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Electron Diffraction and the Imperfection of Crystal Surfaces

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Bragg reflections are obtained by scattering fast electrons (0.05A) from the etched surfaces of metallic single crystals. The surfaces studied are a (100) face of an iron crystal, (111) face of a nickel crystal and (110) face of a tungsten crystal. In each case the reflections occur accurately at the calculated Bragg positions with no displacement due to refraction. A given reflection is found, however, even when the glancing angle of the primary beam differs considerably from the calculated Bragg value —by over 1° in some cases—so that several Bragg orders occur simultaneously. The accuracy with which this glancing angle must be adjusted is a measure of the degree of imperfection of the crystal. From the electron experiments, estimates are made of the widths at half maximum of electron rocking curves. These widths are 0.8° for the iron crystal, 1.5° for the nickel crystal and somewhat over 1° for the tungsten crystal. X-ray rocking curves for these same crystals are much narrower, although the observed widths vary considerably with the treatment of the surfaces. It is concluded that the values obtained from the electron measurements apply to projecting surface metal only, and that *the degree of misalignment is much greater at the surface than deep down within the crystal.* Furthermore, even the x-rays [Mo $K\alpha$ radiation $-$ 0.71A] are not sufficiently penetrating to yield values certainly characteristic of these metal crystals.

X-RAY reflection experiments lead to the well-known conclusion that many physical crystals are not perfect. With parallel and monochromatic radiation the reflection from a crystallographic plane of such a single crystal is of appreciable intensity only for incident angles very close to one of the Bragg angles. As the crystal is turned slightly from such a critical position the intensity of the reflection decreases rapidly, but its location remains unchanged. The apparently non-regular reflection of x-rays, when the crystal is slightly turned from a Bragg position, is attributed to crystal imperfection. Reflections of this sort are produced by regular and selective reflection from constituent parts of the crystal which are not in perfect alignment with the mean orientation. The maximum amount of the angular misalignment is measured by the angle through which the crystal can be turned without entirely destroying the reflection.

I have observed similar evidence of crystal imperfection in the reflection of electrons from metallic single crystals. Experiments have been carried out upon crystals of iron, nickel and tungsten. The imperfection which these experiments indicate are much larger than are found by x-ray methods. The electron experiments yield information concerning only the crystal surfaces, whereas, because of greater penetrating power, x-rays show the imperfection at considerable distances beneath the surfaces. *The present experiments then are interpreted to mean that the misalignment of the constituent parts of these metal crystals is much greater at the surfaces than deep down in the metal.*

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The crystals are prepared first by cutting to expose a surface parallel to an etch plane, and then by careful etching. A sharply defined beam of electrons, of wave-length of the order of 0.05A, is incident upon such a prepared surface at small glancing angle. This glancing angle can be varied by rotating the crystal about a vertical axis lying in its face. The electrons scattered from the crystal register upon a photographic plate located normal to the primary beam at a distance of 365 mm from the axis of rotation.

Fig. 1 is the photographic record obtained with an iron crystal.[1] The four photographs are taken at four different glancing angles. After each exposure a second very short exposure is made with

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[1] A figure similar to Fig. 1 was presented in July, 1932, in a paper by Dr. C. J. Davisson at the International Electrical Congress, Paris, France. This paper is reprinted, in translation, in the Bell System Technical Journal for October, 1932.

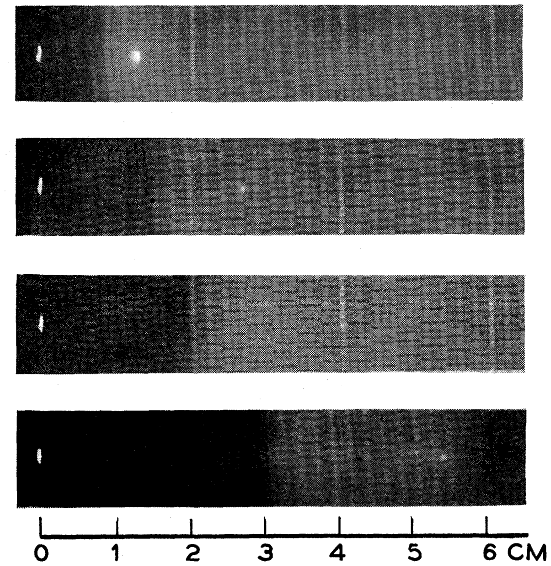

FIG. 1. Bragg reflections of 0.054A electrons from the (100) face of an iron crystal. Photographic plate located at 365 mm from the crystal.

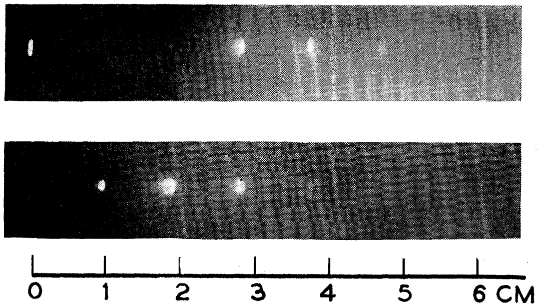

FIG. 2. Bragg reflections of 0.054A electrons from the (111) face of a stationary nickel crystal. The spots occur accurately at the calculated Bragg positions.

the crystal removed, to record the position of the primary electron beam—shown as a spot at the left of each figure. These four figures show the first four orders of Bragg reflection from planes parallel to the (100) surface plane. The reflections occur at just the positions calculated from the known spacing of (100) planes in iron and the independently determined electron wave-length, respectively 1.43A and 0.054A.

On each of these photographs the glancing angle is indicated by the edge of the darkening produced by general scattering. This edge is the intersection of the plane of the surface with the photographic plate. The glancing angle has the Bragg value when the distance from the central spot to this edge is just half the distance from the central spot to the reflection. One notes in each of the photographs that the reflection is produced when the crystal is set at just about the correct glancing angle. Thus no considerable crystal imperfection is indicated by these photographs. When, however, the crystal is set at glancing angle midway between the first and second Bragg angles, both the first and the second reflections can be seen weakly. This indicates that a small part of the surface of the crystal has an orientation differing from its mean orientation by 0.5°. If a curve were obtained similar to an x-ray rocking curve, it would have a total angular width of over 1.0°. The intensities of these first and second order spots appear to be somewhat less than half the intensities at the correct glancing angles. Thus the width of the rocking curve at half maximum is less than 1.0°. I estimate the total width at half maximum to be about 0.8°.

The two photographs of Fig. 2 were obtained from a nickel crystal at slightly different glancing angles.[2] Each of these photographs shows simultaneously four different orders of Bragg reflection from planes parallel to the (111) surface plane. This simultaneous occurrence of different orders indicates that the crystal is very imperfect. Portions of it are rotated with respect to its mean orientation by at least as much as 1.1°. If a rocking curve were obtained its total angular width would be at least 2.2°. Its width at half maximum I estimate to be about $1\frac{1}{2}$°.

The scattering of 0.059A electrons from a tungsten crystal is recorded in Fig. 3. The first three Bragg reflections from the (110) surface plane are indicated by the arrows 1, 2 and 3. By rotating the crystal to a slightly larger glancing angle, the third order becomes stronger and the

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[2] In the lower photograph of Fig. 2 the position of the primary beam was not registered. In both photographs the edge of the darkening due to general scattering is not sharply defined. This poor definition appears to be due to rounding of the crystal surface which has resulted from repeated etchings without repolishing. One is unable to determine glancing angles from observations of the edge, but one does observe that the glancing angles of these two photographs differ by about 1.4°, corresponding to 9 mm in the figure.

fourth order is found. From the general darkening edge one sees that the glancing angle is about midway between the correct angle for the first Bragg reflection and that for the second. As the third order is very weak one calculates that the total width of the rocking curve is just over 2.2°. The width at half maximum would appear to be a little over 1°.

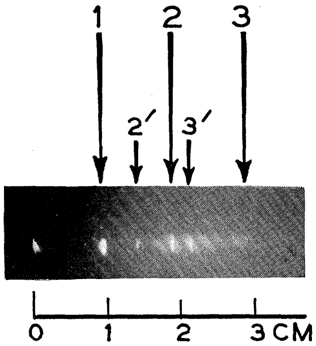

FIG. 3. Bragg reflections of 0.059A electrons from the (110) face of a tungsten crystal. Bragg reflections are also shown from a crystal of unknown composition on the surface of the tungsten. This crystal has crystallographic planes parallel to the surface separated by 3.00A.

In Fig. 3 are shown other reflections designated as 2′ and 3′, which are respectively the second and third order Bragg reflections from another single crystal. By turning the tungsten to about the right glancing angles the first and fourth orders are readily found. These four reflections correspond to crystal planes parallel to the surface separated by 3.00A. This is probably the spacing of some compound of tungsten which has been formed during or immediately after the etch treatment. The relative intensities of the tungsten reflections and these additional reflections have varied greatly after different treatments of the crystal. The latter were, however, never entirely absent.

In x-ray examinations of the iron and tungsten crystals I failed to find any evidence of imperfection. The method was crude and I could have detected, with certainty, only imperfections large enough to produce rocking curves having widths at half maximum of about a fifth of a degree (12′). More recently Mr. F. E. Haworth of these laboratories has obtained x-ray rocking curves for the three crystals used in these experiments. He has obtained 14′ as the width at half maximum for the iron crystal, 24′ for the nickel crystal, and 6′ for the tungsten crystal. In these measurements the $K\alpha$ radiation from molybdenum was used (0.71A).

More extensive measurements have since been made for the purpose of reconciling Mr. Haworth's value of 14′ for the iron crystal with the earlier conclusion that the width at half maximum was definitely less than 12′. These measurements have shown that the width of the x-ray rocking curve is determined, in part at least, by the condition of the surface of the crystal. The iron and nickel crystals were etched a number of times, and after each etch the width of the rocking curve was determined. The widths at half maximum varied considerably, and in some cases they were as large as 0.7°. All of these tests, however, show lesser degrees of imperfection than are found by the electron method. One concludes that the surfaces of the metal crystals used in these experiments are less perfectly aligned than the bodies of the crystals. Furthermore, x-rays of wave-length 0.71A are not sufficiently penetrating to yield a rocking curve which is certainly characteristic of the bulk of a metal crystal.

A possible explanation of the extremely imperfect surfaces suggests itself when one considers the fact that none of the Bragg reflections obtained with electrons shows displacement due to refraction. If the electrons which form the diffraction spots pass in and out of the metal through the same plane surface we would expect to observe considerable displacements due to this cause. For example a potential difference of any value greater than 12 volts between the outside and inside of the metal would result, in the upper photograph of Fig. 1, in a reflected beam which would not emerge above the mean plane of the surface and could not register on the photographic plate. (This calculation is based on the assumption that the gross plane of the surface is made up entirely of etch planes of the various mosaic crystals of which the block is made.) The absence of any observed displacement of the Bragg beams leads to the interpretation that the reflected beams are made up of electrons which have passed entirely through projecting metal,[3]

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[3] See G. P. Thomson, Phil. Mag. **6**, 939 (1928); Thomson, Proc. Roy. Soc. **A128**, 658 (1930).

left exposed presumably as a result of the etching process. Thus one is led to conclude that the considerable misalignment of constituent parts of the crystals, found by electron diffraction, may be limited to this projecting metal. The forces on the atoms in such projections must be unsymmetrical. Possibly such unsymmetrical forces result in twisting small mosaic crystals, which project from the surface, by as much as the observed amount, one or two degrees. In this connection it should be pointed out that the surface metal, which is found to be imperfect, lay before etching far below the crystal surface. From the x-ray observations we know that, before etching, this metal was much more perfectly aligned.

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In experiments similar to the above G. P. Thomson[4] and others have found diffraction patterns from the etched surfaces of metallic single crystals which are essentially like the cross grating *N* patterns first obtained by Kikuchi in the transmission of electrons through mica. It seems to me probable that the failure to observe complete cross grating patterns in the present experiments is due simply to the fact that a crystal was never adjusted in azimuth to put the primary electron beam along an important zone axis.

Recently Kikuchi and Nakagawa[5] have interpreted the Thomson patterns of the Kikuchi cross grating type as due to misalignment of crystals in the projecting crystallites through which the electrons pass. An essentially similar interpretation of the cross grating mica transmission patterns had already been given by W. L. Bragg.[6] Kikuchi and Kakagawa also attribute the occurrence of the surface grating patterns from natural or cleaved crystal surfaces found by Kirchner and Raether[7] to a similar slight variation in the direction of the crystal axes from one point to another on the surface. Kikuchi and Nakagawa estimate the degree of misalignment from the extent of the Thomson cross grating patterns, and from the vertical lengths of the spots in the patterns due to surface gratings. A value of about 1.5° is obtained in each case.

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The tungsten crystal used in these experiments was cut from an ingot which was given to Dr. C. J. Davisson by Dr. Irving Langmuir of the General Electric Company. The iron crystal was produced in this laboratory by Mr. P. P. Cioffi. I am also indebted to Dr. R. M. Bozorth and Mr. F. E. Haworth for advice and assistance in the x-ray measurements, and especially to Dr. Davisson for his supervision and constant interest and assistance.

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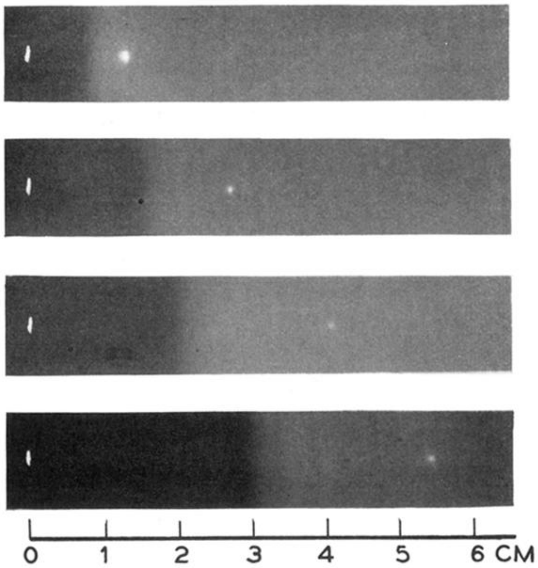
[4] Thomson, Proc. Roy. Soc. **A133**, 1 (1931).

[5] Kikuchi and Nakagawa, Sci. Papers, Inst. Phys. and Chem. Res. **21**, 80 (1933).

[6] Bragg, Nature **124**, 125 (1929).

[7] Kirchner and Raether, Phys. Zeits. **33**, 510 (1932). Raether, Zeits. f. Physik **78**, 527 (1932).



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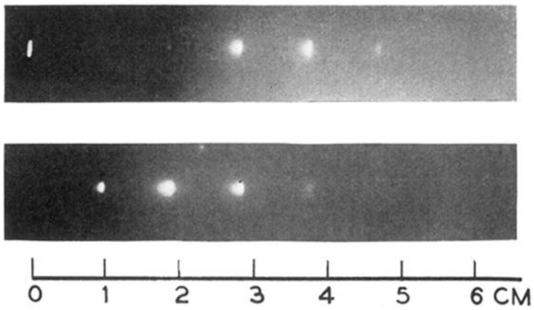

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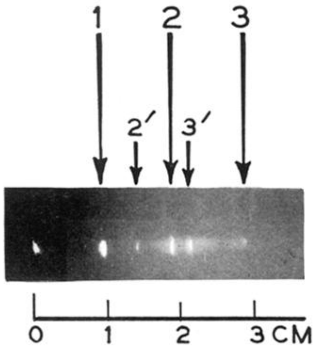

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