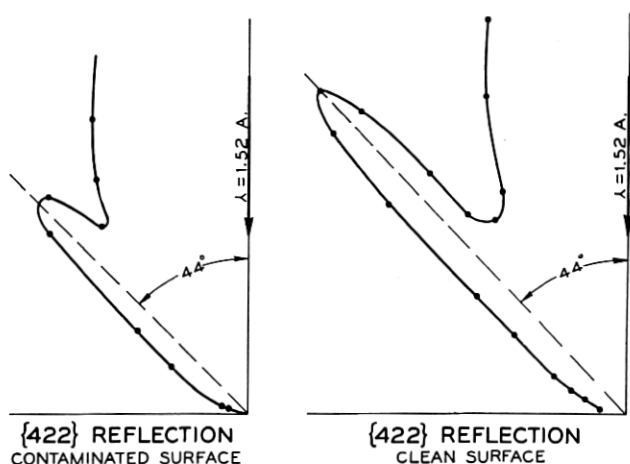
{422} REFLECTION
CLEAN SURFACE

FIG. 1—Showing the effect of the removal of surface gas upon the intensity of the electron diffraction beam whose Miller indices are (422)

surface upon the intensities of diffraction beams arising from the space lattice of the crystal. In these figures the electron diffraction beams have been designated by their Miller indices in accordance with the conventional X-ray nomenclature. Since the refractive index of nickel for electron waves differs from unity by a quite appreciable fraction, in the wave-length range of our experiments, a knowledge of the values of this index was necessary before these Miller indices could be assigned. This knowledge has been supplied by our experiments [5] on electron reflection. (Although Bethe [6] and others deduced refractive indices correctly from the data which we published in the Physical Review (loc. cit.) and assigned the correct Miller indices to the diffraction beams which we observed, these deductions seem to us to have rested upon a rather inadequate experimental basis.)

[5] C. J. Davisson and L. H. Germer, *Proc. Nat. Acad. Sci.*, 14, 619 (1928).
[6] Bethe, *Naturwissenschaften*, 16, 333 (1928).

disappearance of X-ray diffraction beams under similar conditions. In other words, the wave-length resolving power of the crystal is not so good for electron waves as for X-rays of comparable wave-lengths. This is due to the fact that the penetration of electron waves into the metal is very much less than the penetration of X-rays of the same wave-length.[7]

It is, of course, just this slight penetrating power of electron waves which made the diffraction patterns arising from our nickel crystal sensitive to the presence of adsorbed gas, and caused the extraordinary complexity in the observed phenomena. The circumstance, that electron waves are scattered very efficiently by the surface atoms of the crystal and are consequently extinguished on penetrating into the crystal at a very rapid rate, opens up to us the possibility of the use of electron diffraction as a means of studying surfaces.

The first application of this new method of surface study was the analysis (*Phys. Rev.*, loc. cit.) of the two transient diffraction patterns which existed for only a short time after the crystal surface was cleaned by heating. The first of these patterns to appear after the heating was found as soon as the crystal was comparatively cool. This pattern I shall refer to as the electron diffraction pattern of the third type. It consisted of electron beams emerging near to grazing the surface in the principal azimuths of the crystal, occurring in each azimuth just as if the surface of the crystal were a plane diffraction grating. For each diffraction beam the grating constant was equal to the separation between the rows of atoms on the surface of the crystal normal to the azimuth of the beam. Figures showing beams of this type in the principal crystal azimuths were exhibited in our original paper (loc. cit., Figs. 14–16).

The change in intensity with time of a typical beam of this third type after the crystal surface was cleaned by heating is shown by the curve marked "Type-3" in Fig. 5. (The crystal was not cool until nearly twenty minutes after the heating.) From the positions of these "plane grating" (Type-3) beams near to grazing the crystal surface and from their behavior with time after the surface was cleaned, we concluded that, when the beams of this type were most intense, the crystal surface was completely free from adsorbed gas. We concluded also that, until these beams had become quite weak, the surface was not covered by so much as a single layer of gas atoms. The condition,

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[7] The lower curves in Fig. 3 represent the data from which we calculated (*Phys. Rev.*, loc. cit.) the rate of extinction of 54 volt electrons ($\lambda = 1.67$ A.) on penetrating into the metal. A similar calculation cannot readily be made from the data of the lower curves in Fig. 4. These matters were considered in detail in our original paper and need not be discussed here.

which we recognize as a completely clean condition of the crystal surface, could be produced by a comparatively mild heating, to a temperature roughly estimated to be about 900° C. The conclusion that such a mild heating was sufficient to clean the surface completely is of interest, as it appears to be in disagreement with similar evidence concerning gas on surfaces obtained from photoelectric and thermionic measurements.

Transient electron diffraction beams of another type appeared some time after the crystal had become cool following a heating. These beams constitute what I shall call the electron diffraction pattern of the
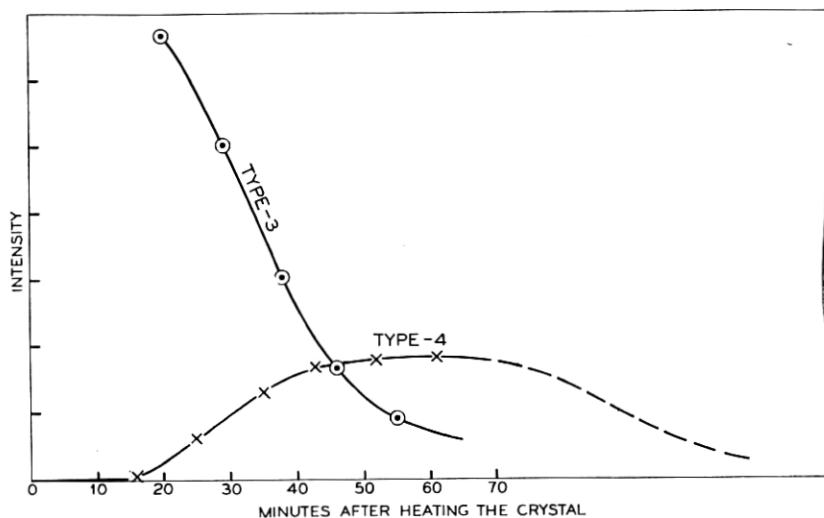

Fig. 5—Change in intensity of a typical "Type-3" beam and of a typical "Type-4" beam as gas settled upon a clean crystal surface. Measurements of the intensities of these two beams were made alternately over a period of an hour.

fourth type. They could not be detected until the diffraction pattern of the third type had become appreciably weakened, and did not attain their maximum intensities until the pattern of the third type had almost disappeared. The curve marked "Type-4" in Fig. 5 shows the life history of a typical beam of this type following a heat treatment of the crystal. In this particular experiment intensity measurements were not made after sixty-one minutes. The dashed continuation of the curve represents its general course as known from other experiments.

The two curves of Fig. 5 represent a single experiment which was carried out at a time when the vacuum condition of our experimental apparatus was intermediate between the best and the worst conditions

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which we were able to realize. Under our best vacuum conditions, the intensity changes took place more than twenty times more slowly than the changes shown in Fig. 5, and under our poorest vacuum conditions they took place so rapidly that the diffraction patterns of the third and fourth types could not be found.
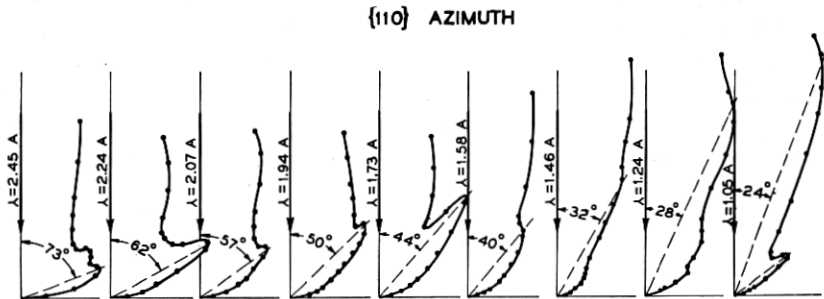
{110} AZIMUTH

FIG. 6—Scattering curves in a (110) azimuth of the crystal showing the transient electron diffraction beams of the fourth type. On each arrow indicating the primary beam is printed the wave-length of the electrons giving rise to the curve.

The entire diffraction pattern of the fourth type is exhibited by the curves of Figs. 6–8.[8] These figures show a series of electron scattering curves in each of the principal azimuths of the crystal. When these
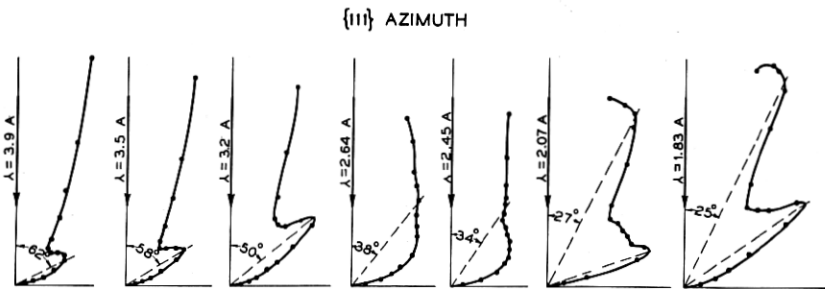
{111} AZIMUTH

FIG. 7—Scattering curves in a (111) azimuth showing electron diffraction beams of the fourth type

curves were taken, the crystal surface was in the transient gas-covered condition corresponding to the maximum of the "Type-4" curve shown in Fig. 5. The vacuum condition of the apparatus was so good at this

[8] It will be remembered that we were bombarding normally a (111) face of a nickel crystal. Each azimuth of the crystal we designated by the Miller indices of the densest plane of atoms the normal of which lies in the azimuth and in or above the surface of the crystal. Diffraction beams were found only in the three most important azimuths, the designations of which are the (111) azimuth, the (100) azimuth, and the (110) azimuth. (Other azimuths were explored without finding diffraction beams.)

time that the intensities of the beams shown in these figures remained
sensibly unchanged for several hours.

The scattering curves near the right-hand ends of these three
figures show weakened diffraction beams of the third type, which we
recognize readily. The curve second from the right in Fig. 8 shows
also a diffraction beam of the first type, a beam arising from the space
lattice of the nickel crystal. This is a (311) reflection according to
X-ray terminology. The other electron beams shown in Figs. 6–8
can be most easily considered by correlating the wave-length of each
beam with the sine of its co-latitude angle. This is the procedure
which was followed in Fig. 17 of our original paper in considering the
diffraction beams of the *first* type. (Loc. cit. Fig. 17.) Fig. 9 is
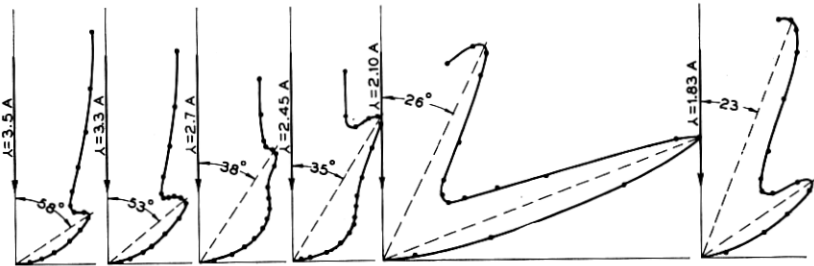
{100} AZIMUTH

FIG. 8—Electron diffraction beams of the fourth type in a (100) azimuth

similar to Fig. 17 of the original paper. The diagonal lines in Fig. 9
are the plots in the various orders of the plane grating formula $n\lambda=d$
$\sin\theta$, where in each azimuth the grating constant d is equal to the
separation between lines of nickel atoms on the surface of the crystal
normal to the azimuth. On this figure are plotted as dots all of the
originally reported diffraction beams of the first type and as crossed
circles the diffraction beams of the fourth type shown in Figs. 6–8.[9]

It is clear from Fig. 9 that the diffraction beams of the fourth type
are "plane grating" beams of "one-half order." The obvious interpre-
tation of the occurrence of such beams is that, for these beams, *the
value of the grating constant is really 2d instead of d.*

It was known from the consideration of data similar to those shown
in Fig. 5 that the diffraction pattern of the fourth type had its origin

[9] In Fig. 9 there is plotted a crossed circle for each of the separate curves shown in
Figs. 6–8. In this respect the crossed circles of Fig. 9 are not similar to the dots.
Each dot represents a diffraction beam of the first type *at its intensity maximum,*
whereas the crossed circles represent all the beams of the fourth type which were
found. The intensities of some of these were very small.

in a film of gas on the surface of the crystal, and that this film of gas was thin.   The last figures show that this gas film consisted of only a single layer of atoms, and that these atoms were arranged in a crystalline structure similar to a parallel layer of nickel atoms but separated by distances twice as great as the separations of nickel atoms (*Phys. Rev.*, loc. cit., Fig. 20).   This arrangement of gas atoms and surface nickel atoms is shown in Fig. 10.

Very interesting information was obtained by taking data similar to those represented in Fig. 5 with the crystal maintained slightly
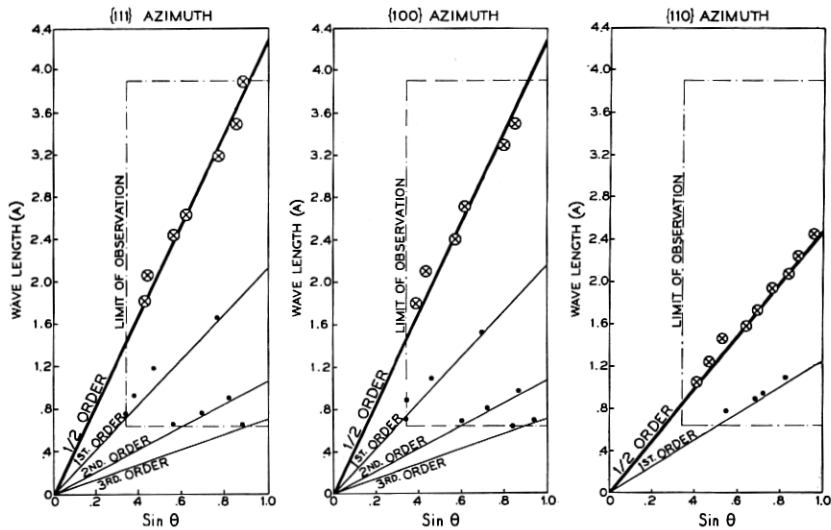

FIG. 9—Plots of the grating formulas in the principal azimuths of the crystal. Positions of electron diffraction beams of the fourth type are indicated by crossed circles and positions of beams of the first type by dots.

warm, at a temperature roughly estimated to be 150° C.   For this slightly warm crystal the life history of a typical "Type-3" beam was substantially the same as that shown in Fig. 5.   The "Type-4" beams, however, did not develop at all.   We concluded that gas atoms settled upon the crystal when warm much the same as when cold, but that upon the warm surface they were unable to take up the regular arrangement which they assumed upon the cold surface.   One is led to say that the temperature of 150° C. was above the melting point of the two dimensional "gas crystal."   It would have been comparatively easy to have found out whether or not the gas crystal melted abruptly at some critical temperature, but this information was not obtained.

One of the most striking features of Figs. 6–8 is the marked change

in intensity of the "Type-4" beams from one curve to another. In our original publication we pointed out a possible interpretation of these intensity differences. The data concerning these beams have now been more carefully studied, and it has turned out that this suggested interpretation gives quantitative results in agreement with the observations.

What we suggested was that the changes in the intensities of the "Type-4" beams were due to interference between the beams diffracted from the layer of gas atoms and the beams arising from the underlying
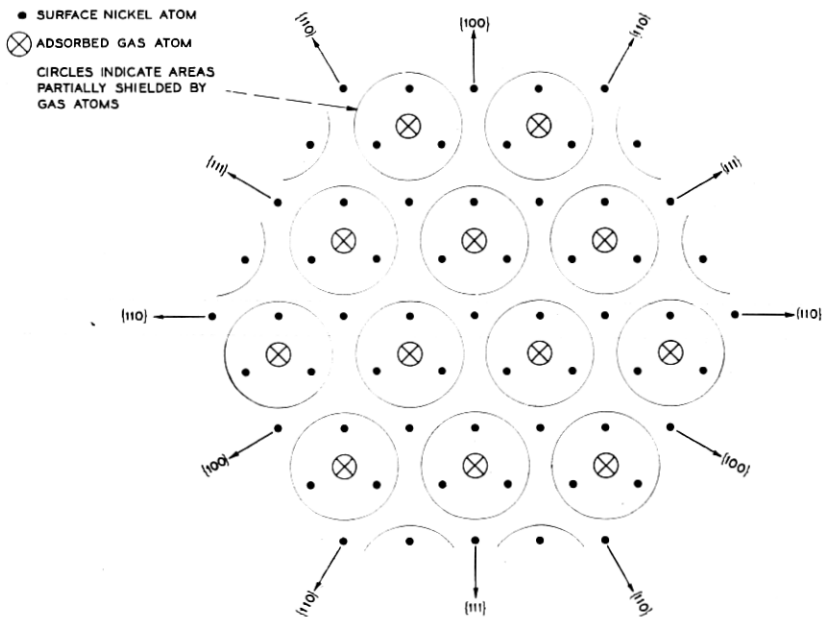

FIG. 10—The arrangement of gas atoms which gives rise to the "Type-4" diffraction beams. The designation of crystal azimuths is the one upon which the calculations of Table I are based.

nickel. That the nickel crystal can produce diffraction beams capable of interfering with the beams from the doubly-spaced layer of gas atoms arises from the fact that the gas atoms divide the surface nickel atoms into two classes. Three-fourths of the surface nickel atoms are adjacent to gas atoms and are presumably partially shielded by these atoms from the incident electron waves (Fig. 10). The other fourth of the nickel atoms on the surface, which are not so shielded, are arranged in a structure similar to that of the gas atoms and having the same scale factor. Thus it is that the surface layer of nickel atoms can give

rise to differential diffraction beams capable of interfering with the "plane grating" beams from the gas atoms.

Believing that the intensity differences of the beams in Figs. 6–8 arise in this manner, one can hope to determine from the intensities of these beams the space relation existing between the layer of gas atoms and the surface layer of nickel atoms. In carrying out the plan of making this determination one naturally assumes a certain relative spacing, and upon this assumption calculates the wave-lengths (and angles) at which the diffraction beams from the gas layer are in phase with the differential beams from the surface nickel layer.[10] These wave-lengths are then compared with the wave-lengths in Figs. 6–8 at which the "Type-4" beams are found to be strong.

Calculations of this kind have been carried out, with the gas atoms placed as shown in Fig. 10, for each of a series of assumed separations between the plane of the gas atoms and the plane of the surface nickel atoms. In comparing the results of these calculations with the observations of Figs. 6–8, the azimuths are to be taken either as shown in Fig. 10 or with the (111) and (100) azimuths interchanged. As far as the first layer of nickel atoms is concerned the (111) and (100) azimuths are identical. When one must distinguish between these azimuths (as in Fig. 10), this distinction is equivalent to a certain definite location of the gas atoms relative to the *deeper layers* of nickel atoms. It turns out that, when the centers of the gas atoms are assumed to lie in a plane separated by 3.0 A. from the plane of the centers of the surface nickel atoms and when the azimuths are chosen as shown in Fig. 10, the calculated wave-lengths of the intensity maxima of the "Type-4" beams agree pretty well with the wave-lengths at which the beams are observed to become strong. These calculated wave-lengths of the intensity maxima are given in Table I.

TABLE I

CALCULATED WAVE-LENGTHS OF THE INTENSITY MAXIMA OF "TYPE-4" BEAMS ASSUMING THE AZIMUTH DESIGNATIONS OF FIG. 10 AND A SEPARATION OF 3.0 A. BETWEEN THE PLANE OF THE GAS ATOMS AND THE PLANE OF THE SURFACE NICKEL ATOMS

(110) Azimuth (compare with Fig. 6)	(111) Azimuth (compare with Fig. 7)	(100) Azimuth (compare with Fig. 8)
2.20 A.	3.07 A.	3.53 A.
1.72	2.10	2.36
1.38	1.57	1.72
1.13		
0.96		

[10] One does not, of course, obtain in this simple manner the intensities of the diffraction beams, but one does obtain the positions and wave-lengths at which these beams reach intensity maxima.

They are to be compared directly with Figs. 6–8. Better agreement could not be expected in view of the fewness of the experimental data. For other assumed separations the calculated wave-lengths of the intensity maxima do not agree so well with the observations.

Designating azimuths as shown in Fig. 10 is tantamount to stating that the gas atoms locate themselves directly over nickel atoms of the third layer. This location appeals to one as inherently probable. The separation of 3.0 A.[11] is greater by about fifty per cent than the separation of layers of nickel atoms parallel to the surface (2.03 A.). This also seems reasonable in view of the fact that the gas atoms are separated laterally by distances twice as great as the separations of nickel atoms.

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Our analyses of the diffraction patterns of the first, third and fourth types seem to us to be fairly satisfactory. The study of the diffraction pattern of the second type has, however, turned out to be futile. This pattern consisted of twelve diffraction beams, one in each of the principal azimuths of the crystal (see Fig. 10). All these beams appeared at the same co-latitude angle of about 58° and for the electron wave-length 1.17 A. We know that this curious pattern had its origin in a heavy layer of adsorbed gas, but we have been unable to determine what were the crystalline regularities in this layer. Our present feeling is that these beams may really have reached their intensity maxima at slightly different angles and wave-lengths in the different crystal azimuths, and that perhaps there may have been other beams belonging to this pattern which we did not detect. We are inclined to believe that we shall not be able to obtain information concerning the crystalline arrangement of a heavy gas layer until further experimental data are available.

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Looking back over the information recorded here concerning gas upon a crystal surface, one should think of it as information which has been obtained by a new method of diffraction analysis. Thinking of it in this way I realize that the observations are of a rather elementary nature. The facts which we have discovered are by no means comparable in complexity with the elaborately detailed information concerning crystal structure which is so readily obtained by X-ray analysis.

Electron diffraction is, however, a new field. At the time when the

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[11] Logically this value of 3.0 A. should perhaps be changed by a few per cent to take into account a refractive index slightly different from unity.

experimental data described here were obtained, we could have learned a great deal more concerning gas upon our crystal surface with comparatively little effort.   In the above pages there are many suggested continuations which were not followed up.   When our measurements were made our interests were quite naturally centered upon the phenomenon that electrons are diffracted, and we neglected many lines of physical investigation which were open to us.   The work described here must be regarded as only the very first application of what may possibly develop into a useful method of crystal analysis, occupying a field entirely distinct from the field of X-ray analysis.