Diffuse Rings Produced by Electron Scattering

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Two diffuse rings produced by electrons scattered from polished metal surfaces have been widely accepted as evidence that such surfaces are amorphous. Similar rings are, however, formed by electrons scattered from vaporized ZnS, and from unpolished surfaces of SiC and Cu_2O, all of which are very probably crystalline. These experiments seem to vitiate the previous interpretation of these rings, although they cannot be construed as definite evidence against an amorphous layer on polished metals.

A NUMBER of experiments have been reported in which electrons incident near grazing have been scattered by highly polished metal targets. The patterns obtained consist of two broad diffuse rings somewhat similar in appearance to rings produced when x-rays are diffracted by a liquid; indeed, the ratio of the radii of the rings (1.8 : 1 approximately) agrees well with prediction based on a simple theory of diffraction by liquids, and with the x-ray patterns of one or two actual liquids.

The obvious inference is that during polishing the material in and near the surface of the target has been rendered amorphous as conceived long ago by Beilby. The surface layer is a supercooled liquid and this is revealed by the pattern of broad rings. This interpretation has been widely accepted, particularly in England, as is evident from the favorable consideration it received at a symposium of the Faraday Society, the papers of which appear in the September number of the Transactions of this society.

In spite of the general acceptance of this interpretation there are certain observations and certain considerations which are not easily reconciled with it, and it is my purpose in this paper to describe still others. Among the difficulties already encountered is the fact that the two diffuse rings are reported to have the same radii for most metals—in the extreme case, for metals for which the cube roots of the atomic densities are in the ratio 1.4 : 1. X-ray diffraction patterns of different liquids do not show such unaccountable similarities.

One of the arguments in favor of the amorphous layer is that if the polished surface were crystalline one would observe the normal Debye-Scherrer pattern of the metal, or possibly the normal pattern as displaced by refraction; since such patterns are not observed the surface cannot be crystalline. The argument is probably not sound, because refraction may easily account for the absence of anything resembling a normal pattern from a crystalline surface from which no points or particles project. This I have attempted to explain in a previous note,[1] and Kirchner also has pointed it out. Kirchner[2] notes that the normal Debye-Scherrer rings should be produced only by projecting roughnesses. If, in reflection experiments, broadening of rings is observed, then any conclusion from this broadening regarding mean size of the crystals must refer only to those portions of the crystal grains which project from the surface, and not to the total sizes of the grains. Kirchner has carried out an instructive experiment upon gold foils in which he shows that the same crystal structure gives, with reflected rays, diffuse rings and with transmitted rays sharp rings. He states finally that "no definite conclusions can be drawn as to the size of crystal grains within the surface layers so far as reflection experiments are used."

DIFFRACTION PATTERNS BY REFLECTION AND BY TRANSMISSION

I have recently repeated Kirchner's experiment using a transparent film of ZnS which had been vaporized in vacuum upon a glass plate. In Fig. 1A is shown the pattern obtained by reflecting electrons from the surface of this film. After this experiment the glass upon which the film had been deposited was broken and, holding the

[1] Germer, Phys. Rev. **43**, 724 (1933).
[2] Kirchner, Nature **129**, 545 (1932); Erg. d. exakt, Naturwiss. **11**, 112 (1932); Trans. Faraday Soc. **31**, 1114 (1935).

A

B

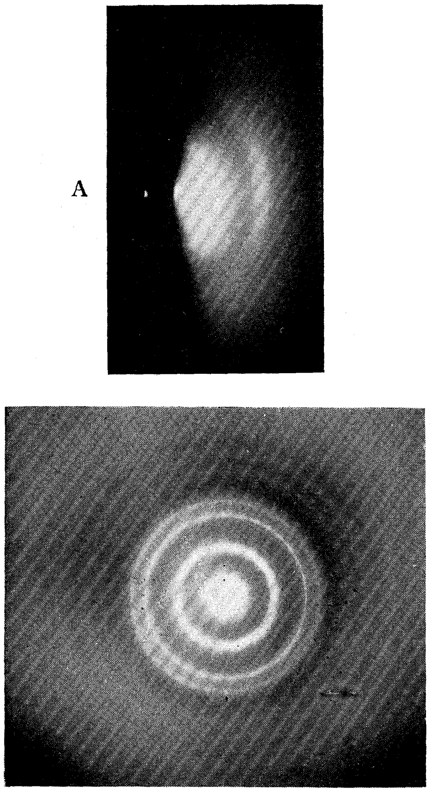


FIG. 1. Diffraction patterns from a ZnS film, deposited by vaporization in vacuum. A, by reflection; B, by transmission.

broken glass under water, portions of the film were chipped off at the edge of the glass. It was easy to capture a minute piece of the film over a 0.1-mm hole in a metal plate. Electrons transmitted through this fragment of film gave the pattern of Fig. 1B.

The ratio of the radii of the rings of Fig. 1A is equal to 1.83. The individual rings correspond, by the Bragg formula, to spacings 2.34A and 1.28A. These values agree well with those of the rings commonly observed from polished metals. The transmission pattern of Fig. 1B, on the other hand, consists of seven sharp rings which correspond both in radii and intensities with rings calculated from the well-known structure of the cubic modification of ZnS,[3] (B3 structure in *Struckturbericht* by Ewald and Hermann). This experiment upon ZnS is substantially a repetition of Kirchner's experiment upon gold mentioned above. It proves again that the occurrence of diffuse rings by reflection cannot be accepted as evidence that the reflecting material is amorphous.

Diffuse Rings from Naturally Formed Surfaces

In the present paper I wish to report other objections to the amorphous layer interpretation of the diffuse diffraction rings. The new difficulties are presented by diffraction by glassy smooth surfaces of carborundum single crystals and by glassy smooth surfaces of polycrystalline cuprous oxide. It is difficult to believe that these naturally smooth surfaces are covered by layers of amorphous carborundum and amorphous cuprous oxide, and yet they produce the same type of pattern as polished metals—two broad diffuse rings.

Carborundum crystals were chosen having natural (0001) faces which appeared very smooth and perfect. These crystals were prepared by washing in Merck's thiophene free benzene, in anesthetic ether and in absolute alcohol. From the alcohol each crystal was dried quickly in a stream of dry nitrogen. After this treatment (as well as before) the (0001) faces had a very high gloss and were exceedingly flat. Electron diffraction patterns from these faces always show two rings which are definitely more diffuse than those of Fig. 1A. In addition to these diffuse rings there are traces of extremely weak sharp rings, and sometimes very weak poorly defined spots lying along the intersection of the plane of incidence with the photographic plate. Sometimes also one can detect patterns characteristic of the carborundum crystal, and in one case the carborundum pattern was strong—almost comparable in intensity with that of Fig. 2B. In this case, as well as the others, the two diffuse rings are clearly shown. Usually they are the predominant feature of the plate. The radii of these rings from different specimens appear to be the same, and

[3] The thickness of the film which produced the pattern of Fig. 1B was about 800A, which is somewhat too great to give the best possible pattern. In printing from the original plate it was necessary to employ translucent shields protecting the outer portion of the plate from the intense light necessary for the very dark region near the primary beam. This may be considered a simplified modification of the sector copying method described by Trendelenburg in Wiss. Veröff. a. d. Siemenskonzern **13**, 48 (1934). The rings do not appear with their correct relative intensities in the reproduction. A similar photographic artifice was used in producing the prints of the other figures. In spite of this the rings of Figs. 1A, 2A and 3A are reproduced badly and are much less definite than on the original plates.

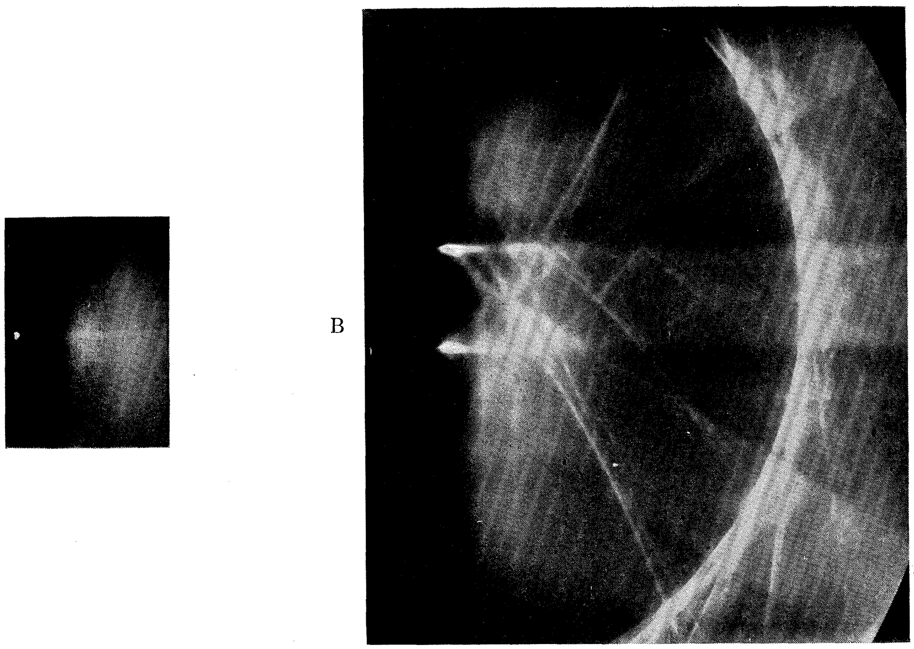
A  B

FIG. 2. Reflection patterns from (0001) faces of SiC crystals. A, smooth, unetched surface; B, surface etched in fused KOH.

the mean values of all the measurements correspond, by the Bragg formula, to spacings of 2.26A and 1.23A. These are in good agreement with values obtained from rings produced by polished metals.

The diffuse rings are destroyed by etching in fused KOH. Figs. 2A and 2B show patterns before and after etching. The strongest features of Fig. 2B are readily calculated from the carborundum structure, and it seems highly probable that the entire pattern is due to this structure.[4]

Similar experiments have been carried out upon sheets of red transparent cuprous oxide. This material was formed by oxidizing sheets of copper completely in air. The surfaces of the specimens used had a glassy smoothness, although they were not flat. The individual crystals were very large and the electron beam was probably incident upon only ten or twenty different crystals. The surfaces were prepared by careful washing in benzene, ether and alcohol, and by drying quickly in a stream of nitrogen. The scattering patterns (Fig. 3A) show two diffuse rings, of which the mean values of the measured radii correspond to spacings of 1.7A and 1.1A. These values are distinctly lower than those calculated from the rings from polished metals.

The two diffuse rings cannot be found after the cuprous oxide has been etched. The new pattern which is produced after etching varies greatly with the type of etch. Microscopic examination of some etched surfaces shows minute roughnesses, the various crystals having different appearances. Such a surface gives a diffraction pattern characteristic of some newly formed, and as yet unidentified, surface layer plus what appear to be separate spots falling on the Debye-Scherrer rings of Cu_2O. Under appropriate conditions an etched surface can, however, be produced on which most of the crystals continue to have a rather smooth appearance. The pattern of Fig. 3B came from such a surface. The streaks in this figure, which are approximately parallel to the plane of incidence, appear to be spots on Debye-Scherrer rings which have been displaced and elongated due to refraction and a variable

[4] The crystal which produced the pattern of Fig. 2B was adjusted to make the plane of incidence upon the (0001) face parallel to a [01$\bar{1}$0] direction. It turns out that the strongest features of this pattern are due to the atoms lying along this direction and to planes which pass through this direction as a common zone axis. The spacings and arrangements of these particular atoms and planes happen to be the same for three of the four different crystalline forms of carborundum. Thus one does not readily determine from the pattern of Fig. 2B which of the three structures B5, B6 or even the cubic B3 (Ewald and Hermann *Struckturbericht*) is that of the crystal used. Intensity relations allow one to conclude that the structure is not that described as B7.

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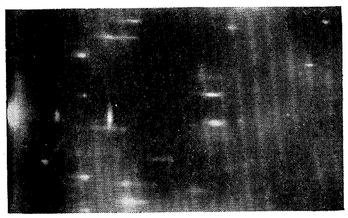


B

FIG. 3. Reflection patterns from Cu_2O. A, smooth unetched surface; B, etched surface.

glancing angle upon the surface of the individual crystal giving rise to each spot. The elongation seems to be like that observed by French[5] for spots from a silver crystal which had been very lightly polished.

The surfaces which produced the patterns of Figs. 3A and 3B were examined microscopically. Both appeared to be relatively smooth, but they were distinctly different. On the former the crystal boundaries were not marked and the entire surface had a uniform glassy appearance. On the latter the boundaries were well defined and, although most of the crystals still seemed rather smooth, this smoothness had become much less perfect. One cannot, perhaps, be certain that this same difference would still obtain if the observations were concerned with roughnesses sufficiently small to be of importance in the diffraction experiments. There is, however, experimental basis for believing that this would be so; visual examination of roughened metal surfaces is a fairly reliable guide to the suitability of the surfaces for electron diffraction.

It is well known that roughened crystalline surfaces do not show refractive effects. These are appreciable only for surfaces which are so smooth that the *true* glancing angles of incidence or emergence are quite small. From the streaks of Fig. 3B one is able to determine that the surface giving this pattern was sufficiently smooth to cause some refractive displacements of diffraction spots, although less than the displacements which one would expect to observe if the surface had atomic flatness. Judging from the microscopic examinations one must conclude that any diffraction pattern arising from the unetched oxide surface would be displaced by refraction to a still greater extent. Nevertheless the rings of Fig. 3A are similar to those reported from polished metals, and have slightly *larger* radii rather than smaller. The amorphous theory requires that the polished surfaces giving rise to such rings be so rough that refractive effects are nonexistant. The microscopic examinations together with the interpretation of Fig. 3B actually indicate, on the contrary, that the diffuse rings are produced by a surface which is so very smooth that refractive effects must be important —unless, of course, the rings arise from some superficial layer of other material.

No adequate explanation of the diffuse rings from very smooth crystalline surfaces is at hand. The careful washing of these surfaces was expected to remove all grease. Tests have, nevertheless, been made upon thick surface layers of grease. These give interesting patterns which are entirely unlike the diffuse rings. Upon the surfaces of the carborundum crystals there must be some extraneous polycrystalline material to account for the traces of sharp Debye-Scherrer rings which are observed. It appears barely possible that the diffuse rings of Fig. 2A may be made up of a large number of sharp rings very closely packed together. In the case of the ZnS and Cu_2O surfaces, however, there are no traces of the resolution of the diffuse rings into constituent parts.

The present experiments do not offer any definite evidence against the amorphous theory. They simply show that the formation of diffuse rings by electrons scattered from polished metal surfaces cannot, at the present time, be construed as evidence that the surfaces are amorphous.

As a speculation regarding the origin of the diffuse rings it seems worth while to point out that fast electrons have never given rise to diffraction patterns which have been attributed to water or gas molecules adsorbed on a surface. Such adsorbed molecules might be expected to produce appreciable diffraction effects only when lying upon exceedingly smooth surfaces, if at all.

[5] French, Proc. Roy. Soc. **A140**, 637 (1933).

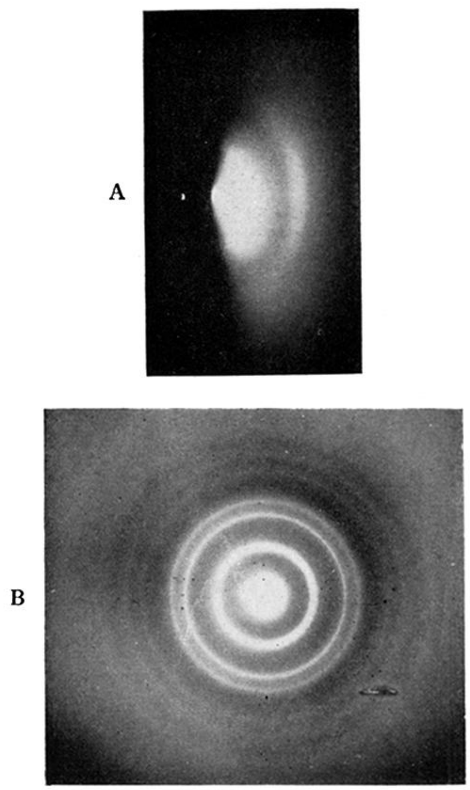


FIG. 1. Diffraction patterns from a ZnS film, deposited by vaporization in vacuum. A, by reflection; B, by transmission.

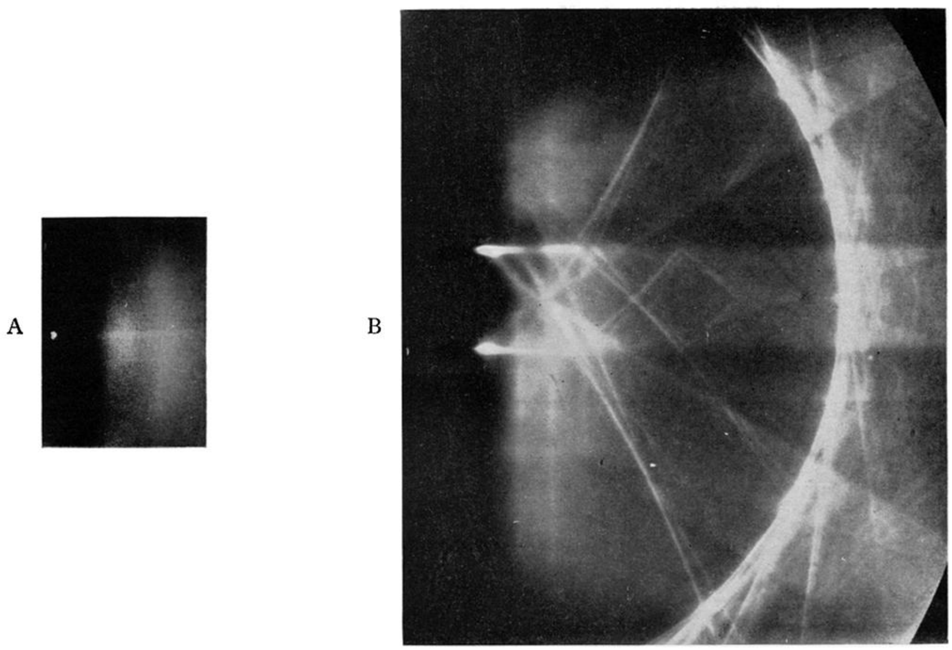
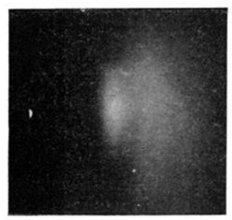


FIG. 2. Reflection patterns from (0001) faces of SiC crystals. A, smooth, unetched surface; B, surface etched in fused KOH.

A



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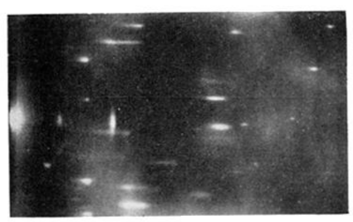

FIG. 3. Reflection patterns from Cu_2O. A, smooth unetched surface; B, etched surface.