ELECTRON MICROSCOPY
OF
THIN CRYSTALS

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PREFACE

In 1963 The Institute of Physics and The Physical Society circulated a questionnaire amongst the members of its Electron Microscopy Group with the aim of discovering the need for courses on electron microscopy. The replies showed that there were a number of people who while being fully conversant with the basic principles and operation of the electron microscope, were unable to use it to the best advantage and would welcome a course on advanced operational techniques, the theory of electron diffraction and the interpretation of diffraction patterns and contrast on electron micrographs. In order to meet this need a Summer School was held in Cambridge in July, 1963, with the present authors as lecturers. The School consisted of a series of twenty lectures backed up by examples classes and demonstrations on the electron microscope.

The School attracted very wide interest not only from the United Kingdom but also from the rest of Europe and from the U.S.A.; the number of places had to be limited and it was heavily over-subscribed. In view of the strong interest in this approach to the subject, it was considered worth while to record the lectures in a more permanent form and the present book is the result. Although there have been several major alterations of the original lectures and the whole course has been streamlined and brought up-to-date, the book inevitably has the same pattern as the Summer School and is aimed at satisfying the same need for fairly advanced instruction in the electron microscopy of crystalline specimens. Thus the book is selective rather than comprehensive in the detailed subject matter; there is no general treatise on the design and construction of the instrument itself; a knowledge of related topics such as crystallography, classical optics and quantum mechanics is assumed, and the various applications to crystalline specimens are considered solely for their intrinsic interest to electron microscopy and not in relation to the wider fields to which they belong.

The examples classes were found to be a very useful part of the Summer School and consequently many of the problems have been reproduced in Appendix 6 with solutions given in Appendix 7. We are grateful to M. F. Ashby, C. Baker, G. R. Booker, L. M. Brown, J. D. Embury, G. W. Groves, P. Hazzledine, J. Jakubovics and J. W. Steeds for providing the material for these problems.

All micrographs reproduced in this book have been taken at an operating voltage of 80 or 100 kV.

CONTENTS

CHAPTER 1

THE ELECTRON MICROSCOPE

1.1. BASIC DESIGN OF THE ELECTRON MICROSCOPE

The electron microscope is now a well-established research tool both in the biological and physico-chemical domains, and there are several authoritative texts and review articles dealing with the special field of electron optics and with the design of the instrument (Zworykin and colleagues, 1948; Cosslett, 1950; Klemperer, 1953; Hall, 1953; Sturrock, 1955; Ruska and Wolff, 1956; Leisegang, 1956). It is not, therefore, the aim of this chapter to give a detailed account of the design of the instrument, but rather to acquaint the reader with the most important electron optical principles which must be clearly understood so that he may utilize the available facilities of a modern high resolution instrument to the best advantage in transmission work with crystalline materials. The reader is therefore assumed to be familiar with the basic principles of electron optics and of the design of the instrument. He who requires knowledge of electron optics on a broad front should consult the references cited above, although for specific (but less explicit) accounts of particular instruments he is advised to study the handbooks issued by various manufacturers.

An electron microscope consists of an electron gun and an assembly of electron lenses as shown in *Figure 1.1*. This depicts schematically the ray paths in a microscope employing three stages of magnification and a single condenser lens system for illuminating the specimen. The lenses may be either of the magnetic or electrostatic type, although, due to the development of electronically stabilized sources of current and beam voltage, the magnetic lens is nowadays used almost exclusively because of its smaller optical aberrations and its freedom from the usual troubles associated with high voltages. Many early electron microscopes employed two stages of magnification. In modern high resolution instruments the use of three stages of magnification (objective, intermediate lens and projector), often with a double condenser lens illuminating system, has become a fairly standard design. For details of the procedure to be followed in aligning the microscope, reference should be made to the handbooks of individual instruments or to Agar, 1961.

The most critical component of a magnetic lens is the soft-iron pole-piece (*Figure 1.4*), which produces an axially symmetric magnetic field for focusing the electrons. The rest of the lens is a magnetic yoke containing the windings for energizing the lens with d.c. current and varying the focal length of the pole-piece system. The specimen to be examined by transmission of electrons is placed near the entrance to the bore of the objective lens pole-piece, the design and perfection of which most influences the electron optical performance of the microscope. The magnified image I_1 (*Figure 1.1*) produced by the objective is called the first intermediate image. This serves as an object for the intermediate lens which produces a second intermediate image I_2, and this is magnified further by the projector lens to produce the final image on the fluorescent viewing screen. The photographic plate for recording the image is placed immediately below this. Typical approximate magnifications produced by the various stages are:

objective lens $\times 25$

intermediate lens $\times 8$

projector lens $\times 100$

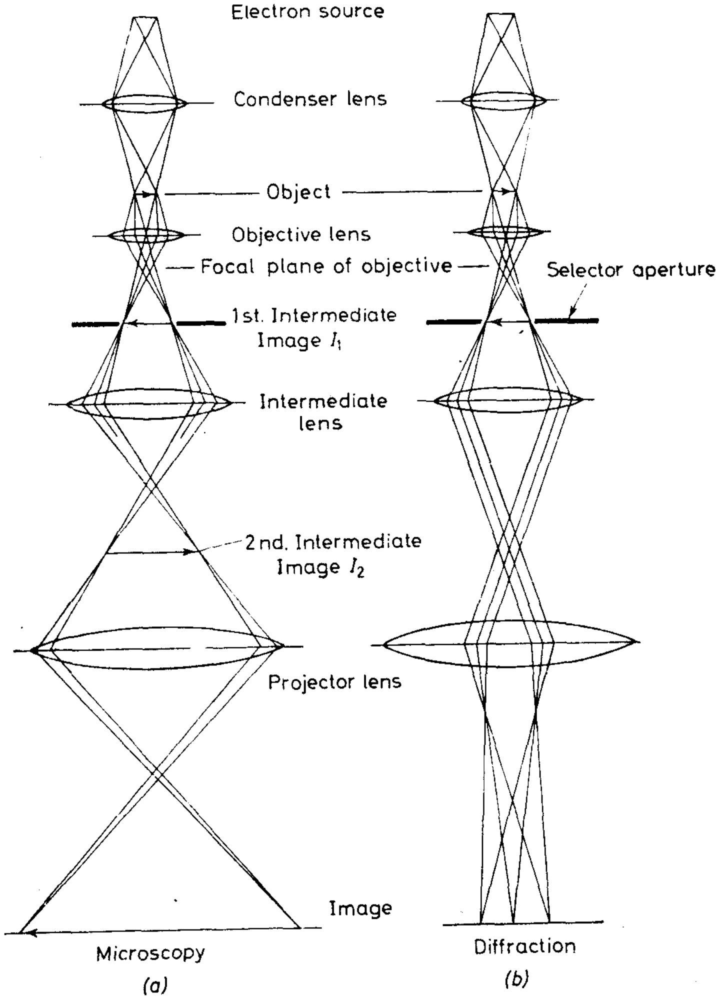

Figure 1.1. Ray paths in the electron microscope (a) under microscopy conditions and (b) diffraction conditions

Thus a total magnification of about 20,000 is obtained on the viewing screen, which is a convenient magnification for examination of many defects in crystalline materials. Since the specimen is usually in a fixed position in the objective pole-piece bore, the magnification of this stage is fixed*. The final magnification may be varied by regulating the energizing currents of either the intermediate or projector lenses. In some microscopes, for example the Elmiskop 1, the projector is for convenience adjusted to a standard magnification, control over total magnification then being obtained by varying the current in the intermediate lens alone. The Elmiskop 1 contains a removable fluorescent screen in the second intermediate image plane, which enables a low magnification image of the specimen to be quickly observed, a feature which is very useful for surveying the specimen to locate thin areas. This instrument also has facilities for exchanging the projector pole-piece during operation, so that low magnification, distortion-free images may be obtained by using a pole-piece of wide bore, while pole-pieces of smaller bore enable total magnifications of up to $\times 160,000$ to be obtained. The pole-piece of widest bore is wide enough to enable both low magnification images ($\times 200$ using the objective lens alone) and transmission diffraction patterns (using the condenser system alone) to be obtained without dismantling the column. In this last case, however, for optimum results the objective pole-piece should be removed, since its residual magnetization causes slight distortion of the pattern.

Facilities are also provided for introducing apertures into the bores of the various lens pole-pieces. Platinum and molybdenum apertures are the most common. With a double condenser lens system (Section 1.7) condenser 1 usually contains a fixed aperture of about 400 μ diameter. Condenser 2 may be equipped with a range of interchangeable apertures of about 100 to 400 μ diameter. The objective lens also has interchangeable apertures of about 10 to 50 μ diameter. For selected area diffraction, apertures are inserted in the first intermediate image plane during examination of the specimen.

1.2. IMAGE FORMATION AND CONTRAST. SELECTED AREA DIFFRACTION

Figure 1.2 illustrates the mechanism of production of contrast on transmission micrographs. The almost parallel illuminating beam of electrons is scattered by the specimen. In the case of crystalline materials this scattering takes the form of one or more Bragg diffracted beams travelling at small angles (~ 1 or 2 degrees) with the incident beam, which are focused by the objective to form a transmission diffraction pattern in its back focal plane. If the objective lens were perfect, it would be possible to form a resolved image of the crystal lattice planes giving rise to the diffracted beams by allowing all the beams to reach the final image and interfere according to the usual Abbe theory of image formation of a periodic object (see for example, Jenkins and White, 1951). However, the spherical aberration of the objective lens and other effects combine to make this difficult to achieve except in the case of thin specimens with large lattice spacings (Menter, 1956, see Chapters 7, 15). In work with metal foils the lowest order Bragg reflections encountered correspond to lattice spacings of about 2 Å and the effects mentioned above make

* This statement applies specifically to the selected area diffraction condition where the intermediate image I_1 coincides with the selector aperture plane (see Section 1.2). The magnifications of the various stages quoted above would be typical of this condition for the Siemens Elmiskop 1. In other circumstances a somewhat higher intermediate lens magnification and a lower projector lens magnification might be typical.

direct resolution of the lattice difficult. The image contrast is therefore usually produced by an entirely different mechanism which does not aim at revealing the atomic structure.

An aperture is inserted in the objective lens as shown in *Figure 1.2.* This aperture does not allow Bragg reflections to pass through to the final image, which is therefore formed by the direct beam and any low angle inelastic scattering. This type of image is called a *bright-field image.* The contrast is therefore produced by differences in intensities of electrons scattered into Bragg reflections from various parts of the thin specimen and is consequently called 'diffraction contrast'. A 30 μ diameter objective aperture would correspond to a semi-angular aperture of about 5×10^{-3} rad in a typical objective of focal length about 3 mm. A typical 2θ value for the angle of deflection of a low order diffracted beam is $\sim 2 \times 10^{-2}$ rad. It is seen that the diffracted

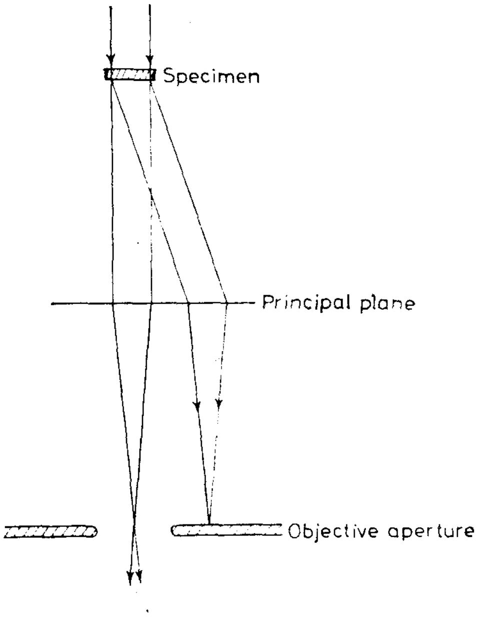

Figure 1.2. Mechanism of diffraction contrast

beam does not pass through the aperture. In discussions involving the objective aperture it is usually assumed that the objective aperture lies in the back focal plane of the objective as shown in *Figure 1.2.* In practice it is not convenient to place it there, because this plane usually lies in the bore of the lower pole-piece (*Figure 1.4a*). The objective aperture is usually positioned centrally in the pole-piece gap. However, the diffracted beams from an area a few microns in diameter are sufficiently well separated in the central gap plane to enable the aperture to be just as effective in the raised position.

Images can be formed by any one diffracted beam by either displacing the aperture to receive this beam, or by tilting the illumination so that the required beam passes down the axis of the objective. The resulting image is known as a *dark-field image.* Much useful information can be obtained by this technique and it will be discussed in detail in Chapter 13.

Figure 1.3 illustrates the production of the first intermediate image by the objective lens. Under microscopy conditions the intermediate plus projector system is focused on the I_1 plane, and produces a magnified image of this plane on the final screen. The intermediate lens can, however, be reduced in strength so that the back focal plane of the objective is focused on the final screen. Thus, the transmission diffraction pattern of the illuminated area of the specimen will then be observed. If an aperture of diameter D is placed in the I_1 plane and if the objective lens behaves as a perfect lens, only those electrons passing through an area of diameter D/M on the specimen will reach the final screen, where M is the magnification of the objective. In practice, D may be about 25 μ and since M is about 25 in a typical case, the diameter of the area selected on the object is about 1 μ. The diffraction pattern of this area only is therefore observed. This technique, first developed by Le Poole, 1947, is known as selected area diffraction. It enables diffraction patterns to be taken from small areas of the specimen, so that a correlation between the features observed on the micrographs and the crystallography of the specimen

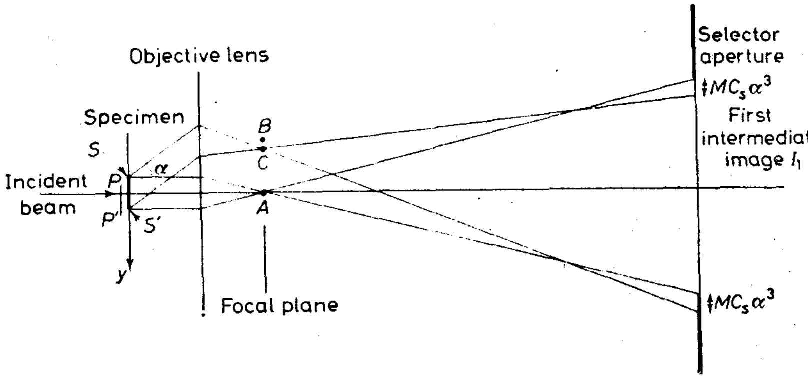

Figure 1.3. Formation of the first intermediate image by the objective lens

can be made. It is also very useful for identifying phases in an inhomogeneous specimen. The technique is subject to certain errors, both systematic and random, which are discussed in Section 1.8.

It should be noted that for correct operation of selected area diffraction, the intermediate image plane is fixed, because the intermediate aperture drives are usually in a fixed position. The intermediate lens is focused on this fixed plane and the final magnification (for constant projector current) is therefore invariant. In the Elmiskop 1, for example, this final magnification is $\times 20{,}000$. At other magnifications it is necessary to change the strength of the intermediate lens to achieve this magnification and to refocus the objective before taking the selected area diffraction pattern, otherwise errors are incurred which are equivalent to incorrect focusing of the objective (Section 1.8). The procedure for selected area diffraction is as follows. The intermediate lens is first focused on the intermediate image aperture. The correct position is easily found by removing the objective aperture so that wide angle scattering contributes to the image I_1. If the intermediate lens is incorrectly focused, the image of the selector aperture is surrounded by halation due to the wide angle scattering. At correct focus the halation disappears and the selector aperture appears clean and sharp. The objective aperture is then replaced and the image is refocused with the objective. This ensures that the image I_1 and the selector aperture are coincident. The correct conditions for selected area diffraction are now obtained. *Figure 1.1b* shows the ray paths through the lenses of a three-stage microscope for the selected area diffraction condition.

1.3. PROPERTIES OF MAGNETIC ELECTRON LENSES AND THEIR ABERRATIONS

The performance of a magnetic lens depends on its pole-piece, the essential geometry of which is illustrated in *Figure 1.4a*. The important parameters are the spacing S of the upper and lower pole-pieces and the radii R_1 and R_2 of the bores of the upper and lower parts. It can be shown (see Hall, 1953) that electrons travelling at small angles to the axis are focused by the magnetic field

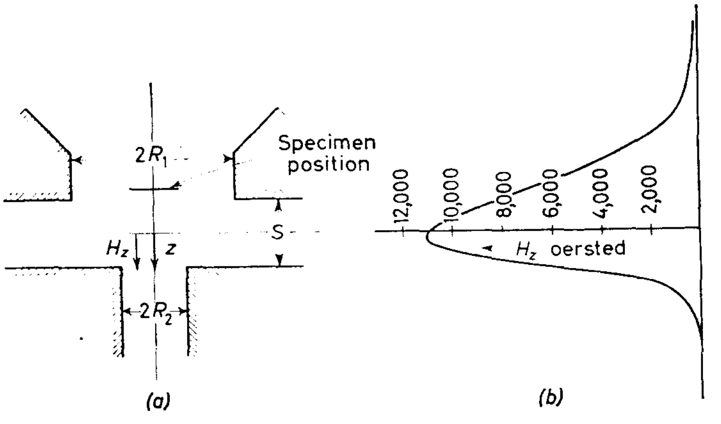

Figure 1.4. (a) The geometry of the objective pole-piece. (b) The axial distribution of the z-component of magnetic field. The geometry is for the Siemens Elmiskop 1 for which $2R_1 = 6{\cdot}5$ mm, $2R_2 = 2{\cdot}6$ mm *and* $S = 2{\cdot}7$ mm

H of the pole-piece. The equations of motion of the electron in the axially symmetric magnetic field lead to the well-known paraxial ray equation, which predicts quite generally the image-forming properties of the field. When the axial extent of the magnetic field is small compared with the focal length f, we obtain the thin lens formulae

$$\frac{1}{f} = \frac{300e}{8mc^2E} \int_{\text{gap}} H_z^{\,2}\,\mathrm{d}z = \frac{0{\cdot}022}{E} \int_{\text{gap}} H_z^{\,2}\,\mathrm{d}z \qquad \ldots. \; (1.1)$$

where e, m and c have their usual meaning; e is in e.s.u. E is the electron energy in volts; H_z is the z-component of the field in oersteds; f is in centimetres. Owing to the radial velocity component of the electron and the axial field H_z, the plane of motion of the electron also rotates. The rotation of a thin lens is given by

$$\theta = \left(\frac{300e}{8mc^2E}\right)^{\frac{1}{2}} \int_{\text{gap}} H_z \, \mathrm{d}z = \frac{0{\cdot}148}{\sqrt{E}} \int_{\text{ap}} H_z \, \mathrm{d}z \qquad \ldots\ldots (1.2)$$

where θ is in radians. We see that the properties of a thin lens depend on the distribution of the z-component of the magnetic field in the gap. Similar formulae, including certain constants to take account of geometry, also hold for thick lenses (see Section 1.5). The axial distribution of magnetic field in the objective pole-piece of the Elmiskop 1 under normal operating conditions is shown in *Figure 1.4b*. The geometry of this pole-piece and specimen position is that shown in *Figure 1.4a*.

Electron lenses have aberrations which limit the resolution attainable in various ways. As in the case of the optical microscope, the aberrations in the objective lens are by far the most important. Hall, 1953, lists a total of eight third-order aberrations for a magnetic lens. We shall be concerned solely with the aberration which does not vanish on the axis of the lens, namely spherical aberration. In addition, we are also concerned with the aberration caused by defects in the pole-piece (astigmatism) and that introduced by the specimen itself, or by instability in the beam voltage supply (chromatic aberration).

Spherical aberration is the chief defect in the objective lens since at present there is no convenient way of correcting it. In *Figure 1.5* electrons leaving a

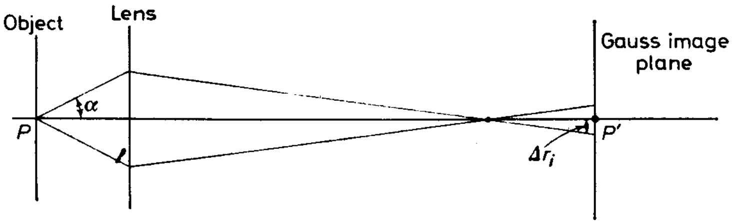

Figure 1.5. Illustrating the phenomenon of spherical aberration

point P on the object at an angle α to the axis arrive at the Gaussian image plane at a distance $\Delta r_i = MC_s\alpha^3$ away from Gauss image point P'. A pencil of semi-angle α thus gives rise to a disc of confusion of radius Δr_i in the image plane. Referred back to the object, the corresponding disc of confusion is of radius

$$\Delta r_s = C_s\alpha^3 \qquad \ldots\ldots (1.3)$$

C_s is the spherical aberration constant of the lens and is usually of the order of two or three millimetres in high resolution objectives. It should be noted that the spherical aberration of a magnetic lens is always positive. The off-axis ray is always bent more than it should be and marginal rays are always brought to a focus closer to the lens than axial rays.

Astigmatism results from asymmetry in the objective lens field produced either by inaccuracies in manufacture or by inhomogeneities in the soft-iron pole-piece. The lens effectively has different focal lengths for paraxial rays in the two principal planes of asymmetry as shown in *Figure 1.6.* In order to obtain a resolution of about 5 Å limited only by astigmatism, a typical objective pole-piece would have to be machined and aligned to an accuracy of about 1/20 μ, assuming absence of inhomogeneous effects. Since this is difficult to achieve, an adjustable correcting device known as a stigmator is usually built into the lens for producing equal and opposite astigmatism to the residual astigmatism of the pole-piece. Stigmators may be of the magnetic slug type or of the electrostatic type. The Metropolitan Vickers EM6 microscope has an electrostatic stigmator, while the Siemens Elmiskop has a magnetic stigmator. For further information regarding stigmators and their adjustment the reader should consult the manufacturers' handbooks, the book by Klemperer, 1953, and the article by Leisegang, 1956. It is usual in a modern high resolution microscope to have a stigmator in the objective and one also in the second condenser for correcting the astigmatism in the illumination.

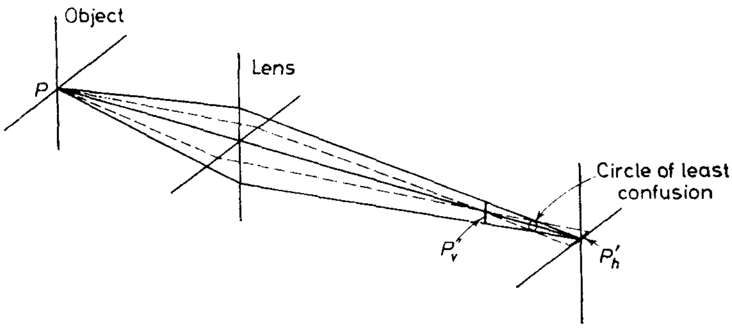

Figure 1.6. Illustrating the phenomenon of astigmatism. A conical pencil of rays forms two different line foci P_h' and P_v' at right angles

As already mentioned, chromatic aberration arises if there is an energy spread of the imaging electrons. In terms of equation 1.1 the focal length of the objective varies if E varies. Electrons which have lost energy are bent more by the objective field and therefore give rise to a disc of confusion in the image plane. It is easy to show from equation 1.1 and the usual thin lens formula, that the radius of this disc referred to object space is

$$\Delta r_c = f\alpha \frac{\Delta E}{E} \qquad \ldots. \; (1.4)$$

where ΔE is the energy spread. For a thick lens

$$\Delta r_c = C_c\alpha \frac{\Delta E}{E} \qquad \ldots. \; (1.5)$$

where C_c is the chromatic aberration constant, usually of the same order but slightly less than f. In the Elmiskop 1, for example, C_c is 2·2 mm at 100 kV compared with a focal length of 2·74 mm.

1.4. RESOLVING POWER. DEPTH OF FIELD AND DEPTH OF FOCUS

Since at present there is no convenient way of correcting the spherical aberration of the objective lens, the effect of this on resolving power can be limited only by stopping-down the aperture of the lens. This is in contrast to the case of the optical microscope where suitable aberration-free lenses of large numerical aperture can be obtained, so that the resolution is limited to the order of the wavelength of light by the diffraction effect occurring at the aperture. In the electron microscope we have to consider both the aperture diffraction aberration Δr_d (referred to object space) and the spherical aberration Δr_s given by equation 1.3. It is shown in books on physical optics (Jenkins and White, 1951) that the former aberration is given by

$$\Delta r_d = \frac{0{\cdot}61\ \lambda}{\alpha} \qquad \ldots. \ (1.6)$$

where λ is the De Broglie wavelength of the electron (see Chapter 4). The aberration of equation 1.6 increases with decreasing α whereas that of equation 1.3 decreases. Thus there is an optimum semi-aperture angle and minimum aberration given by

$$\alpha_{\text{opt}} = A\lambda^{1/4}C_s^{-1/4} \qquad \ldots. \ (1.7)$$

$$\Delta r_{\text{min}} = B\lambda^{3/4}C_s^{1/4} \qquad \ldots. \ (1.8)$$

The exact values of the constants A and B depend on the method of combination of the aberrations of equations 1.3 and 1.6, i.e. whether they are simply added or whether we take the square root of the sum of squares. It is hardly worth worrying about the exact procedure here, since a proper treatment would consider the lens aberrations in terms of wave optics and not in terms of ray optics. It suffices to state that the values of A and B are about unity, and equations 1.7 and 1.8 with A and B equal to unity may be taken as definitions of the optimum angle and minimum instrumental resolving power respectively. For a typical objective with $C_s = 3{\cdot}3$ mm at 100 kV ($\lambda = 0{\cdot}037$ Å), the resolving power Δr_{min} is about 6·5 Å, while α_{opt} is about 6×10^{-3} rad. This corresponds roughly to a 40 μ diameter objective aperture. This discussion has neglected the fact that the pole-piece may be astigmatic. In practice it is difficult to adjust a stigmator so that the astigmatic difference in focal length (referred to object space) is less than $\sim 10^{-5}$ cm. For the above aperture angle this would imply a disc of confusion of about 6 Å diameter, which is comparable with the estimate of instrumental resolving power. Therefore a more conservative estimate of resolving power would be in the range of 8 to 10 Å. Resolving powers of this order have been demonstrated for several modern instruments using suitable test specimens. The above estimate of resolving power depends on formula 1.6, which in turn assumes the applicability of the Rayleigh criterion to the images of two points just resolved. This criterion assumes that the waves emitted by two point objects are incoherent, and that the aperture of the objective lens is filled with scattered waves. This assumption is clearly inapplicable to cases where Bragg diffracted beams are formed. Discussion of