SYMPOSIUM on ELECTRON DIFFRACTION STUDIES of SOLIDS and GASES

. . . *an impression* . . . *By James A. Ibers*

A SYMPOSIUM on Electron Diffraction Studies of Solids and Gases was held July 17–19 at McGill University, Montreal, Canada, following the Fourth General Assembly and International Congress of the International Union of Crystallography. This is the first meeting at which there has been wide representation of laboratories active in the field of electron diffraction, and there can be no doubt that the participants have obtained both a better understanding and appreciation of one another's work and also a better oriented view of the field as a whole. This Symposium was typical in the sense that much more was learned from informal discussions than from formal papers. For this reason in this review an attempt is made to summarize current problems and areas of research in the field of electron diffraction, rather than to review one by one the papers presented. It seems expedient to discuss the developments in electron diffraction of gases separately from those in electron diffraction of crystalline solids, since the experimental and theoretical problems are generally quite different.

The study of molecular structure by the gas diffraction method has been pursued actively in many laboratories since the mid 1930's. The diffraction pattern, which contains the molecular scattering of interest superimposed upon the rapidly changing background of incoherent and atomic scattering, has until recently generally been interpreted visually, the eye being able to discern changes in intensity even on a rapidly decreasing background. Moreover, the first Born approximation, that is the assumption that the primary wave is perturbed but little by the atomic field, has served as the basis for the calculation of the theoretical scattering functions to be compared with the visually perceived molecular scattering curves. In the hands of careful investigators (since the visual method of interpreting electron diffraction patterns requires both skill and experience) the details of the structures of hundreds of molecules have been elucidated in this way, and bond distances have been determined typically to an accuracy of 0.02 to 0.05 A.

The major experimental advance of the last five years has been the perfection by O. Bastiansen and co-workers at Oslo and Trondheim, Norway, of the rotating sector method to replace the visual method. A sector or disk, shaped in such a way that when rotated the background due to incoherent and atomic scattering is flattened out, is interposed between the sample and the recording plate. The resulting diffraction pattern, which now contains the molecular scattering on a rather smooth background, can be interpreted with the aid of a microphotometer. At the Symposium Bastiansen summarized his feelings about the current status of the sector method. For molecules containing atoms of approximately equal atomic number (see below) he can obtain internal consistencies of bond distances of 0.001 A and an estimated accuracy of determination of 0.003 to 0.005 A. Although there is not complete agreement as to procedure, most workers in the field who have sector cameras do appear to agree that accuracies of the order of 0.005 A for bond distances can be obtained.

The important theoretical development of the last five years has grown out of the realization by V. Schomaker and R. Glauber at Caltech that the first Born approximation is not valid for heavy atom–light atom molecules. Schomaker and his collaborators have shown that UF_6 and other heavy atom–light atom molecules give diffraction patterns which may be interpreted correctly only if the atomic scattering functions for electrons are complex, as predicted by approximations of higher order than the first Born approximation. Using this latter approximation, which yields only real atomic scattering functions, molecules such as UF_6 appear to be asymmetric in disagreement with the results of other physical methods. At this Symposium Schomaker com-

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pared the results obtained experimentally from visual data with the calculations of J. A. Hoerni and J. A. Ibers. In these calculations the atomic scattering factors were obtained from the partial waves scattering theory on the assumption of a Thomas-Fermi potential function, and the molecular scattering was obtained from the atomic scattering factors essentially by a Born approximation method, a procedure which Hoerni has shown to be valid. Unfortunately, it is only in the region where the difference in phase between heavy and light atoms approaches 90° that the visual data allow a sensitive test of the theoretical calculations, and here the agreement between theory and experiment is good. More adequate tests of various scattering models should be possible when sector data become available for heavy atom–light atom structures.

In summary the electron diffraction method incorporating the rotating sector now appears to be the most accurate general method for the elucidation of the molecular structures of compounds containing atoms of approximately equal atomic number. Furthermore, sector data on heavy atom–light atom compounds should enable us to learn more about scattering processes, and ultimately to determine bond distances in these compounds to comparable accuracy.

THE study of crystalline solids by electron diffraction techniques has developed rapidly in the last few years. Electron diffraction cameras of high resolution and stability have been developed primarily as a result of experience gained in the construction of commercial electron microscopes. Two applications of high resolution electron diffraction cameras reported at this Symposium were the precision determination of lattice constants by H. Raether of the University of Hamburg, Germany, and the study of fine structure in the diffraction spots from single crystals by K. Moliere of the Fritz-Haber Institute, Berlin. These studies are of great interest in themselves, but the major subject of discussion at the Symposium was the determination of crystal structures by electron diffraction techniques.

Techniques of structure determination by electron diffraction were developed for polycrystalline materials by Z. G. Pinsker and co-workers at the Institute of Crystallography, Moscow, USSR, and for single crystals by J. M. Cowley and A. L. G. Rees at CSIRO, Melbourne, Australia. Structure analysis by electron diffraction is complementary to structure analysis by x-ray diffraction: Two important advantages of the electron diffraction method are first that with this method exceedingly small crystals can be studied, and second that electrons are scattered relatively better by light atoms in relation to heavy atoms than are x-rays. In his introductory lecture Pinsker reviewed the Russian work in this field and gave many examples of successful structure analyses of inorganic compounds, organic compounds, and alloys. Other interesting determinations reported upon were the structure of cubic ice by G. Honjo and S. Miyake of the Tokyo Institute of Technology, and the structure of an anti-phase domain in the ordered alloy Au_3Mn by S. Ogawa and D. Watanabe of Tohoku University, Sendai, Japan.

Most of the discussions both in and out of the Symposium were concerned with attempts to reconcile the apparently unfavorable predictions of scattering theory on the one hand with successful structure determinations on the other. Structure determinations to date have been based on the familiar kinematic scattering approximation in which it is assumed that the primary beam is disturbed but little by the crystal field and from which it follows that the intensity of scattering is proportional to the square of the structure amplitude. This kinematic approximation is strictly valid only in the limiting case of crystals of zero thickness. With crystals of thickness greater than perhaps a few hundred Angstroms effects are observed which have been explained on the basis of a dynamic scattering theory in which the interaction of scattered waves with the crystal is taken into account. Most calculations of dynamic effects have been based on the two-wave approximation to Bethe's dynamic scattering theory; such an approximation in the case of polycrystalline material leads to the result that the intensity of scattering should be proportional to the first power of the structure amplitude. Some evidence for such a dependence has been found. Usually, however, the dependence of intensity of scattering on structure amplitude lies between the kinematic and dynamic limits, and therefore means of deriving the kinematic intensities must be found. At this Symposium several methods were advanced to allow correction of the intensities for dynamic scattering effects. B. K. Vainshtein of the Institute of Crystallography, Moscow, USSR, discussed a method of correction in which an average over the crystallite size is

The 4th General Assembly and International Congress of the International Union of Crystallography, held July 10–17 in Montreal, was followed by two major symposia: one on physical techniques of crystallographic interest, and the second (which is reported above) on electron diffraction. At right are shown the members of the new Executive of the Union: (front row, left to right) N. V. Belov (USSR), J. Wyart, president (France), P. P. Ewald (USA), D. Smits, secretary (Netherlands); (second row) I. Nitta (Japan), A. J. C. Wilson (UK), Miss C. M. MacGillavry (Netherlands), F. Laves (Germany); (third row) R. W. G. Wyckoff (USA), A. Guinier (France), and O. Bastiansen (Norway).

made. Miyake described a method due to Honjo and Kitamura in which extrapolation to zero thickness of the crystallites is achieved by studies of the intensities over a range of wavelengths. Honjo described the application of a procedure due to Nagakura, based on Wilson's intensity statistics, for the correction of the intensities. In addition to corrections for dynamic effects other corrections seem necessary in some cases. J. A. Hoerni of Shockley Semiconductor Laboratory, Mountain View, California, pointed out that analogous to the case of gas molecules if the crystal contains both heavy and light atoms the first Born approximation is not valid and it is then necessary to employ complex atomic scattering functions in the calculation of intensities. Vainshtein discussed the necessity of taking into account a Lorentz factor in the reduction of intensities. Raether of Hamburg and L. Marton of the National Bureau of Standards, Washington, D. C., indicated that inelastic scattering contributes appreciably to the intensities of Bragg reflections. It remains to be seen whether or not corrections for inelastic scattering will be important, since it may be that the inelastic contribution is proportional to the elastic one.

The gross details of many structures have been elucidated by electron diffraction techniques in the past without taking into account all of these corrections. On the other hand the discussions at this Symposium served to indicate that the intensities of electron diffraction patterns must be considered much more carefully in the future if the accuracy of structure determinations is to approach the accuracy possible in the x-ray diffraction case.

The requirements for the determination of crystal structures by electron diffraction studies of single crystals are more exacting both in experiment and theory. At this Symposium considerable discussion was devoted to the theoretical problems involved. The two-wave approximation to the dynamic theory leads to fundamental difficulties when applied to the case of finite single crystals. On the other hand more accurate calculations from the dynamic theory are both exceedingly tedious and extremely dependent upon the assumed orientation and shape of the crystal. For this reason new approaches to the problem of the scattering of electrons from single crystals are needed, and two such approaches were discussed at the Symposium. L. Sturkey of the Dow Chemical Company, Midland, Michigan, assumed the crystal to be broken up into a large number of thin layers and then considered Fraunhofer diffraction of both the incident and scattered waves from each such layer. He concluded that considerable deviations from kinematic intensities were possible for quite thin crystals, and suggested that observed intensities could not be used for structure analysis. Cowley discussed an approach developed in collaboration with A. F. Moodie. In this approach a similar subdivision of the crystal was assumed, and Fresnel diffraction from each individual layer was considered. Cowley and Moodie also concluded that there would be considerable deviation of the intensities from those predicted from the kinematical approximation, but that these deviations should provide additional information which would facilitate structure determinations. Both of these calculations apply to ideal, perfect crystals, but experience has shown that in practice one deals almost exclusively with imperfect crystals. Real crystals contain imperfections in the form of dislocations, stacking faults, mosaic structure, etc., and there is an obvious need for calculations of scattering of electrons from crystals with such imperfections. In general the presence of imperfections will in effect extend the range of applicability of the kinematic approximation. This is undoubtedly the principal reason why structure analysis from single-crystal data has been successful. On the other hand increased accuracy of such structure analyses must await more complete theoretical studies of scattering from imperfect crystals, and must take into account many of the corrections mentioned above for polycrystalline materials.

The field of electron diffraction has long suffered due to lack of interchange of ideas among people of widely different background and experience, and the real value of the Symposium at Montreal was to facilitate such an interchange. There is now a much better general understanding of the problems of importance and the directions in which progress may be made in electron diffraction. The general enthusiasm for continued interchange of ideas was high at this meeting, and there was a desire on the part of most of the participants from all countries for the establishment of an international organization of electron diffractionists. To that end a Commission on Electron Diffraction within the International Union of Crystallography has been established with the following members: L. O. Brockway (USA), Chairman; O. Bastiansen (Norway); M. Blackman (UK); J. M. Cowley (Australia); S. Miyake (Japan); Z. G. Pinsker (USSR); H. Raether (Germany); and J. J. Trillat (France). It was hoped that through the agency of the Commission further International Symposia on Electron Diffraction could be organized, the first, perhaps, in about two years.

Members of the Commission on Electron Diffraction of the International Union of Crystallography: (front row, left to right) Z. G. Pinsker (USSR), L. O. Brockway, chairman (USA), H. Raether (Germany); (back row) O. Bastiansen (Norway), M. Blackman (UK), J. M. Cowley (Australia), S. Miyake (Japan). The eighth member of the Commission, J. J. Trillat (France), was not present at Montreal.