Electron Diffraction Experiments Upon Crystals of Galena

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Cleaved surfaces of galena crystals yield electron diffraction patterns made up of Kikuchi lines, and spots which are drawn out into streaks by refraction. After etching, the spot pattern predominates and the individual spots are sharp. The lines are then rather diffuse and ill-defined. Rocking curves upon various Bragg reflections from the surface plane prove that the imperfection of a certain crystal does not exceed about 15 minutes, and that the projections through which the electrons pass are relatively thick. Estimates of imperfection and thickness made from rocking curves are in approximate agreement with those obtained from widths of Kikuchi lines.

A galena crystal which has been filed or ground parallel to a cube face exhibits two different sorts of surfaces. There are smooth "mirror" surfaces from which large blocks of the crystal have been mechanically torn, and there are very deeply scratched portions of the surface. The "mirror" surfaces give diffraction patterns which are qualitatively similar to patterns from cleaved surfaces, although there are notable differences. From mirror surfaces produced by filing Kikuchi lines are very diffuse or are entirely missing, and diffraction spots form an extended array. The diffuseness of the lines and the extent of the array of spots correspond to great crystal imperfection, or to exceedingly thin projections. Reasons are advanced for believing in imperfection rather than extreme thinness.

The deeply scratched portions of the surface of a galena crystal give diffraction patterns which are entirely unlike patterns from cleaved surfaces. Before etching, Debye-Scherrer rings are produced. After a light or moderate etch a complex pattern appears, the nature of which is related to the angle between primary beam and direction of filing. The pattern is that of a mass of minute crystallites which have been rotated about an axis in the surface normal to the direction of filing, and in the sense determined by imaginary rollers which would be turned by slipping on the (0 1 0) plane. The magnitude of the rotation varies for different crystallites over a range from 5 to about 35 degrees. By alternate etching and examination by electron diffraction it is found that this layer of rotated crystallites extends beneath the surface to a depth of 0.003 mm.

Rotation of crystallites accompanying slip along slip planes is the mechanism reported to account for strain hardening in metals. This same rotation is observed in the present experiments on galena. It seems altogether possible that the simple technique of these experiments can be applied directly to study the disturbance in surface layers of metal crystals produced by abrasion. It may thus be a useful way of studying strain hardening in metals

GALENA crystals were chosen for examination by electron diffraction because of the simplicity of the crystal structure of galena, because the crystals are fairly good electrical conductors, and because they cleave readily. The testing of such a simple crystal as galena seemed desirable after unexplained and complex phenomena had been discovered in the investigation of less simple crystals. It was thought that experiments upon galena might aid in clarifying our views.

The simple experiments recorded here have fulfilled this purpose. At the same time they have revealed a type of strain in these crystals which is of interest in itself, and which seems to be related to the mechanism believed to account for strain hardening in metals. They suggest, in fact, a possible means of investigating slip and strain hardening.

Diffraction by Mirror Surfaces Produced on Galena Crystals by Abrasion

Galena is the mineralogical name for lead sulphide (PbS) occurring in nature as cubic crystals of the rocksalt type. These crystals cleave very easily. The cube face, {100}, is both the cleavage plane and the slip plane.

The crystals upon which the first experiments were carried out were cut to expose {100} faces. The final mechanical operation upon one of these faces was filing or grinding parallel to a cube edge, and in one direction only. After this abrasion the appearance of a crystal is similar to that shown in the photomicrograph, Fig. 1. There are frequently occurring areas from which large blocks of the mineral have been torn out to expose mirror surfaces which have the appearance of cleavage surfaces. Between these are areas which have been plowed up by the filing or grinding and are covered by very deep scratches. Electron diffraction examinations show that these two areas, which have such different appearances, differ also in other interesting ways.

By abrasion with a coarse file, it is easy to tear out a block of galena so large that a mirror

FIG. 1. Cube face of a galena crystal which has been filed from left to right, parallel to a cube edge. Magnification 90×.

surface of two or three square millimeters is exposed. A surface of this sort, after being brushed with a camel's hair brush to remove powdered galena, gave the electron diffraction pattern shown in Fig. 2. The crystal was then etched very lightly in a mixture composed of two parts HCl and one part HNO_3, then boiled vigorously in water to remove deposited lead salts, washed in absolute alcohol, and dried quickly in a stream of dry nitrogen. Following this treatment it was remounted in the camera and the diffraction pattern shown in Fig. 3 obtained from its surface.[1]

The spots of Fig. 3 constitute the diffraction pattern which one expects to observe from the surface of a galena crystal oriented, as is this crystal, with a cube edge parallel to the electron beam. The elongation of the spots of Fig. 2 is apparently due to refraction and appears because the unetched surface of the crystal is very flat, but not perfectly so.[2]

Some mirror surfaces produced by abrasion give, before etching, traces of diffuse Kikuchi lines in addition to the elongated spots of Fig. 2. *Cleaved* galena surfaces produce patterns in which the Kikuchi lines are very much stronger. Such a pattern is shown in Fig. 4. A light etch changes a cleaved surface, or a mirror surface formed by abrasion. After etching, Kikuchi lines are no longer prominent in the diffraction pattern. The pattern is then always rather similar to that of Fig. 3, although cleaved surfaces usually still show Kikuchi lines.

These experiments indicate a marked similarity between cleaved galena surfaces and mirror surfaces produced by abrasion; diffraction patterns are formed which are essentially alike, although differences exist which indicate that cleaved surfaces are more nearly perfect. Entirely different patterns are produced by those parts of an abraded surface which show the roughnesses and scratches appearing in Fig. 1. These different, and more interesting, patterns will be described in later sections of this paper. It is desirable first to give more consideration to square arrays of diffraction spots such as that shown in Fig. 3.

THE SPOT PATTERN

One cannot say from casual inspection whether the pattern of spots shown in Fig. 3 is due to diffraction by extremely thin projections from a perfect crystal, or to diffraction from many relatively thick crystals which are well but not perfectly aligned; whether, that is, we have a "cross grating" pattern or a pattern due to crystal imperfection.

If the roughnesses extending above the surface of a perfect crystal were sufficiently thin they would give rise to a pattern of diffraction spots the positions of which, in the neighborhood of the primary beam, could be calculated by assuming the crystal to consist of a single plane of scattering centers normal to the direction of this beam.[3] This equivalent plane of scattering centers is not necessarily a physical plane of atoms in the crystal, but it is obtained from the structure of the physical crystal by projecting upon a plane at right angles to the electron beam all of the atoms in one of the very thin projections. An absolutely perfect crystal would produce this

[1] The rectangular light patch which appears strongly in Figs. 2 and 3, and weakly in some later figures, is without important significance; it is due to electrons scattered from the slit system.

[2] See French, Proc. Roy. Soc. **A140**, 637 (1933); Darbyshire, Phil. Mag. **16**, 761 (1933); Kikuchi and Nakagawa, Sci. P.I.P. & C.R. (Japan) **21**, 256 (1933); Germer, Phys. Rev. **49**, 165 (1936).

[3] Bragg and Kirchner, Nature **127**, 738 (1931).

FIG. 2. Electron diffraction pattern from such a mirror surface of galena as that marked A in Fig. 1. Surface brushed to remove powdered galena, but not etched. Primary beam nearly parallel to a cube edge.

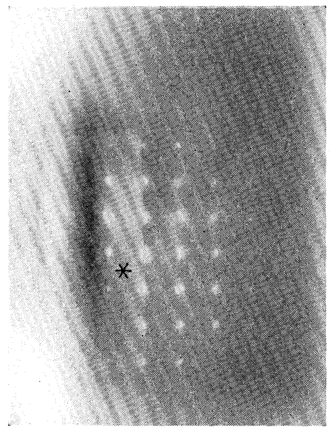


FIG. 3. Diffraction pattern from the surface which gave the pattern of Fig. 2 after a very light etch.

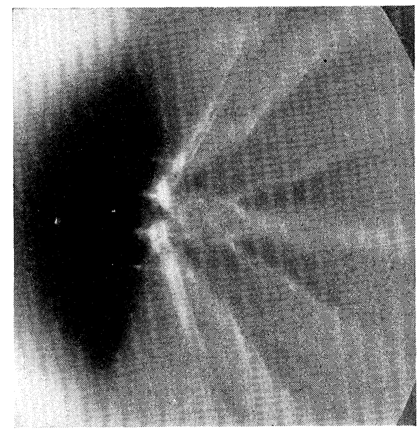


FIG. 4. Pattern from a cleaved surface of galena.

pattern of diffraction spots, if only the crystal were sufficiently thin in the direction parallel to the electron beam. The actual thickness determines only the *extent* of the "cross grating" pattern of spots, the radius of the pattern R being related to the thickness T, the electron wave-length λ and the separation L between crystal and photographic plate by the formula

$$R = L(2\lambda/T)^{\frac{1}{2}}. \tag{1}$$

If the crystal is aligned with an important crystallographic direction parallel to the primary electron beam this radius of the pattern is measured out from the intersection of the primary beam with the photographic plate. For slightly imperfect alignment this formula may still hold approximately with R measured out from the intersection of the important direction.

The alternative interpretation of such patterns as that of Fig. 3 as due to crystal imperfection rather than thinness was first given by W. L. Bragg.[4] He showed that substantially the same diffraction pattern would be produced by a slightly imperfect single crystal in which the electron paths need not necessarily be sufficiently short to give rise to the cross grating effect. If the spots of the square array are due to crystal imperfection they can be regarded as Bragg reflections from all of those crystal planes which pass through the cube edge, which is nearly parallel to the primary beam, as a common zone axis. In order that reflections from these planes appear it is necessary only that the imperfection be so great that cube edges of various crystallites are inclined to the direction of the primary beam by angles equal to the Bragg angles of the various planes. For the planes giving rise to the outermost spots which are clearly visible along the center line in Fig. 3 these angles are about 3°.

It is interesting and important to note that this angle of 3° is somewhat larger than the Bragg angles of several crystal planes which are inclined by approximately these angles to the common crystallographic zone axis of those planes which produce the square array of spots. Diffraction spots from these other planes do not appear near the center line, although some of them can be seen clearly along the upper edge of the pattern. From the unsymmetrical distribution of these "additional" spots we conclude that, due to imperfect alignment of the crystal, the cube edge of the mean orientation is not exactly parallel to the primary beam direction. It must intersect the photographic plate at a point somewhere in the square array of spots and below the center line. (The same conclusion is reached when one attempts to explain the

[4] W. L. Bragg, Nature **124**, 125 (1929).

square array of spots as due to a crystal which is perfect but extremely thin.)

Use of the Ewald Reciprocal Lattice

A more critical analysis and some further experimentation seem necessary to discriminate between these two possible explanations of the diffraction pattern shown in Fig. 3. The analysis is best supplied by an application of Ewald's conception of a reciprocal lattice.[5] As this will be almost indispensable later, it will be developed at once.

A vector is drawn from a fixed origin normal to each of any three pairs of planes which enclose a smallest possible unit of structure in a crystal lattice, the lengths of the three vectors being made numerically equal to the reciprocals of the separations of their corresponding planes. These vectors chosen as primitive translations define a new point lattice which is said to be reciprocal to the original physical lattice. The vector from the origin to any point of this new lattice can be written as

$$\mathbf{F} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C},$$

where **A**, **B** and **C** are the primitive translations and h, k and l are whole numbers. The fundamental Laue conditions for coherent scattering are very simply expressed in terms of the vector **F**. These conditions are contained in the single equation

$$\mathbf{S} - \mathbf{S}_0 = \lambda \mathbf{F}, \tag{2}$$

where $\mathbf{S}_0$ is a unit vector in the direction of the primary beam and **S** a unit vector in the direction of a diffraction beam. Every unit vector **S** which can satisfy Eq. (2) represents the direction of a diffraction beam, and conversely all diffraction beams are included in this assemblage. Eq. (2) has a simple geometrical interpretation which is very useful. Choosing any point of the reciprocal lattice as origin, we draw the vector $-\mathbf{S}_0/\lambda$ (which is of length $1/\lambda$ and opposite in direction to the primary beam direction). A sphere is constructed of radius $1/\lambda$ about the endpoint of this vector as center. This sphere is called the sphere of reflection ("Ausbreitungskugel"). Eq. (2) states that the directions of all diffraction beams are obtained by drawing vectors from the center of the sphere to those points of the reciprocal lattice which fall upon its surface.

In the case of the galena crystal, we need consider scattering from the lead atoms only. These form a cubic face-centered structure with cube edge $a = 5.93$A. It is easy to show that the lattice reciprocal to this is body centered with a cube edge b numerically equal to $2/a = 0.337$. A cross section of this lattice is represented in Fig. 5. The plane of the paper is a cube face, which was approximately the plane of incidence of the primary electron beam upon the crystal when the pattern of Fig. 3 was produced. The large arc is the intersection of this plane with the sphere of reflection, assuming the primary beam to lie accurately along a cube edge. (The electron wave-lengths was 0.054A, which makes the radius of this sphere numerically equal to 18.5.) The solid circles are points of the reciprocal lattice of the galena crystal (lead atoms only) which fall in the plane of the paper, and the hollow circles are points which fall above and below this plane by distances equal to half the smallest separations of the solid circles. It is convenient to designate the points of the reciprocal lattice by the indices of corresponding planes of the physical crystal. If the direction of the primary electron beam is [100] and the normal to the crystal surface [010], then the points of Fig. 5 directly above the origin (000) are (020), (040), etc. and other points have the indices which appear in the figure.

This construction, which corresponds to a large perfect crystal, can be readily modified to indicate the pattern to be expected when the crystal is not perfect and is not large. In particular, to represent diffraction from a powder we image a great number of reciprocal lattices all with common center (000) but oriented entirely at random. The points of these lattices are scattered over a family of spherical surfaces about the point (000). The sphere of reflection cuts these other spheres in circles, and the diffraction beams form continuous circular cones, the apex angles of which are readily calculated from this construction.

[5] Similar applications to electron diffraction have been made by: Kirchner, Ann. d. Physik **13**, 38 (1932); Aminoff and Broomé, Zeits. f. Krist. **89**, 80 (1934); **91**, 71 (1935); Darbyshire and Cooper, Proc. Roy. Soc. **A152**, 104 (1935); and by others.

If the diffracting material is a collection of small (but not too small) crystals with nearly the same orientation—the case of an imperfect single crystal—then instead of the single reciprocal lattice of Fig. 5 one has a collection of such lattices with the same distribution of orientations as the crystals. The points of given indices form a cluster which occupies a small cap on the corresponding lattice sphere. If the distribution is random all such caps subtend the same solid angle at (000). The sphere of reflection may cut through many caps, thus giving rise to such a considerable array of diffraction spots as that exhibited in Fig. 3.

To represent diffraction by a number of perfectly aligned but extremely thin crystals, the simple reciprocal lattice is altered in a different manner. Kirchner has pointed out[5] that thinness in the direction of the primary beam can be represented by making each point of the lattice the center of a line segment parallel to the beam direction and of length inversely proportional to the thickness. It is easy to show that the line segments have a common length equal numerically to twice the reciprocal of the thickness. This modified reciprocal lattice is generated by moving the original lattice back and forth parallel to the primary beam direction through a total distance numerically equal to $2/T$. One sees that, in this case also, the sphere of reflection will intersect many reciprocal lattice line segments if their common length is comparable to the constant of the lattice—that is, if the crystals are sufficiently thin. Thus thinness is also capable of accounting for such an array of spots as that shown in Fig. 3.

With the designation of crystal axes given in Fig. 5, the spots of the principal array of Fig. 3 have indices of the form $(0\ k\ l)$, with k and l even and k having positive values only. It is easy to estimate from Fig. 5 the degree of imperfection required to explain the extent of the pattern in Fig. 3. The rotation of the lattice of Fig. 5 required to bring to the sphere of reflection a point of the form $(0\ k\ 0)$ is readily estimated from the figure, and it is easy to show that the rotation required to bring in the $(0\ k\ l)$ reflection is

$$\theta=\sin^{-1}((\lambda/2a)(k^2+l^2)^{\frac{1}{2}}).$$

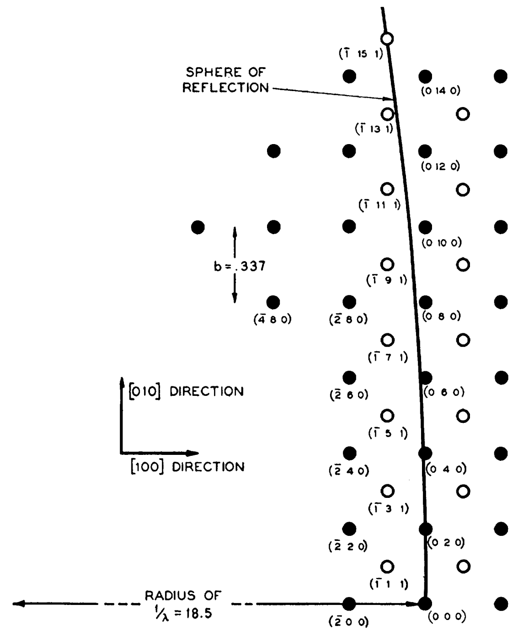


FIG. 5. Cross section of the reciprocal lattice of galena and the sphere of reflection, with the primary electron beam in the [100] direction.

Still more generally, the reflection $(h\ k\ l)$ requires a rotation of

$$\theta=\tan^{-1}(h/(k^2+l^2)^{\frac{1}{2}})+\sin^{-1}((\lambda/2a)(h^2+k^2+l^2)^{\frac{1}{2}}). \quad (3)$$

(The correct sign must be assigned to the number h.)

From Eq. (3) one calculates that the reflection (0 12 0) requires a rotation of about 3.1° and the reflection $(\bar{1}\ 11\ 1)$ about $-2.3°$. The former reflection appears clearly in Fig. 3 although the latter, which should lie nearby, is entirely missing. Other diffraction spots with high odd indices, which one expects to find near the center line in Fig. 3, also are missing. Those spots with odd indices which actually appear are located in the upper part of the figure. The obvious interpretation of the unsymmetrical occurrence of odd-ordered diffraction spots is that Fig. 5 does not correctly represent the reciprocal lattice corresponding to the mean orientation of the crystal. For this mean orientation the lattice of Fig. 5 should be turned slightly. In Fig. 6, for example, is represented the same lattice rotated by an angle of 3° about an axis through (0 0 0) and normal to the plane of the paper. One sees that, if this lattice represented the mean orientation of the crystal, a very slight imperfection, or equally well a small elongation of lattice points due to thinness, could account for the appearance of even-ordered diffraction spots of the form $(0\ k\ 0)$ and the odd-ordered spots $(\bar{1}\ k\ 1)$ would not appear unless the imperfection were quite large, or elongation of lattice points due to thinness very great.

It is not difficult to determine the actual orientation of the crystal required to account for the pattern of Fig. 3. If, for example, one goes out from the primary beam position along the 45° line in the upper half of Fig. 3 one comes first to the position of the missing $(0\ 2\ \bar{2})$ diffraction spot, then successively to the spots $(0\ 4\ \bar{4})$, $(0\ 6\ \bar{6})$, $(\bar{1}\ 7\ \bar{7})$, $(\bar{1}\ 9\ \bar{9})$ and $(\bar{1}\ 11\ \overline{11})$. The weak spots $(0\ 6\ \bar{6})$ and $(\bar{1}\ 7\ \bar{7})$ seem to be equally intense. This equality means that the sphere of reflection passes between the corresponding reciprocal lattice points, and that these points are located at equal distances from the sphere. It can be shown that this is sufficient to locate the intersection of the [100] axis with the photographic plate upon a straight line normal to the line of diffraction spots just considered and passing very close to the primary beam position, but slightly on the other side from the $(0\ 6\ \bar{6})$ and $(\bar{1}\ 7\ \bar{7})$ diffraction spots. Other simple considerations modify the indicated position of this line slightly, and finally locate the intersection of the [100] axis at about the position of the star in Fig. 3.

Although these considerations seem to show that the extended array of spots in the pattern of Fig. 3 can appear as a result of imperfection or as a result of thinness, it is of course true that a pattern due to thinness cannot be identical with one which results from imperfection. Yet the differences are not so marked that one can by inspection always attribute a pattern to one cause or the other.

It should, in principle, be possible to reach a conclusion regarding the state of the material producing the pattern shown in Fig. 3 from a study of widths of rocking curves.

Rocking Curves from a Cleaved Galena Crystal

A crucial experiment from which one might distinguish between imperfection and thinness is suggested by the ways in which the simple reciprocal lattice must be modified to represent these different conditions. If one rotates the crystal its reciprocal lattice rotates with it, and one sees that a given diffraction beam will persist through whatever angle the lattice feature representing this beam remains in contact with the sphere of reflection. For a slightly imperfect crystal each lattice feature is the small cluster of points already described. Each of these clusters subtends the same angle at the origin. If the crystal is rotated about an axis normal to the plane of incidence the clusters which represent the $(0\ k\ 0)$ beams will remain in contact with the sphere through equal angles; the "rocking curves" of these beams will have equal widths. For a thin perfect crystal the case is different. The lattice features are line segments of equal lengths. These do not subtend equal angles at the origin, and if the crystal is rotated about an axis normal to the plane of incidence the "rocking curves" of different beams of the form $(0\ k\ 0)$ will not have equal widths.

These two cases are illustrated by the lattice features of Fig. 7. In 7A are drawn the reciprocal lattice line segments of the form $(0\ k\ 0)$ corresponding to a perfect crystal only $3a = 17.8$A in thickness. To compare with this are drawn in 7B arcs representing the loci of reciprocal lattice points of the form $(0\ k\ 0)$ corresponding to the various crystallites of a thick crystal of which the maximum imperfection is 3°. It is evident that, if one attempts to measure "crystal imperfection" by the rocking crystal method, he will obtain results which are dependent upon which of these figures represents the true condition of the crystal. If the condition is that represented by Fig. 7B one will obtain 3° for the total width of rocking curve, quite independently of the diffraction spot upon which the measurements are made. If, however, the condition is that represented by Fig. 7A one will also obtain 3° if the measurements are carried out upon the diffraction spot $(0\ 12\ 0)$, but a larger value will be found if a lower ordered spot is chosen for measurements. In general, for a crystal of thickness $T = na$, a spot of the form $(0\ k\ 0)$ will give a total rocking curve width equal to

$$W = 2a/kT = 2/kn \tag{4}$$

in circular measure.

Unfortunately rocking curves of various dif-

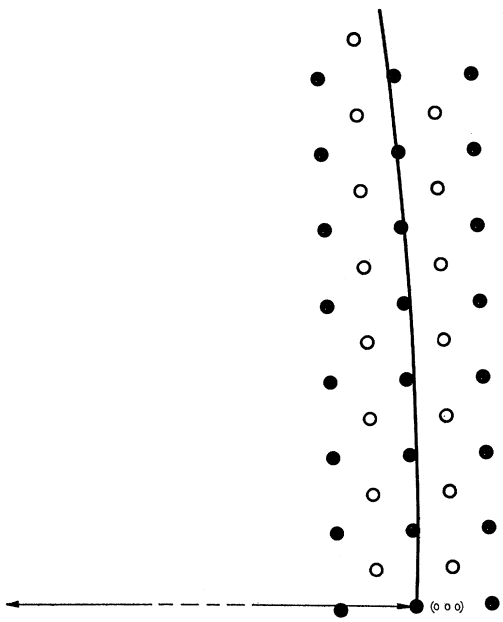


FIG. 6. The reciprocal lattice and sphere of reflection of Fig. 5, with the primary electron beam lying in the (001) plane of the galena crystal and inclined by 3° to the [100] direction.

fraction spots appearing in Fig. 3 cannot be obtained; the widths of these curves would be so great that the crystal itself would intercept the primary electron beam on one side, and the diffraction beam under examination on the other. The proposed crucial experiment could be carried out only by the transmission method.

Although this investigation of the variation of rocking curve width with order cannot be made upon the crystal which produced the pattern of Fig. 3 it can be carried out upon a crystal which gives rise to *narrower* rocking curves. The cleaved surface of a galena crystal does give curves which are sufficiently narrow to permit direct measurements. But unfortunately the curves are so narrow and exhibit such anomalies that no certain conclusion can be drawn from them concerning the condition of the surface. They do, however, supply us with data from which we can decide regarding the condition of material on the surface of a filed crystal. The conclusion is that such an extended pattern of spots as that shown in Fig. 3 is due to imperfection, and not to thinness.

In Fig. 8 are reproduced nine rocking curves for a cleaved and etched crystal. These curves represent the variation of intensity with angular crystal setting, respectively, of the diffraction spots (0 2 0), (0 4 0), (0 6 0), (0 8 0), (0 10 0), (0 12 0), (0 14 0), (0 16 0), and (0 18 0). The abscissae are the angular positions of the crystal, measured from the position of grazing incidence, as determined by a lamp and scale and a mirror attached to the crystal holder.[6]

The first five of the curves of Fig. 8 were obtained by measuring directly the intensities of diffraction spots upon the fluorescent screen by means of a Macbeth illuminometer manufactured by the Leeds and Northrup Company. Because of the small size of the fluorescent screen, spots beyond (0 10 0) could not be observed directly. Rocking curves of the spots beyond this were obtained photographically as described below. The spot (0 18 0) fell near the edge of the photographic plate, and higher ordered spots were beyond the range of observation.

In using the illuminometer a color match was established by the use of suitable filters. The ordinates of the first five rocking curves are readings taken directly from the illuminometer. Nearly three hours were required to obtain the data of these curves; voltage, current and direction of the primary beam remained constant throughout this time.

The photographic method of obtaining rocking curves of diffraction spots beyond (0 10 0) consisted of several steps. With stops in front of the photographic plate so adjusted that 23 exposures could be made upon one plate, preliminary estimates of intensities and approximate widths were easily made. After such preliminary estimates a series of exposures at constant time shows clearly the variation of intensity of a diffraction spot with crystal position. Such a series of photographs is exhibited in Fig. 9. The electron beam current has been adjusted to a rather low value so that the uniform exposure time of 7 seconds gives suitable darkening of the photographic plate. On Fig. 9 the diffraction spots (0 12 0) and (0 14 0) reach their maximum intensities, and the spots (0 8 0), (0 10 0) and (0 16 0) can be observed. Various diffuse Kikuchi lines also appear weakly.

Each final rocking curve exhibited in Fig. 8, beyond the (0 10 0) curve, was obtained from a

[6] For the means of rotating the crystal see Germer, Rev. Sci. Inst. 6, 138 (1935).

series of exposures in which approximately constant photographic intensities were maintained by varying exposure time with crystal position. In this way it was unnecessary to make estimates of relative blackness. A photographic comparison of intensities of different diffraction spots was also carried out, and all curves of Fig. 8 have been reduced to readings upon the illuminometer. The photographic estimations of rocking curves involved altogether a total of 424 exposures upon 19 plates.

In Fig. 10 are plotted the widths at half maximum of the various curves shown in Fig. 8 against the reciprocal of k, the order of reflection. If the diffracting material is an aggregate of "thick" crystals imperfectly aligned the points of Fig. 10 should fall along a straight line parallel to the axis of abscissae; if it is an aggregate of thin projections from an essentially perfect crystal they should fall along a straight line passing through the origin. The line drawn on the figure corresponds to a perfect crystal having a thickness of about 350A.[7] The range of the measurements is so small, and their anomalies are so great, that one cannot decide between imperfection and thinness. One can, however, at once conclude that the imperfection of the crystal is at least *as small as 10 or 15 minutes* and that the average thickness is *350A or more.*

In addition to measurements upon diffraction beams of the form $(0\ k\ 0)$ the rocking curve of the beam $(\bar{1}\ 15\ 1)$ also was determined. This beam was found to be about equal to $(0\ 18\ 0)$ in intensity, and the rocking curve width at half maximum was measured to be 14′. This width is represented on Fig. 10 by an open circle at an abscissa of 1/15, which is approximately the correct value to make this point comparable with the others.

The maximum of the $(\bar{1}\ 15\ 1)$ rocking curve occurred at glancing angle 0.49°. From Eq. (3) one calculates that this should come at 0.27°. Slightly incorrect azimuth adjustment of the crystal is undoubtedly responsible for the discrepancy. The calculation assumes that, at zero glancing angle, the primary beam lies accurately along the [100] direction. It is easy to show from the lattice of Fig. 5 that an azimuth rotation of the crystal through a small angle θ will result in changing the glancing angle of a diffraction beam of the form $(\bar{1}\ k\ 1)$ by an amount equal to θ/k. If the glancing angle of the beam $(\bar{1}\ k\ 1)$ is increased, the angle of the beam $(\bar{1}\ k\ \bar{1})$ will be decreased by an equal amount. Thus we might expect to find the beam $(\bar{1}\ 15\ \bar{1})$ at 0.05° glancing angle. It was not looked for. The *positions* at which diffraction beams occur are not perceptibly changed by slight rotation of the crystal in azimuth.

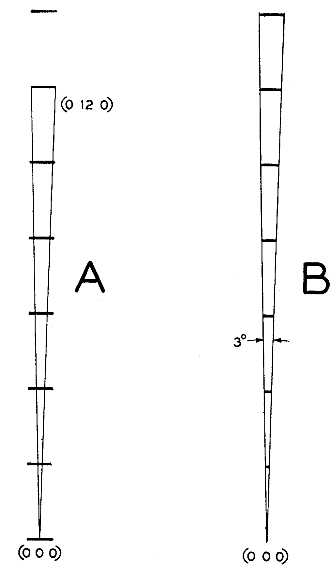


FIG. 7. Reciprocal lattice line segments of the form $(0\ k\ 0)$. *A*. For a perfect crystal having a thickness of only 17.8A in the direction of the primary beam. *B*. For a thick crystal with a total imperfection of 3°.

No explanation has been given of the curious relative intensities of the beams of Fig. 8, or of the anomalous broadness of the $(0\ 4\ 0)$ curve. (This broadness is so striking that it could be readily observed on the fluorescent screen, entirely without the aid of the illuminometer.) Other anomalies were also observed. For example, rocking curves of beams of the form $(0\ k\ 0)$ were not the same for different crystal azimuths. Several such curves were obtained with the crystal rotated 180° about the normal to its face. In this position the $(0\ 4\ 0)$ beam was considerably more intense than in the original azimuth, and its rocking curve was not unusually

[7] The value 350A is not obtained by direct substitution of the slope of the line of Fig. 10 into Eq. (4). The quantity W in this expression is total rocking curve width, whereas the ordinates of Fig. 10 represent widths at half maximum. From the latter, estimates are made of total widths, under the simplifying assumption of uniform thickness for all the projections from a perfect crystal.

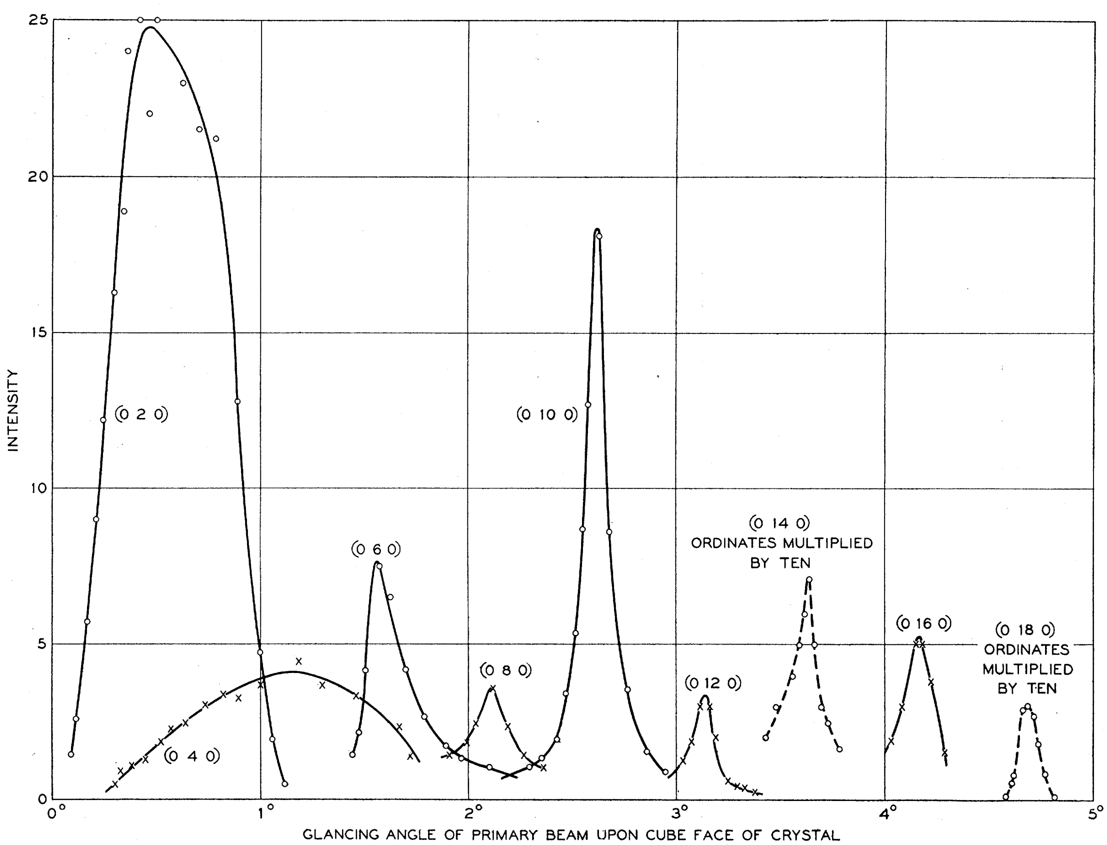


FIG. 8. Rocking curves of various Bragg reflections from the cube face of a cleaved and etched crystal.

broad. In the new azimuth it was found, however, that the (0 12 0) beam was very weak and had a rocking curve which was broad. This curve had, in fact, two maxima the stronger of which occurred at the correct glancing angle.

General Conclusions Concerning Thinness and Imperfection

In the above section two conclusions have been drawn from rocking curve measurements upon a cleaved galena crystal: (1) The imperfection of the surface of this crystal does not exceed about 10 or 15 minutes. (2) Those projections from its surface, which are most effective in scattering electrons of 0.054A wave-length, are not thinner than about 350A. Less extensive measurements upon a number of other cleaved crystals of galena have indicated that for these also the general surface imperfection does not exceed a small fraction of one degree, and that effective projecting portions are quite thick. The rather good definition of Kikuchi lines from cleaved, but unetched, crystals supports this conclusion regarding relative perfection of cleaved surfaces.

On the other hand, galena crystals which have been filed, and which have subsequently been deeply etched, show *extended* spot patterns. Clearly defined Kikuchi lines are not found even before etching.

All of these data are consistent with the hypothesis that the surface of a galena crystal which has been filed is, even after very deep etching, much more imperfect than the surface of a cleaved crystal. On the other hand, the data can also be understood if we are willing to believe that projections are always thinner upon the surface of a filed and deeply etched crystal than upon the surface of a crystal which has been

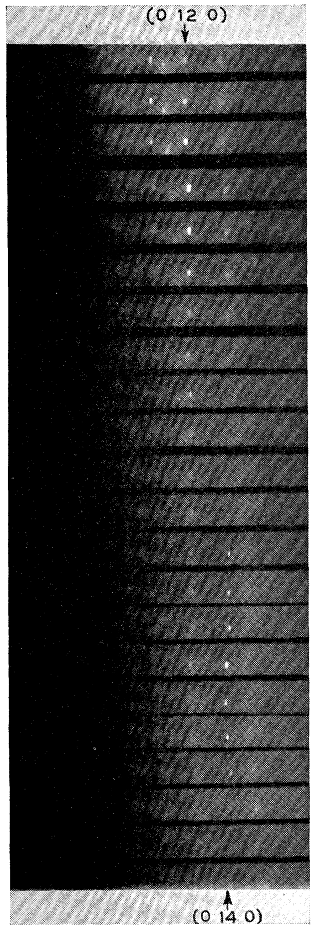


FIG. 9. Series of exposures at progressively varied glancing angles, showing the (0 12 0) and (0 14 0) diffraction spots.

cleaved and etched.[8] This latter hypothesis seems so unlikely that the former can be regarded as thoroughly established. It seems altogether reasonable to generalize further. Any extended spot pattern from a galena crystal, which would correspond to an indicated imperfection as large as 2 or 3 degrees, is really due predominantly to imperfection and not to thinness.

In some earlier experiments[9] upon metal crystals diffraction patterns of this sort were explained in this manner, but G. P. Thomson[10] has taken exception to this explanation and believes that these patterns should be attributed mainly to thinness. Further study of spot patterns from metal crystals seems desirable.

One predicted feature of the considerable imperfection indicated by the extent of the diffraction pattern of Fig. 3 does not appear in this figure, and requires explanation. One might expect that the total indicated imperfection of over 4° would result in diffraction spots drawn out into arcs of this length. *Such arced spots are actually found in many cases.* It seems probable that the imperfection is not uniform around different axes, but that it is related to the direction in which a crystal was filed. The experiments of the next section are concerned with this matter.

DIFFRACTION BY DEEPLY SCRATCHED SURFACES

All of the diffraction patterns which have already been described were obtained from "mirror" surfaces of galena. Entirely different patterns are obtained from abraded areas, either before etching or after moderate etching.

The diffraction pattern of Fig. 11 was produced by a filed but unetched galena crystal so adjusted that the electron beam was nearly parallel to a cube edge and was scattered mainly by deeply scratched portions of the surface, of the type marked B in Fig. 1. The predominant part of the pattern consists of Debye-Scherrer rings. Thirty-one of these rings are observable on the plate from which the figure was made. Their radii and, as far as one can estimate easily, their intensities have the values predicted for randomly oriented

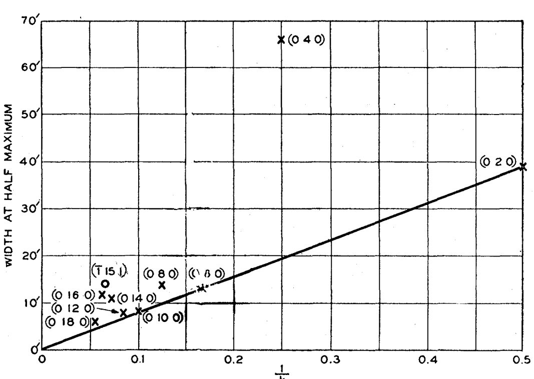


FIG. 10. Widths of rocking curves of diffraction beams of the form (0 k 0), as taken from Fig. 8.

[8] If this second hypothesis is correct the projections upon the surface of a filed and deeply etched crystal must quite generally be of the order of 20A in thickness.

[9] L. H. Germer, Phys. Rev. **44**, 1012 (1933).

[10] G. P. Thomson, Phil. Mag. **18**, 640 (1934).

crystals of galena. The rings are very sharp. One estimates that the average linear dimensions of the small galena crystals cannot be less than about 100A, and that the individual crystals are not greatly strained. Superposed on this ring pattern is a weak pattern of the type shown in Fig. 2. From this one infers that a small fraction of the B-type surface is really of type A.

Etching a crystal, which gives a pattern like that of Fig. 11, changes the surface in such a way that a subsequent diffraction pattern shows an array of spots in place of the weak streaks of Fig. 11. If the etch is rather light the Debye-Scherrer rings persist. Examples of these "combination" patterns showing diffraction from two different sorts of galena surfaces are shown in Fig. 12. The relative intensities of the two patterns depend upon a number of factors, dominant among which are, of course, the relative extents of the two sorts of surfaces in the area upon which the beam strikes. (See, for example, Figs. 12A and 12B.) Other factors are the depth of the etch, the glancing angle of the primary electron beam upon the surface, the amount by which the surface of the crystal deviates from a cube face, and the direction in azimuth of the plane of incidence. Some of these factors are of importance because the galena surface is extremely rough, and the mirror surfaces from which the spot patterns come are below the general plane of the abraded areas. The difference in level is of the order of 0.02 mm.

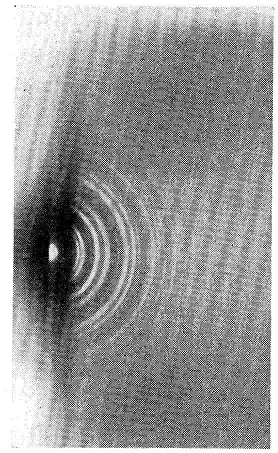
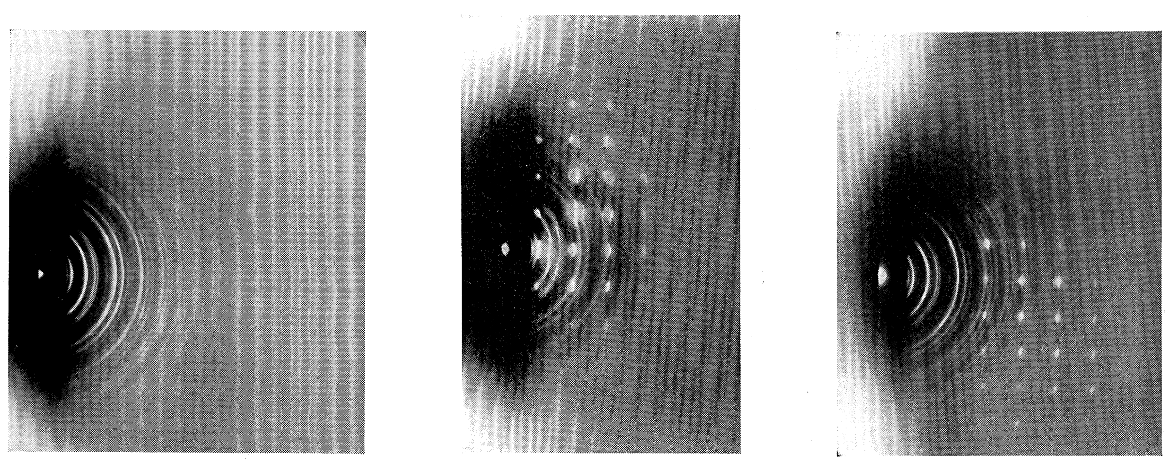


FIG. 11. Diffraction pattern from such a filed galena surface as that marked B in Fig. 1.

The higher parts cast shadows upon the photographic plate. A clear example of this is shown in Fig. 12C. Here the spot pattern fails to come up to the general shadow of the galena surface by a distance which corresponds to an angle at the specimen of about 2°. Various "shadowing" effects of this nature have been observed, some of which are not entirely understood.

Deeper etching of a crystal, which gives diffraction patterns more or less like those of Fig. 12, results in a surface from which strikingly different patterns are obtained. Two of these are reproduced in Figs. 13 and 14. These two patterns were produced by the same crystal without



A B C

FIG. 12. Combination patterns from galena crystals which have been first filed, then very lightly etched.

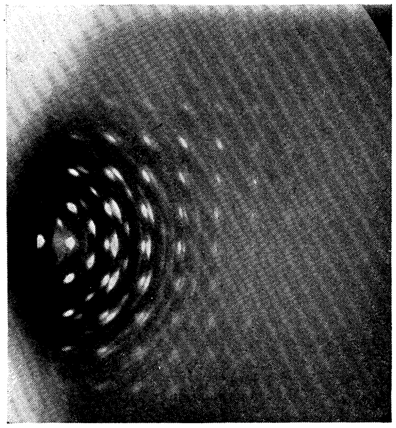


FIG. 13. Pattern from a crystal which has been filed and moderately etched. The primary electron beam was approximately parallel to the direction of filing.

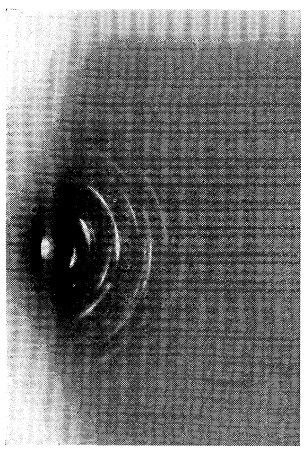


FIG. 14. Another pattern from the crystal which produced Fig. 13, after rotating the crystal so that the electron beam direction lay normal to the direction of filing.

alteration of its surface condition. In both cases the electron beam direction was approximately parallel to a cube edge. In the former the beam direction was the direction of grinding, while in the latter the crystal had been rotated so that the grinding direction was normal to the beam direction.

Both in Fig. 13 and in Fig. 14 we recognize two different sorts of diffraction patterns. The square array of spots which arises mainly, if not entirely, from the etched mirror surfaces has remained unchanged; the Debye-Scherrer rings from the deeply scratched areas have been replaced by new diffraction spots in Fig. 13 and

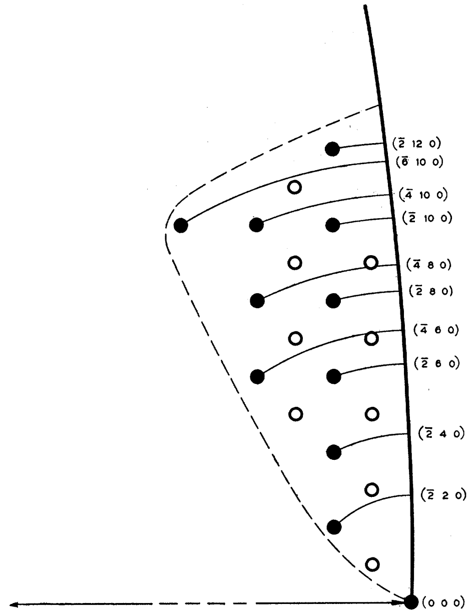


FIG. 15. Reciprocal lattice of the lead atoms of galena, representing only those points of the form $(0\,k\,0)$ and $(\bar{1}\,k\,1)$ which correspond to reflections observed in Fig. 13.

by arcs in Fig. 14. It is easy to see that the latter correspond to crystallites which have been rotated from the orientation of the galena crystal about an axis approximately parallel to the primary beam and by amounts varying from 5 to about 35 degrees. The sense of the rotation is that of imaginary rollers on the surface of the crystal which have been rotated by motion of the grinding wheel. The new spots of Fig. 13 are also attributed to these same rotated crystallites.

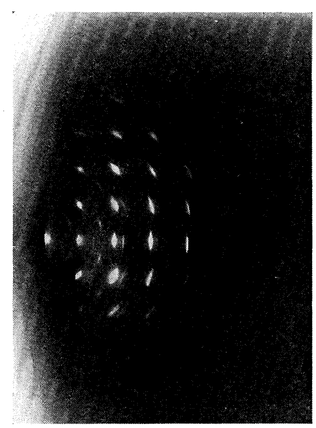


FIG. 16. Pattern like that of Fig. 13, from a crystal which has been more deeply etched.

The axis of rotation is now normal to the electron beam. The sense of the rotation is not readily determined from Fig. 13.

Fig. 15 represents again the reciprocal lattice of the galena crystal and the sphere of reflection. The solid circles are those points of the reciprocal lattice which lie in the plane of incidence and the open circles points located at the distance $1/a$ either side of this plane. Only those points are drawn which correspond to reflections actually observed in Fig. 13 among the *new* array of diffraction spots. (Lattice points corresponding to the square array of spots are not indicated.) The rotations of the original crystal about an axis normal to the plane of incidence required to bring various reciprocal lattice points to the sphere of reflection are immediately estimated from Fig. 15. Arcs are drawn from those lattice points which lie in the plane of incidence. The intersections of these arcs with the sphere of reflection represent the locations of the corresponding diffraction points on the photographic plate, and the lengths of the arcs, the rotations of the crystallites from the mean orientation of the large galena crystal. Indices of those diffraction spots appearing in the plane of incidence are marked on the figure. The dashed curve represents an approximate envelope of the reciprocal lattice points which correspond to observed diffraction spots.

Repeated etching of the crystal which produced the patterns of Figs. 13 and 14 resulted in further modifications of these patterns. The new spots became relatively much weaker, as in Fig. 16, and finally disappeared entirely indicating that the etching had at last removed all of the material which had been disturbed by the abrasion. A crude estimate of the depth of this disturbed layer was obtained in a series of experiments in which a crystal was alternately etched and examined by electron diffraction until, after ten etchings, only the square array of diffraction spots was produced. The amount of material removed was estimated by chemical analysis of the etching solutions for amount of dissolved lead. These experiments indicated that the rotated crystallites extended to a depth of about 0.003 mm below the surface. The mean rotation, as estimated from patterns like those of Figs. 13 and 14, was about 20°. The interesting observation was made that this mean rotation was about the same after different amounts of material had been removed.

In Fig. 13 one observes clearly that the "spots" due to the rotated crystallites are actually arcs extending several degrees along the corresponding Debye-Scherrer rings. This means that, in addition to the considerable rotation about an axis normal to the direction of grinding, the crystallites have suffered also slight rotations about other axes.

A Possible Application to Metallurgy

It is known from x-ray examinations that when the surface of a metal crystal is filed, or polished on abrasive material, the regular arrangement of atoms near the surface is profoundly disturbed; but, so far as I am aware, no systematic investigation of the nature of this disturbance has been made.

The results of the present experiments suggest that a similar investigation of metallic crystals might be interesting and valuable. The observed rotation of crystallites is similar to the mechanism postulated to account for strain hardening of metals,[11] and it seems possible that the simple experimental technique used here could be applied to metal crystals and might yield readily important data regarding slip and strain hardening.

I am glad to thank Dr. C. J. Davisson for his interest and advice throughout the course of these experiments, and Mr. K. H. Storks for doing a great deal of the experimental work and helping considerably with the interpretation of data.

[11] See e.g. Burgers, *Int. Conf. Physics*, London, 1934, Vol. 2, pp. 139–160.

FIG. 1. Cube face of a galena crystal which has been filed from left to right, parallel to a cube edge. Magnification 90×.

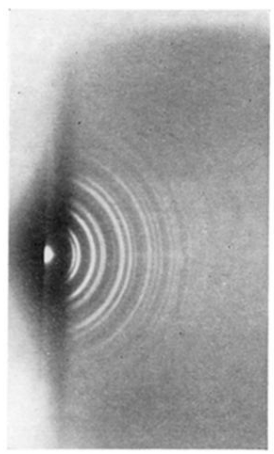
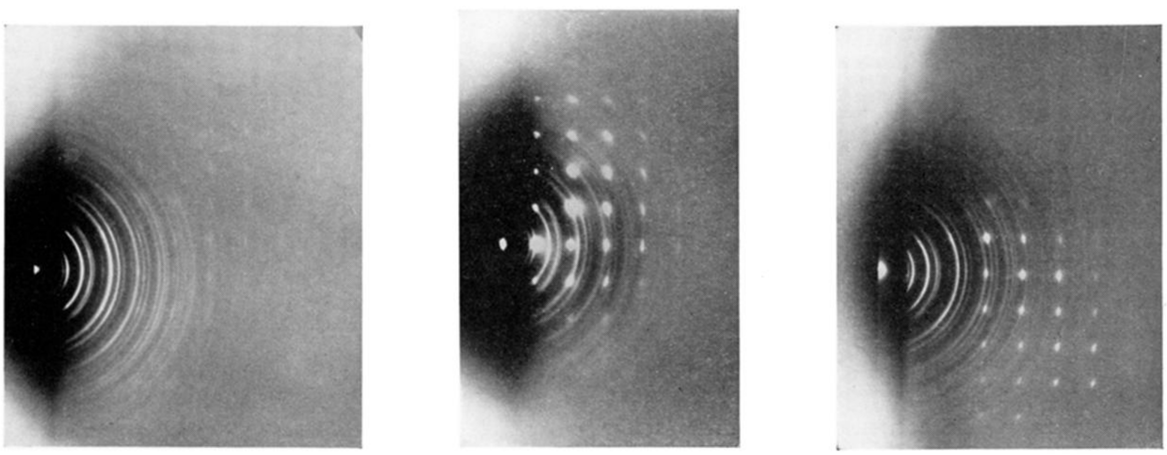


FIG. 11. Diffraction pattern from such a filed galena surface as that marked *B* in Fig. 1.



A B C

FIG. 12. Combination patterns from galena crystals which have been first filed, then very lightly etched.

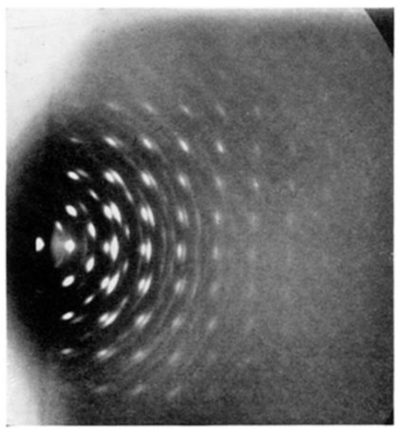


FIG. 13. Pattern from a crystal which has been filed and moderately etched. The primary electron beam was approximately parallel to the direction of filing.

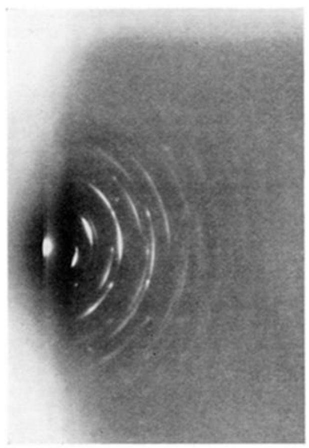


FIG. 14. Another pattern from the crystal which produced Fig. 13, after rotating the crystal so that the electron beam direction lay normal to the direction of filing.

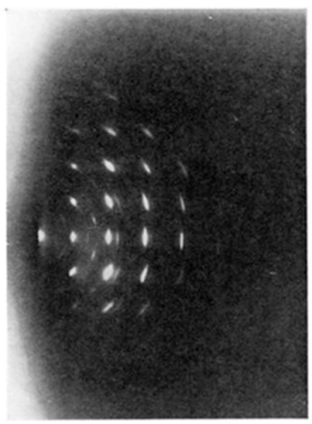


FIG. 16. Pattern like that of Fig. 13, from a crystal which has been more deeply etched.

FIG. 2. Electron diffraction pattern from such a mirror surface of galena as that marked A in Fig. 1. Surface brushed to remove powdered galena, but not etched. Primary beam nearly parallel to a cube edge.

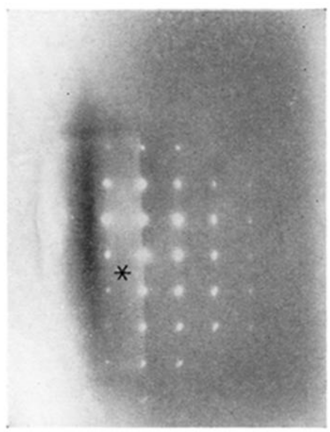


Fig. 3. Diffraction pattern from the surface which gave the pattern of Fig. 2 after a very light etch.

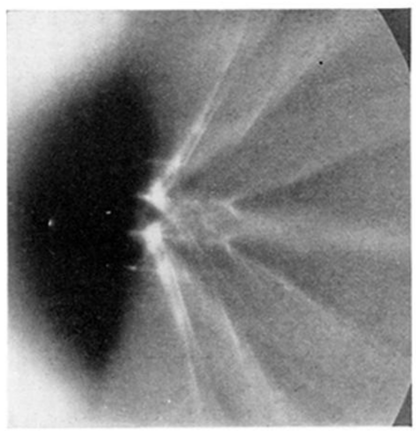


FIG. 4. Pattern from a cleaved surface of galena.

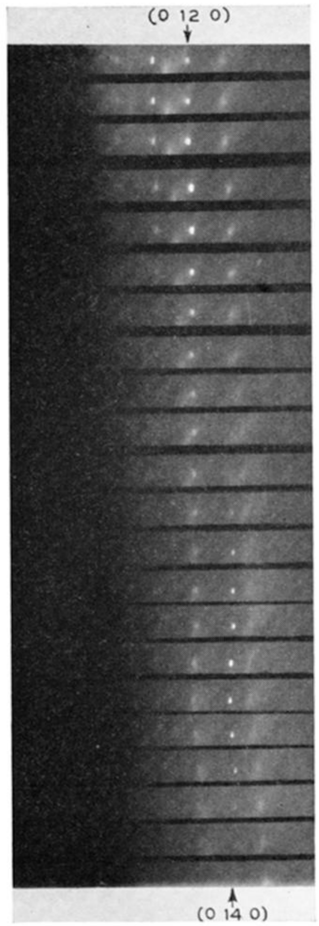


FIG. 9. Series of exposures at progressively varied glancing angles, showing the (0 12 0) and (0 14 0) diffraction spots.