THE INVESTIGATION OF THE STRUCTURE OF CRYSTALS
BY ELECTRON DIFFRACTION METHODS.

By

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Being a collection of published works, with explanatory notes, submitted in support of his candidature for the degree of Doctor of Science of the University of Adelaide.

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PREFACE.

During the years 1945 to 1947 and 1949 to 1956 the candidate has worked in the laboratories of the Chemical Physics Section, Division of Industrial Chemistry of the Commonwealth Scientific and Industrial Research Organisation. In this period most of his time has been spent in research of a fundamental nature in the field of electron diffraction, with emphasis on the development of new experimental and interpretative techniques, rather than on the application of existing techniques to problems of surface physics or chemistry. The publications herewith submitted contain reports of some of this work.

As far as can be ascertained, none of this work reproduced or duplicated work carried out in any other laboratory, and was original with the candidate except to the extent indicated by the acknowledgements given in the text or mentioned in the notes on individual papers given below.

In the few years preceding the inception of the electron diffraction group within the Chemical Physics Section in 1945, the increasing interest in electron microscopy lead to the development of precision electron-optical techniques. Rapid progress was made in the design of electromagnetic lenses of short focal length, and very stable power supplies were developed to provide the energising currents for the lenses and the voltages of 20 to 100 kV used to accelerate the electron beams. At that time, such precision techniques were not applied in electron diffraction work except in a few isolated cases where diffraction patterns were obtained by introducing electron diffraction adapters into electron microscopes. These rather limited experiments had indicated that patterns could be obtained in this way having much better resolution than was possible with the electron diffraction instruments then in use.

The first electron diffraction work in the Chemical Physics Section was carried out using the diffraction adapter of the RCA electron microscope, type EMU, modified to improve its performance. The resolution of the diffraction patterns was sufficiently good to allow us to study previously unresolved detail in the fine structure of diffraction spots given by small crystals of regular shape. This work is reported in papers 1 and 2.

Our experience in the use of the electron microscope diffraction adapter influenced the design of the electron diffraction camera which was built in the Section (paper 7). The resolving power of this instrument was superior to that of any other then existing. Especially after the electron-optical system was modified (in 1950-51), the resolving power could be taken to the practical limit set by the brightness of the available electron sources. More recently a second and more elaborate instrument has been designed and built to allow the full range of electron microscopy and electron diffraction techniques to be applied to the examination of any sample. No description of this instrument has yet been published.

The unique properties of the former instrument have been exploited in the development of two new fields of application of electron diffraction. By focussing the electron beam on the photographic plate we have obtained good resolution of the fine structure detail of diffraction spots from very small crystals. In this way we have studied the effects of the shapes, structures and defects of crystals on the shapes and subdivisions of diffraction spots. A more complete study (not yet published) has been made of the fine structure given by small cubic crystals of magnesium oxide. This work provided a valuable test for the dynamic theory of the diffraction of electrons and led to the development of a method for deducing the potential distribution in a crystal lattice from the fine structure dimensions. Studies of crystals of zinc oxide smoke (paper 4) and copper oxide (paper 13) have been made, giving, in each case, information on the relation of the crystal morphology to the lattice structure.

Alternatively, the precision of the electron-optical system could be exploited in focussing the electron beam on the specimen so that a diffraction pattern could be obtained from a very small area of the specimen, no more than a few microns in diameter. In this way single crystal patterns were obtained from very small crystals, some of them not more than a few hundred Ångstroms thick. It was confirmed that the intensities of the spots given by such crystals are directly related to the crystal lattice structure. The spot intensities may then be used as a basis for the structure analysis of crystals by Fourier series techniques similar to those used in the structure analyses of crystals based on the intensities of x-ray diffraction spots.

A group of workers in Russia have, since 1949, made structure analyses from electron diffraction data, but they have used patterns from polycrystalline material almost exclusively. There are inherent limitations in this method. Structure analyses based on single-crystal electron diffraction data had not previously been attempted and, indeed, were generally considered impossible principally because, when electron beams of comparatively large cross-section are used, as is customary in electron diffraction cameras, the probability that an appreciable part of the pattern is given by very thin crystals is very small. The intensities of the spots given by the thicker regions of the crystals are not simply related to the crystal structure, and so can not be used as a basis for structure analyses.

The practicability of crystal structure analysis from the spot patterns given by very small single crystals has been examined, and experimental and interpretive techniques have been developed for its exploitation (papers 5, 8, 10, 14, 15), These techniques have been employed in investigations of the structure of very small crystals of boric acid (papers 9, 10), oxides of alumina (papers 6, 11), basic lead carbonate (paper 16) and a graphite - ferric chloride compound (paper 17).

Apart from these two principal fields of research work, various applications of electron diffraction techniques to chemical problems have been made (e.g., paper 3), some theoretical work on the physical optics of electrons has been done (paper 12, and other work submitted for publication) and attention has been given to the design and construction of computing devices for carrying out the arithmetical manipulations involved in the processes of structure analysis by Fourier series methods.