On the Contribution of A. McL. Mathieson to Crystallography*

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Abstract

We briefly describe some of the main contributions of Dr A. McL. Mathieson to various aspects of X-ray crystallography, including his contributions to: (i) crystal structure determination; (ii) the development of X-ray diffraction instruments; and (iii) measurement procedures.

1. Introduction

Alexander McLeod Mathieson was born in 1920 in Aberdeen, Scotland, where he attended the Central School and, later, the University, graduating in 1942 with the degree of B.Sc. in Chemistry. He was introduced to the field of chemical crystallography at the University of Glasgow, where he studied under Professor J. Monteath Robertson, graduating with a Ph.D. in 1948. In 1947 he came to Australia to join a newly formed section of the CSIR Division of Industrial Chemistry (later to become the CSIRO Division of Chemical Physics).

From the mid-1940s Mathieson has been an extremely active researcher in the area of X-ray crystallography and has also led, for more than 30 years, what has arguably been one of the most influential X-ray diffraction groups for its size in the world. The principal thrusts of Mathieson's work lie in the directions of X-ray structural studies of molecules $^{1-73}$) and of the associated development of instruments and measurement procedures⁷⁴⁻¹²⁴). The unifying force which binds together these seemingly disparate aspects of his work has been the fervent desire to assess and improve the accuracy of measurements of X-ray structure factors, in order both to lead to more reliable structure determinations and to the derivation of bonding-electron density information and atomic thermal vibration properties. This unyielding quest for accuracy led him to design new types of X-ray diffractometers, goniometer heads and monochromator arrangements. In each case the design for a new instrument appears to have arisen out of an intense desire to understand the underlying physical principles operating in a given experimental configuration. Often this driving curiosity provided the impetus for careful experiments to isolate the key physical factors and, in the important case of extinction (multiple scattering), led in turn to the development of a new general

* Dedicated to Dr Mathieson on the occasion of his 65th birthday.

principle for the elimination of extinction from structure factor measurements.

Mathieson's scientific achievements gained early recognition when, for example, in 1954 he was awarded the David Syme Medal and in 1956 he received a D.Sc. from the University of Melbourne. These were followed by the H. G. Smith Memorial Medal of the Royal Australian Chemical Institute in 1965 and election to the Australian Academy of Science in 1967. Mathieson served as a member of Council of the Australian Academy of Science from 1975–8 and as a member of the Australian National Committee of Crystallography from 1956–74 (and as Chairman 1965–74). He has been a member of two Commissions of the International Union for Crystallography (IUCr): the Commission on Crystallographic Apparatus (1960–72, Chairman 1963–72) and the Commission on Structure Reports (1960–72). He has also chaired the organizing committees of two international meetings; namely, the 1968 IUCr 'Accurate Determinations of X-ray Intensities and Structure Factors' (Cambridge, U.K.) and the 1974 IUCr/Australian Academy of Science meeting, 'Diffraction Studies of Real Atoms and Real Crystals' (Melbourne, Australia).

In the following sections we describe briefly some of Mathieson's key contributions to crystallography.

2. Structural Studies

Background

X-ray diffraction has long been recognized as a tool for crystal-structure determination^{125,126}). That is, it can be used to locate the positions of atoms within the unit cell of a crystal. These positions cannot, however, be located in a direct way. Rather, the Fourier transform of the diffracted intensities gives the Patterson function P(u), which is the convolution

$$P(u) = \int \rho(r) \rho(r+u) \, \mathrm{d}r, \qquad (1)$$

where $\rho(r)$ is the electron density distribution at position r and may be considered to be a set of discrete atomic densities peaking at each atomic centre. It can be seen that P(u) then has peaks whenever u is an interatomic vector.

Structure determination from the Patterson function is then a matter of choosing the correct atomic arrangement from a distribution of interatomic vectors. Although this process can be intractable, especially for very large molecules consisting of light atoms, there are several techniques which may render it amenable to solution. One of these is the 'heavy-atom' technique, in which a heavy-atom derivative (hopefully isomorphous with the original) of the structure to be solved is synthesized. Alternatively, a heavy atom may already be present in the structure. Then interatomic vectors from the heavy atom can be distinguished in the Patterson function because they link the strongest peaks.

At present, with automatic diffractometers for data collection and powerful computing facilities, the structure determination of small molecules may typically be accomplished on a time scale of the order of weeks. However, in the 1940s and early 1950s the situation was quite different. The most advanced computing devices were electromechanical desk calculators and primitive aids, such as Beevers-Lipson strips¹²⁷) (see the article on p. 263 of this issue). It was clearly essential to progress at that time to find methods to simplify the numerical task of structure determination and so two-dimensional projections of the Patterson function were used [see, e.g., ref.¹²⁸)].

Contributions to Structure Determination

From the late 1940s to the 1970s, Mathieson's contribution to the field of structural crystallography was substantial. The structures which he tackled were mainly complex organic molecules, usually natural products. Such compounds were difficult to study by standard chemical methods, because of their intrinsically complex stereochemistry and, in many cases, because only small quantities of the materials had been isolated.

As well as extracting the maximum chemical information from the structures he solved, Mathieson was concerned with improving or developing new techniques of structure analysis. Thus, he extended the scope and developed the power of generalized projections, first introduced by Cochran and Dyer¹²⁹) in which non-equatorial reciprocal lattice-layer data is manipulated mathematically to give projected Patterson and electron-density distributions. He also considered the implications for structure determination resulting from the use of different deconvolution and image-seeking functions⁸²).

In his early work Mathieson often relied on the heavy atom technique, as in the case of lanostenyl iodoacetate^{11,13}), a product of wool wax. In time he accepted the daunting challenge of keeping the heavy atom as light as possible, so that the reliability of the structure of the organic moiety would be correspondingly high; for example, in gliotoxin⁴³) (a fungal product with anti-biotic properties) he used the disulfide bridge as the heavy atom. In addition, the anomalous dispersion of the sulfur atom was used to determine the absolute configuration (whether the molecule points up or down with respect to the macroscopic polar axis), thus establishing the chirality of the disulfide bridge and of the skew diene chromophore. The chirality of the skew diene, taken in conjunction with the circular dichroism of gliotoxin⁴¹) (as determined by the rotation of polarized light), was thus shown to be at variance with the prediction of a previously accepted 'rule'¹³⁰).

During the course of his long series of structural studies, Mathieson was confronted by and overcame virtually every trick of Nature designed to tax the perseverance and ingenuity of the crystallographer: partial solvation of sporidesmin by methylene bromide³⁵); misleading elemental analysis²⁸); unsuspected water of crystallization²⁵); space-group-imposed false symmetry²⁸); more than one molecule per asymmetric unit^{31,43}); efflorescing solvated crystals⁴³) and many others.

One of Mathieson's techniques in structure solving involved making comparisons amongst related structures. In time he was able, by making a survey of known structures, to assign preferred conformations to commonly occurring molecular fragments; for example, in the case of ester groups in relation to saturated ring systems³⁷). Other structural problems addressed by Mathieson included the clay minerals [e.g. vermiculite^{10,15,17})], minerals of the hollandite family⁵), peptides [e.g. tosyl-L-prolyl-L-hydroxyproline²⁵)] and α -amino acids [e.g. DL-methionine⁸)]. In the case of DLmethionine, which is a sulfur bearing amino acid and an essential constituent of keratin, the structure determination problem was extremely difficult because this substance crystallizes in two forms, each with a different monoclinic space group.

Mathieson enjoyed a fruitful collaboration with staff from the CSIRO Division of Applied Organic Chemistry, in particular C. C. J. Culvenor, S. R. Johns and J. A.

Lamberton, spanning some 25 years, during which he and coworkers determined the molecular structure and absolute configuration of no less than 14 alkaloids, most of them representing new ring systems.

Mathieson's profound influence on the course of crystallography in Australia is further demonstrated by his many and varied collaborative efforts with scientists from other CSIRO Divisions [A. D. Wadsley, Mineral Chemistry⁵); G. F. Walker, Mineralogy^{10,15}); H. K. Welsh, Applied Physics^{9,34}); B. J. Poppleton, Forest Products^{38,46,48})] and Australian Universities [N. C. Stephenson, Sydney⁷); J. F. McConnell, B. P. Schoenborn and J. C. Taylor, New South Wales^{22,26,29,33}); M. F. Mackay, Latrobe^{32,44,45,49-54,64,65}); L. F. Power, Cook⁵⁵)].

Undoubtedly, his closest associate in structural studies was Janis Fridrichsons with whom he published 23 papers over a 22 year period. Other members of his laboratory for varying lengths of time included A. F. Beecham, B. Dawson, W. Denne, D. J. Sutor and J. A. Wunderlich. Moreover, his laboratory was the milieu for a constant stream of Australian and overseas crystallographers wishing to learn at first hand how and where so many complex crystal structures were being elucidated.



Fig. 1. Zero-layer Weissenberg photographs of lanostenyl iodoacetate at (a) room temperature and (b) -160° C [see ref.⁷⁸)].

3. Diffraction Procedures and Instrumentation

Until the 1960s nearly all diffracted intensity data were collected on film, rather than with counters, often using a Weissenberg camera. This moving film device allows one to record a subset of the total data (actually a layer of reciprocal space) instead of crowding and superimposing all the data on one film (see Fig. 1). Lacking such a camera on his arrival at the CSIR Division of Industrial Chemistry, Mathieson immediately set about building one⁷⁴). At about the same time, Mathieson conceived, in a moment of deep insight, an ingenious design for an automatic diffractometer based on a physical analogue of the reciprocal space condition for Bragg diffraction (Mathieson, CSIR Internal Rep. 1948). This device, independently developed later by Arndt and Phillips¹³¹) and called the linear diffractometer, could record one line of a diffraction layer at a time, and thus offered to minimize the amount of numerical computation required to collect a data set. These were the first in a long series of contributions by Mathieson to the field of diffraction apparatus design and procedures⁷⁴⁻¹²⁴).

A serious problem in determining the structure of organic molecules is the weakness of the diffracted intensities. This results from (i) the proportionality of the X-ray scattering cross section to atomic number and (ii) the diminution of intensity caused by thermal motion of the atoms. Mathieson attacked the weak intensity situation on two fronts. Firstly, with Dai Davies and Geoffrey Stiff, he constructed⁷⁹) a rotating anode X-ray generator. Secondly, to minimize the effect of thermal vibration the obvious approach is to cool the sample. With X-ray diffraction the design of cryostats requires windows of large solid angle to be constructed of a material transparent to X rays, such as beryllium foil. Mathieson and Fridrichsons⁷⁸) used an adaptation of Fankuchen's method¹³²), employing a cold stream of air fed into a sealed-off chamber within a Weissenberg camera. The enhancement of intensity at -160° C over that at room temperature is clear from Fig. 1.

By the late 1950s Mathieson had established in his laboratory the most favourable set of conditions possible at the time for collecting and analysing X-ray diffraction data. These conditions enabled his group to carry out a large number of highquality structure determinations throughout the next decade, with the result that the group became established as a centre of excellence in chemical crystallography and crystal-structure analysis. The time scale for a complete determination was gradually diminishing over that time, due largely to improved computer facilities. In the late 1950s a time span approaching a year was required, including sample preparation and data collection, but by 1970 this had been reduced by an order of magnitude.

Throughout this period the international scene had also been developing. Probabilistic methods had become powerful tools in small molecule crystal-structure analyses and were challenging the 'direct method' based on heavy-atom phasing, because they had the additional advantage of not requiring derivative formation. Computers were also becoming faster and more powerful. Taken in conjunction, the chemistry and the intellectual challenge appeared to be fading from chemical crystallography, at least in the short to medium term.

Two alternative and obvious frontiers for future research lay open. Firstly, the pursuit of the heavy-atom technique into protein crystallography or, secondly, the pursuit of the elusive bonding information which may be contained in the diffracted X-ray intensities. The monumental advances already achieved in the United Kingdom, the local historical precedent, and the large infra-structure required, but not available, to satisfactorily prosecute the protein problem all probably influenced Mathieson's own choice of research direction toward the quest for accuracy in X-ray structure factor measurements (a prerequisite to the derivation of bonding-electron density information). Thus, in the early 1970s Mathieson's interests were turning more towards the physics of X-ray diffraction, beginning with his works on polarization^{87,91,92,99,104}) and attenuation^{94,96,97}) of X rays.

Polarization and Extinction

Diffraction from a crystal causes polarization of the diffracted beam, with a resulting modification of the reflected intensity depending on the level of interaction of the X rays with the crystal. The level of interaction (intimately related to 'extinction' level) depends on many physical factors, including the X-ray wavelength and the perfection of the crystal. Mathieson's first concern with polarization came in 1968 with his design for a post-crystal monochromator-polarizer, in which the detector and monochromator could be rotated about the diffracted beam emanating from the sample⁸⁷). This arrangement had the advantage that the system was easy to align, since it could first be aligned in a conventional fashion with the detector alone, and also allowed for the investigation of the effect of modifying the interaction of the beam incident on the monochromator with respect to polarization effects.

At about the same time, Mathieson's interest in the accuracy of structure factor measurement was brought to a focus by his organization and chairmanship of the Cambridge Meeting on the 'Accurate Determination of X-ray Intensities and Structure Factors'. Leading speakers at that meeting included W. L. Bragg, N. V. Belov, B. Dawson, W. H. Zachariasen, N. Kato, M. Hart and P. P. Ewald.



Fig. 2. Bragg-reflexion scattering geometry illustrating for the Bragg angle θ_B a (a) negative, (b) zero and (c) positive asymmetry angle a.

One of the important innovations of the time was the establishment of Intensity and Structure Factor Measurement Projects^{88,89}) under the auspices of the IUCr, in which the same and also different samples of the same substance were used in structure measurements in different laboratories. A key finding from the analysis of these data was that (Mathieson, CSIRO Internal Rep. 1969) '... the magnitude of errors introduced by the operational factors of a diffractometer correctly handled, is of smaller significance than the errors which can be associated with the individual characteristics of a given crystal. In particular, the influence of internal morphology revealed as abnormal absorption effects appears to be frequently the most important factor.' It would appear difficult to overestimate the significance of this conclusion upon Mathieson's own viewpoint of the problem of accuracy in structure measurement and to the later course of his work. In fact, the very next sentence of this report goes on prophetically to say: 'To attempt to reduce or correct for the influence of such features on the measurements of intensities and so derive structure factor values which are of improved accuracy, it will be necessary to re-investigate the procedure for the measurement of integrated intensity and also to study procedures by which the specific characteristics of crystals can be diagnosed and estimated.'

An early influence on Mathieson's approach to *experimentally* exploring the problem of extinction was provided by the classic experiments in 1921 by Bragg *et al.*¹³³)



Fig. 3. Two-dimensional distribution of intensity in the Bragg reflexion, in terms of two variables, the crystal rotation $\omega_0 + \omega$ and the detector rotation $2\theta_0 + 2\theta + \sigma\omega$. The distributions $I(\omega, 2\theta)$, in contour form, correspond to (a) the ω scan ($\sigma = 0$), (b) the ω/θ scan ($\sigma = 1$) and (c) the $\omega/2\theta$ scan ($\sigma = 2$). In each case, the origin of the offset 2θ ordinate is associated with the centre of the peak of the α_1 component. The lines AA', BB' and CC' correspond to the trends associated with crystal mosaic and fragment character, the source distribution and the spectral distribution respectively [see ref.¹¹⁰)].

which consisted of measurements of integrated reflectivity on a series of plates of different thicknesses. This stimulated Mathieson to consider, in the years 1975–80, the influence on extinction of four key parameters, namely: (i) the sample thickness; (ii) the asymmetry parameter α , which measures the angle between the Bragg planes and the crystal surface (all taken in the plane of diffraction, see Fig. 2); (iii) the polarization, and (iv) the wavelength of the X rays.

Mathieson achieved variation in thickness using only one sample by the ingenious device of tilting it in Laue configuration¹⁰⁰). Similarly, the asymmetry parameter α could be varied in a precisely controllable manner by rotating the sample about the scattering vector⁹⁵). Mathieson's first foray in the area of asymmetry actually came with a design for a 'defocussing monochromator' from which the diffracted beam has a broader cross section than the incident beam. The contents of this brief laboratory note⁹³) were regarded as being so contentious that it passed through the hands of no less than five separate referees before being accepted. This episode stimulated Mathieson to a deeper consideration of the role of asymmetry in affecting the integrated intensity from extended face crystals and ultimately led to the classic work⁹⁸) in which he presented the integrated intensity measurements from a LiF crystal as a function of asymmetry and, in addition, outlined a means for obtaining extinction-free measurements for X-ray structure factors by extrapolation of data to the asymmetric limits. Works on extrapolation to zero extinction limits by controlled variation of plate thickness and incident wavelength of a plane polarized beam, with wavelength chosen such that the Bragg angle is made to approach 45°, followed rapidly, as also did an exposition of the general philosophy of experimentally eliminating extinction from structure factor measurements^{99-101,106}). Guided by the general philosophy of extrapolation to extinction-free limits, Mathieson and Mackenzie¹⁰⁵) [see also ref.¹²¹)] were able to show that γ -ray data¹³⁴) for Cu, which had been claimed to be extinctionfree, gave an anomalously low value for the 220 structure factor because of residual extinction effects.

Anatomy of Bragg Reflexions

On a somewhat different front of the same battle for accuracy in structure determination, Mathieson's careful measurement of the two-dimensional intensity distribution around a Bragg reflexion from BN, in which a fine slit was placed in front of the detector and the detector scanned for each setting angle of the crystal, led him to a thorough and elegant analysis^{110,112,114,115,117-119}) of the instrumental and crystal factors affecting the intensity distribution. This analysis provided simple diagnostic procedures for assessing the resolution of the instrument and the quality of the crystal (see Fig. 3), and thereby an improved prescription for conventional, onedimensional, intensity-profile measurements for routine data collection. By adopting an improved experimental technique¹²⁰), the two-dimensional examination of Bragg reflexions is capable of yielding reflectivity curves of imperfect crystals¹²³), these being of fundamental importance and intimately related to the crystal mosaic spread¹¹⁹). Extension of the same basic ideas also led Mathieson to an elegant analysis of the two-crystal case¹²⁴).

4. Epilogue

The above description constitutes but a skeletal outline of almost 40 years of continuous research by Mathieson, spanning a wide range of important problems in X-ray crystallography. Mathieson's work has been characterized by clear insight, a tenacious grasp of fundamental principles and an eschewing of mathematical embellishments. Not only may one measure his achievements by those works bearing his name, but also by the very great number of ideas which arose through his patient guidance and inspiration of others. In these and many other ways Mathieson has had a profound influence on a whole generation of Australian crystallographers.

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