phous (or if it contains microcrystals, their orientation must be completely random). On the other hand, the investigators in disagreement with the author, and with each other in respect to line breadth, may have used *crystalline graphite more or less fortuitously orientated* so as to produce narrower Compton lines. In this connection it is interesting to note that on the author's theory *any departure from perfectly random electron momenta will have some narrowing effect.*

3. If the results are positive it may be possible from this experiment to obtain exceedingly valuable information as to the behavior of the outer electrons in crystalline graphite. If these electrons in preferentially orientated orbits form an isolated class well differentiated from the remainder, it may be possible to determine their number relative to the total number of electrons by comparing the area of the sharp peak they contribute with the area of the broader structure associated with the remainder. The interesting bearing of this experiment on the explanation of diamagnetism in crystals is also evident. The breadth of the narrow peak will give perhaps some evidence as to the degree of flatness of these preferentially orientated graphite crystal orbits. Many interesting considerations bearing on the nature of the solid state of matter and the mechanical properties of solid bodies may be closely connected with just such questions.

Second, if the results are negative and no narrow line appears:

1. This will decidedly *not* be negative evidence for the author's theory of Compton line breadth as an effect of atomic electron velocities. *That theory is the only one yet proposed which satisfactorily explains the observed behavior of the breadth as a function of scattering angle and primary wave-length* and this is the strongest possible argument for its correctness.

2. A negative result can be interpreted only as evidence that the outer *electron momenta* in the graphite crystals are not preferentially orientated as postulated above. It will not necessarily mean that the outer electron orbits are not conditioned geometrically by the crystal structure for they may each depart so far from flatness as to approximate an almost random distribution of direction. Or again they may be flat but have such a large number of quantized orientations as to approximate a random distribution to within the power of detection afforded by this method. Thus even a negative result will be to some extent information as to the dynamics of outer electrons in solids.

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December 5, 1931.

The Production of Large Artificial Graphite Crystals

There are two problems brought into the focus of interest very recently which seem to make it desirable to obtain single crystals of graphite of several cm³ size free from occlusions and chemical impurities.

One problem because of which possible methods of producing such crystals had to be considered is the investigation of the dependence of crystal diamagnetism on the size of crystals below certain "critical" dimensions as has been studied by Vaidyanathan,[1] Rao,[2] Mathur and Varma,[3] and in our laboratory in connection with other effects influencing crystal diamagnetism.[4]

The desirability of producing crystals of graphite was furthermore enhanced by the experiments on the Compton radiation from Acheson graphite by Dr. DuMond of this Institute, where the spectral breadth of the modified line has been interpreted by him[5] as due to the fact that the momenta of the electrons of the atoms of the scatterer are oriented at random in a microcrystalline material such as artificial graphite. These considerations led to the planning of the use of single crystalline scatterers as described by him in detail in a letter in this issue of the PHYSICAL REVIEW.

Since the occurrence of single crystals of graphite in nature, sufficiently large and perfect for the proposed types of experiments, is too scarce, (for DuMond's multicrystal spec-

[1] V. L. Vaidyanathan, Ind. Journ. of Phys. **5,** 559 (1930).

[2] S. R. Rao, Ind. Journ. of Phys. **6,** 241 (1931); Nature **128,** 153 (1931).

[3] R. N. Mathur and M. R. Varma, Ind. Journ. of Phys. **6,** 181 (1931).

[4] A. Goetz and A. B. Focke, Phys. Rev. **38,** 1569 (1931).

[5] J. W. M. DuMond, Phys. Rev. **33,** 643 (1929).

trograph not less than 50 equal crystals of ca. $10\times10\times30$ mm are needed) a method for artificial production had to be developed.

The usual ways of crystal growth by crystallization out of the liquid phase or by recrystallization however are unfeasible because of the high vapor pressure of graphite in these temperature regions. One way out of this difficulty is given by the abundant natural occurrence of almost single crystalline graphite powder, represented by the flake-like consistency of the Ceylon-mineral. The particles of this powder are thin plates, only a few microns thick and 3–0.01 mm in diameter; the planes of these plates coincide more or less with (0001) which is the principal cleavage plane. A system of lines on these planes indicates the existence of twinning or gliding planes of rhombohedral character.[6] The imperfection of these planes of the natural graphite is however very large and causes the thickness of the plates to be very irregular. A high powered microscope shows that this is due to adhering lamellae of other individuals, as shown in the microphotograph Fig. 1. In order to obtain large crystals it was planned to pile these flakes in such a way as to orient their principal axes all parallel and to fix them in this position by means of a neutral adhesive. Experiments however showed that this was not possible because of the mentioned imperfection of the (0001) planes.

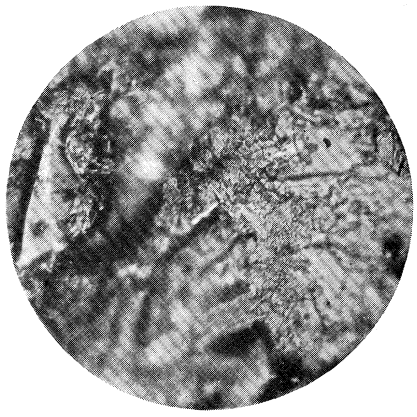

Fig. 1. Microphotograph of the surface of a flake of untreated Ceylon graphite, $495\times$ magnified. It shows the inhomogeneity due to adhering crystal fragments.

The conjecture that the imperfections of the flakes were due to impurities proved to be right, since the measurements of the magnetic susceptibilities by Mr. Focke of this Institute on those crystal cakes showed large amounts of iron which necessitated the use of a thorough extraction method with HCl worked out by Dr. Faessler. Repeated magnetic and chemical tests proved the necessity of extracting for periods of several days after which time no ferromagnetic susceptibility could be traced. The microscopic observations however did not show much improvement of the cleavage planes but the presence of SiO_2 deposits on the (0001) planes was found with the polarization microscope. Therefore the graphite underwent first a treatment in HF before the iron was extracted. Now the cleavage planes were almost perfect although the size of the flakes had decreased considerably by the chemical process. Fig. 2 shows a microphotograph of such a plane which shows now only a pattern of small holes similar to etching figures.

Fig 2. Microphotograph of the surface of a flake from which SiO_2 and Fe were removed (0001) plane, $495\times$ magnified. The surface is much more uniform and shows a pattern indicating the crystallographic symmetry.

From the investigations of Honda and Soné[7] it is known that graphite crystals show an unusually large diamagnetic anisotropy, such that the susceptibility parallel to the axis [0001] is 7 times large than perpendicular to it, whereas the azimuthal variation of the susceptibility is apparently zero, a phenomenon

[6] P. Niggli, Spezielle Mineralogie Pag. 361.

[7] K. Honda and N. Soné, Sc. Rep. Tohoku Univ. **2**, 1 (1913).

which now is almost to be expected from the knowledge of the lattice arrangement. This large anisotropy suggests immediately a method of lining up the perfected flakes: the purified flake powder was suspended in a solution of 3 percent gum Damar in benzene and was then allowed to settle within the inhomogeneous field of a strong electromagnet. After the flakes had settled, the benzene was evaporated and a cake was obtained which possessed considerable rigidity due to the adhesive qualities of the gum. It is obvious that it is very easy to produce such artificial crystals of any size desired. A large advantage of this method is the possibility of using the Gouy method for the exact determination of the magnetic qualities of the graphite crystals with respect to the orientation, which measurement can also serve as indicator of how well the flakes are lined up.

Mr. Focke performed these measurements which show the effect the perfection of the cleavage planes have on the anisotropy of the artificial crystals, being largely influenced by quartz deposits. Crystal blocks free from Fe, however, in presence of SiO_2 showed anisotropy $(\chi_\parallel/\chi_\perp)=4$ which is much less than Honda's observation on a natural crystal. If however the quartz is removed by HF *the anisotropy is increased to 13.2.* There can be little doubt that the line-up of the flakes is still imperfect and estimates of the possible variations seem to indicate that the true anisotropies may reach values up to 20, assuming the validity of the relation:

$$\chi_\perp = \chi_\parallel - (\chi_\parallel - \chi_\phi)/\sin^2\phi,$$

where ϕ designates the mean deviation of the flakes from the correct direction. Fig. 3 shows a photograph in almost natural size of such an artificial crystal broken so as to show the arrangement of the flakes. With the exception of the tin-alloyed Bi crystals[4] these crystals show by far the largest anisotropic diamagnetism known so far.

The method described can be modified in order to measure the oriented susceptibilities of very small crystals, as is essential for the investigation of the dependence of crystal diamagnetism on the dimensions of the particle. For this purpose the purified flakes are ground under special precautions and the powder obtained is settled in an agar solution in order to segregate in different sizes. As soon as the largest particles have settled, the agar solution is solidified, thus fixing each particle in its position. If the whole process is performed in an inhomogeneous magnetic field, all particles are forced into positions which are crystallographically parallel. Thus the agar block forms a kind of a graphite single crystal in which each horizontal layer consists of parallel particles of the same size, the susceptibility and anisotropy of which is easy to determine.

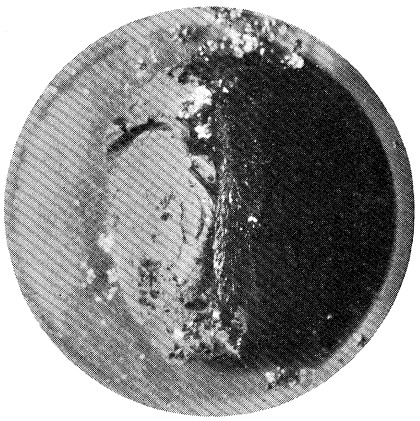

Fig. 3. Photograph of an artificial graphite crystal of approximately natural size. The crystal was broken to show the alignment of the flakes.

The results obtained from these "crystals" are thought to contribute an interesting addition to our knowledge of the nature of the crystal electrons.

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December 7, 1931.

Some Remarks on the Theory of Photoelectric Effect on Metals

In the July, 1931, issue of this Journal appeared a paper by Frenkel,[1] containing among other matters a criticism of a theory of photoelectric effect on metals, advanced recently by Mr. Schubin and me.[2] It is easy to see that

[1] J. Frenkel, Phys. Rev. **38,** 309 (1931).

[2] Ig. Tamm und S. Schubin, Zeits. f. Physik **68,** 97 (1931).

Fig. 1. Microphotograph of the surface of a flake of untreated Ceylon graphite, 495× magnified. It shows the inhomogeneity due to adhering crystal fragments.

Fig 2. Microphotograph of the surface of a flake from which SiO_2 and Fe were removed (0001) plane, 495× magnified. The surface is much more uniform and shows a pattern indicating the crystallographic symmetry.

Fig. 3. Photograph of an artificial graphite crystal of approximately natural size. The crystal was broken to show the alignment of the flakes.