owing to rapid changes in the Lorentz factor. At that time we tried to use the trend, that is the rate of change, of the profile. We now use an ω scan where this is not worth while since we measure the reflexions in an orderly sequence along a zigzag path through the lattice. The reciprocal lattice lines are very crowded, and so the change in profile from one reflexion to the next is slow. With more widely separated reflexions it might be necessary to take the trend into account.

COPPENS: How do you start the process?

DIAMOND: The program is primed with a hypothetical profile. The first one or two reflexions are thus badly matched until the program has learnt a better approximation.

HAMILTON: Is it necessary to be connected on-line to a computer? You are not using the computer to make running alterations.

DIAMOND: You could record the 128 ordinates of each reflexion on an off-line magnetic tape; the computer is most useful in reducing the output.

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Present Problems and Future Opportunities in Precise Intensity Measurements with Single-Crystal X-ray Diffractometers*

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Considerable progress is foreseen toward the precise determination of integrated X-ray reflection intensities from small single crystals. High on the list of presently-limiting problems are multiple reflection, extinction, thermal diffuse scattering, unnecessary other background, counting statistics, effective integration and specimen change. Specific recommendations for equipment design and use are made which will partially alleviate each of them. Opportunities for better utilization of existing equipment through improved strategies for data collection and employment of small on-line computers are pointed out.

Introduction

Accurate determination of Bragg intensities and structure factors depends both on well-designed diffractometric experiments and on application of corrections for factors not subject to experimental control. In the context of integrated intensities and small single crystals, this paper is concerned with the good design of the experiments, of which there are two principal and interacting aspects, equipment design and measurement strategy. Recent years have brought considerable progress, particularly in equipment design, and precision in the 2 or 3% range has become almost routine (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967; Ladell, 1965; Young & Sudarsanan, 1968; Zachariasen & Plettinger, 1965). However, there are several only partially solved problems and a number of opportunities for which significant progress can yet be expected in the foreseeable future. The problems discussed here are multiple reflection, extinction, thermal diffuse scattering, other background content, counting statistics, effective integration, and specimen change, *e.g.* annealing, radiation damage or deterioration. For each problem, one or more directions for experimental progress are indicated and, where appropriate, forward reference is made to other papers in this conference. Areas of opportunity discussed include (1) improvements in diffractometer design to provide more efficient use of the incident flux, (2) optimization of the data-collection strategy for the particular purpose (*e.g.* parameter) of interest and to assist in data validation, handling and reduction, and (3) control of specimen-environmental parameters as part of the diffraction experiment. Some comments about the purposes to be served by, and requirements of, on-line computers are included.

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Multiple reflection

Though recognized for many years (Renninger, 1937), multiple reflection has only recently begun to be seriously considered as a source of significant errors in 'routine precision' measurements of Bragg intensities. When two or more reciprocal lattice points are in contact with the Ewald sphere at the same time, intensity is reflected out of the stronger beams into the weaker ones. The degree to which this occurs depends on the number of reflections operating at once, the strengths of the coupling reflections, and on much the same parameters, especially mosaic spread, as are important to secondary extinction (Zachariasen, 1967). In a hypothetical extreme case, as Zachariasen (1965*a*,*b*) has pointed out, the result could be to make all reflections appear to have the same intensity. In practice, as Zachariasen has shown theoretically and Post (this

conference) experimentally, the intensity errors resulting from multiple reflection range all the way from trivial ($\ll 1\%$) to very significant, *e.g.* several percent to several hundred percent for weak reflections. The likelihood that multiple reflection will occur unless consciously avoided is, in fact, quite high. Obviously, the probability that some second reciprocal lattice point, H_2, will touch the Ewald sphere while measurements are being made on the first, H_1, will increase with increasing unit-cell size; for very large cells it will be effectively unity (Arndt, 1968). Further, multiple reflection is intrinsic to many commonly used geometries. In the equi-inclination Weissenberg case all intensity measurements are made under conditions of multiple reflection (Yakel & Fankuchen, 1962). With 3 and 4 circle diffractometers the common practice of mounting the specimen with a symmetry axis coincident with the diffractometer θ axis produces intrinsic multiple reflection in many cases (Burbank, 1965).

However it may be accomplished with a given instrument, in net result the one thing that the experimenter can do to avoid, or to assess, multiple reflection is to rotate the specimen about an axis (here to be designated σ) parallel to the vector $\mathbf{H}_1$ extending from the origin of reciprocal space to the reciprocal-lattice point corresponding to the reflection being measured. Fig. 1, taken from the literature (Cole, Chambers & Dunn, 1962) illustrates the result of such rotation for a particularly graphic case. Intrinsic multiple reflection can be avoided through straightforward modifications to the geometric arrangement [*e.g.* (1) dropping equi-inclination in favor of equal-cone geometry in the Weissenberg case (Santoro & Zocchi, 1966), (2) mounting the crystal in a random choice of orientation or one chosen not to permit any simple crystallographic direction to coincide with the φ-axis in 3 and 4-circle diffractometers (Busing & Levy, 1967), or (3) simple offsetting of the crystal orientation about $\mathbf{H}_1$, *i.e.* σ-axis offset]. However, avoidance of accidental multiple reflection (*i.e.* to the maximum degree possible) requires individual consideration of each reflection; an appropriate rotation angle about $\mathbf{H}_1$ must be chosen corresponding to a flat portion of a plot, for the reflection, like that of Fig. 1. Three degrees of freedom for specimen rotation are thus required for the general case and may be instrumentally provided for in several ways.

In the usual 4-circle diffractometer they are provided, at least in principle, by the χ, φ and ω axes. Busing & Levy (1967) have given the general solution to the problem of choosing χ, φ, and ω to give a specified rotation about a given reciprocal-lattice vector. Santoro & Zocchi (1964) and Powell (1966) have made computer programs for the pre-calculation, for each reflection, of the combinations of settings of χ, φ, and ω which will place the desired reciprocal-lattice point on the Ewald sphere while keeping all others off (unit-cell size permitting). Willis (1963), among others, has made use of this feature of the 4-circle diffractometer for several years and has used it to produce plots of neutron diffraction intensity *vs* rotation about $\mathbf{H}_1$, analogous to Fig. 1. While very useful for producing rotations about $\mathbf{H}_1$, the 4-circle diffractometer does have some shortcomings: (1) The large ω-motions sometimes required produce excessive χ-circle shadowing in reciprocal space and danger of collision with collimation and beam tunnels. (2) Unless a well-programmed computer is on line with the 4-circle diffractometer, dynamic use of rotation about $\mathbf{H}_1$ is not convenient.

An additional mechanical axis arranged to be always parallel to the diffraction vector, **S**, can provide the needed rotation directly and avoid most of the objections. We have called this axis the σ-axis (because of its parallelism with **S**) and have built several instruments which embody it (Young, Goodman & Kay, 1964). One σ-axis instrument with the other 4 axes automated is shown in Fig. 2. In our instruments the φ and χ axes are carried by the σ-axis and, hence, their settings for a given reflection are independent of σ. With ω fixed at zero, the standard $\theta-2\theta$ motion maintains this special axis parallel to **S**. A particular advantage is that neither (1) change or recalculation of crystal-setting angles initially calculated for some simple (symmetrically aligned) initial orientation nor (2) remounting of the crystal, are required to permit scanning of any (and every) reflection for the σ angle(s) at which multiple reflection effects are minimized. Fig. 3 demonstrates this feature in that it shows results ob-

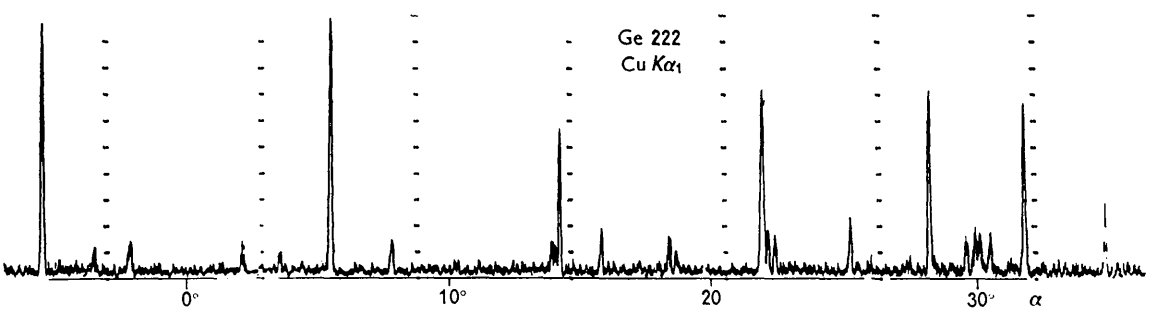

Fig. 1. Rotational-angle dependence of multiple reflection contributions to apparent reflection intensity of the 222, a forbidden reflection, in germanium. (Reprinted with permission from H. Cole *et al.*, 1962.)

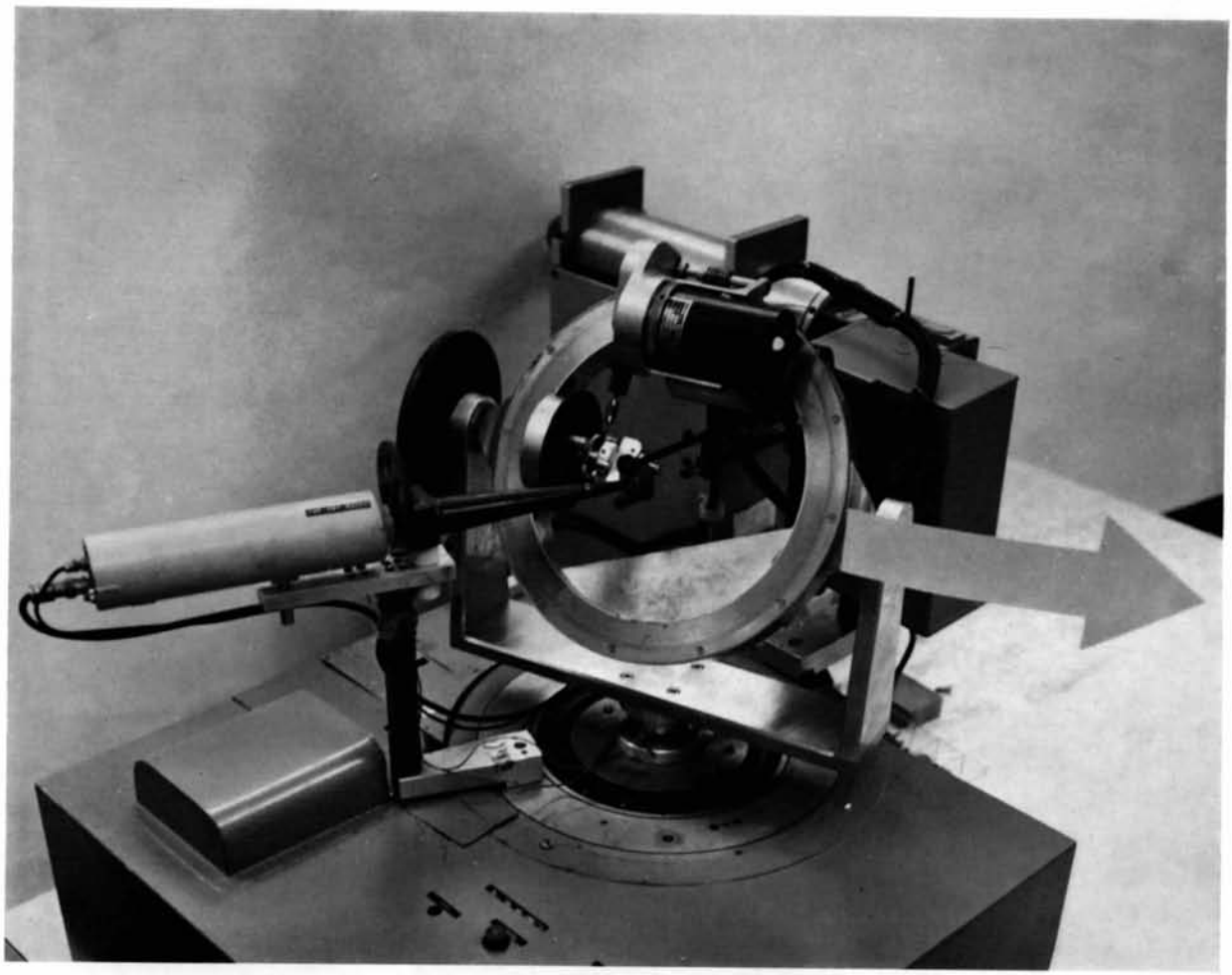

Fig. 2. σ-axis goniostat. Action of the σ-axis can be seen here as a tilt of the χ circle.

[*To face p.* 56

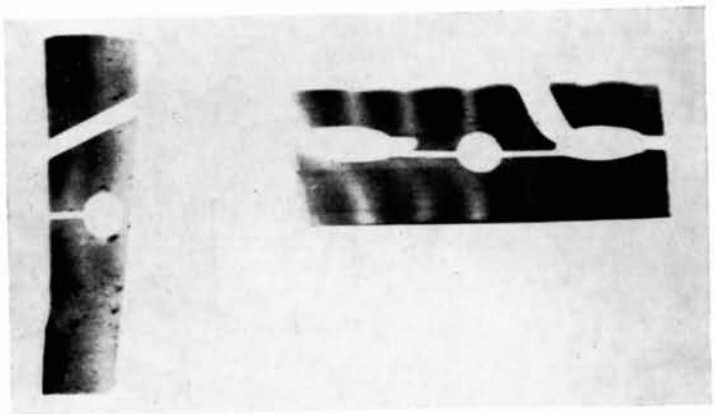

Fig. 4. Extinction anisotropy as shown by two X-ray topographic views of a quartz plate resonating at a particular ultrasonic frequency. The experimental conditions for the two topographs differed only by 90° rotation about the diffraction vector, as axis, here perpendicular to the page. Solid white areas are shadows of mounting wires. (Reprinted with permission from Young & Wagner, 1966.)

Fig. 13. Photograph of beam diffracted from a doubly-bent LiF monochromator.

tained for several unrelated reflections from a hydroxyapatite ($P6_3/m$) specimen in a single, symmetric ($c||\varphi$) mounting. ω was kept at zero; φ, χ, and 2θ were kept fixed during each σ scan. Incidentally, Fig. 3 also is indicative of the magnitude of the multiple reflection effect that might be expected in a practical case.

Extinction

It has long been generally recognized that reflections affected in large degree by extinction must either be discarded or corrected for the effect. It is much less widely recognized that correction for even small degrees of extinction becomes important when physically significant precision is demanded. An example occurs in a recent set of refinements based on different hydroxyapatite specimens of the same origin (Sudarsanan & Young, 1969). Before an extinction correction was applied, the largest R (based on $|F|^2$) value was 5·4% which would have seemed quite satisfactory by the standards of a few years ago. The disagreement among the different results (from different specimens) for the same parameter was 4σ in some cases, but these were anisotropic thermal parameters and σ was only $\sim 5\%$ of the parameter value. However, application of Zachariasen's (1963) extinction correction ($c=0{\cdot}0080$) reduced R from 5·4% to 3·5% for the specimen most affected and reduced the disagreements from 4σ in some cases to $\sim 1\sigma$ in all cases. Thus, in this case at least, the physical significance of the apparent precision was much enhanced by the application of extinction corrections in a case which already appeared to have attained 'good' precision.

The practical calculation of small (*i.e.* <25%) extinction corrections seems to be well in hand, thanks to Zachariasen's (1963) work, and is now widely used. There is also evidence that much larger extinction corrections can be made successfully (Zachariasen, 1967, and this conference). A quantitative experimental method of directly assessing extinction is still much to be desired both for itself and to complement and to direct the theoretical approach. The most notable example of an experimental direct method is Chandrasekhar's (1960; this conference) method based on the polarization-factor difference between kinematic and dynamical theory. We may anticipate that in this conference he will describe a practical experimental arrangement for the application of his method.

Another aspect of extinction which may be helpfully assessed experimentally is that of anisotropy. It is, perhaps, not yet widely appreciated that extinction depends on the orientation of the plane of incidence, not on S alone. This anisotropy was experimentally shown for quartz by Pringle (1955). More recently, X-ray topography and ultrasonic standing waves in a quartz plate were used to demonstrate (1) the reality of extinction anisotropy and (2) that its dependence on the orientation of the plane of incidence was in accord with a simplified interpretation of the full theory (Young & Wagner, 1966). Fig.4 is the principal figure making the point qualitatively in the referenced paper. It should be expected, therefore, that in a case in which extinction is anisotropic (due, perhaps, to anisotropy in the mosaic spread or in coherent-domain shape) the integrated intensity obtained for a reflection will depend on just how the plane of incidence happens to be oriented about S, as axis, during the scan. (Since different instrument geometries will produce different orientations of the plane of incidence during a scan, it is evident that tw oexperimenters could consistently obtain differing results for the intensities of the same reflections from the same specimens if anisotropic extinction is present.) Since this axis is the previously mentioned σ-axis, it is thus clear how the incorporation of a σ-axis in the instrument design can contribute to experimental assessment of extinction aniso-

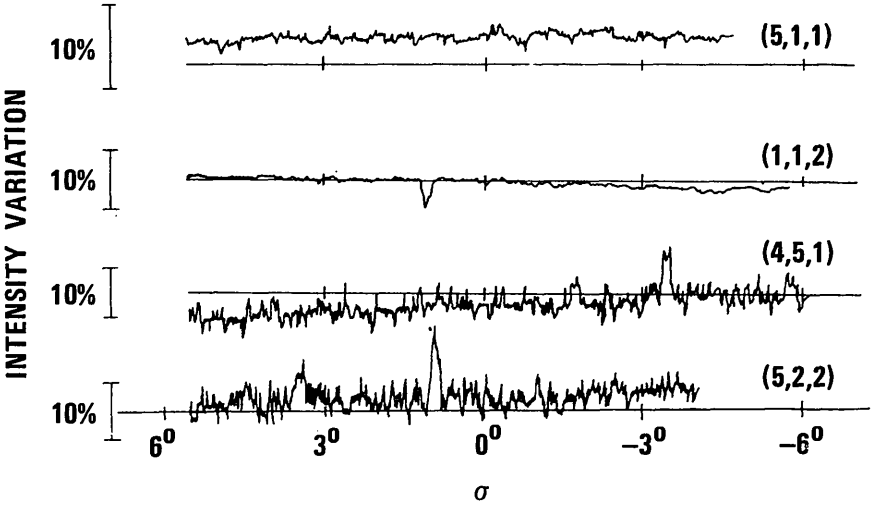

Fig. 3. Multiple-reflection effects as assessed for several unrelated reflections with the σ-axis goniostat shown in Fig. 2.

tropy. The experimental demonstration that, for several non-coplanar reflections, the integrated intensity did not depend (in a slowly varying way) on σ would constitute proof that extinction anisotropy was not a significant source of error. Practically, it probably would be necessary only to show that the peak intensities, rather than the integrated intensities, did not depend on σ.

Thermal diffuse scattering

Thermal diffuse scattering (TDS) is rapidly becoming recognized as the contributor of one of the major remaining sources of uncorrected error in precision single-crystal diffractometry. Thermal diffuse scattering contributes to apparent Bragg intensities largely because the rather slowly varying distribution of one-phonon TDS in reciprocal space peaks at the Bragg position and, hence, is not all included in the measured background. The resulting Bragg-intensity errors can be quite large, easily several % (Nilsson, 1957; Young, 1965). At present it appears that corrections for TDS must be based largely on theory and Professor Cochran (this conference) will give us the present status and recent developments in that area. However, the design of the experimental apparatus and well-chosen procedures for its use can contribute in several ways, *e.g.* (1) by operating at reduced temperatures where the TDS contribution is reduced, (2) by using narrow-profile geometry to minimize the scan-range and, hence, the TDS correction needed, (3) by permitting easy assessment of TDS anisotropy near the reciprocal-lattice point and (4) by lending themselves to experimental tests of the calculated corrections.

The first point rests primarily on the fact that the one-phonon contribution depends approximately linearly on temperature. However, the desired crystalline phase may not exist at the low temperature. Further, the specimen temperature may be otherwise specified as a requirement of the study.

The second point follows from the fact that the one-phonon TDS is intrinsically much less sharply peaked than is the Bragg peak. Thus, as the breadth of the instrumental profile or the width of the scan range is increased, relatively more TDS is included. Chipman & Batterman (1963) have made the point that, for highly perfect crystals and instruments with such narrow instrumental profiles that they sample only the immediate neighbourhood of the (very small) reciprocal lattice point, the TDS contribution is negligibly small. With a double-crystal spectrometer having such an extraordinarily narrow instrumental profile, Renninger (1967) has been able experimentally to display almost separately the TDS (mostly one-phonon) and the Bragg reflection. Fig. 5 shows some of his results. An instructive feature of this experimental figure is that one may readily note the amount of TDS that would be included if the observed Bragg peak profile (including instrumental broadening effects) were the usual $\frac{1}{4}$ to $\frac{1}{2}$ degree wide at half height instead of being only a few seconds wide. The difference between $\frac{1}{4}$ and $\frac{1}{2}$ degree may often be subject to practical control in a single-crystal diffractometer system designed for intensity-data collection. Contributing to the reduction of observed profile breadths are the use of (1) small (but brilliant) X-ray focal spots, (2) specimens no larger than necessary, and (3) source-to-specimen distances as large as are consistent with adequate intensity.

The third point concerns assessment of anisotropy in the TDS. That anisotropy should be expected, even near the reciprocal-lattice point, is clear. It is primarily the one-phonon contribution from the acoustic modes of lattice vibration that will be important, as the optic mode contributions may generally be expected to be much less peaked because of high dispersion. The

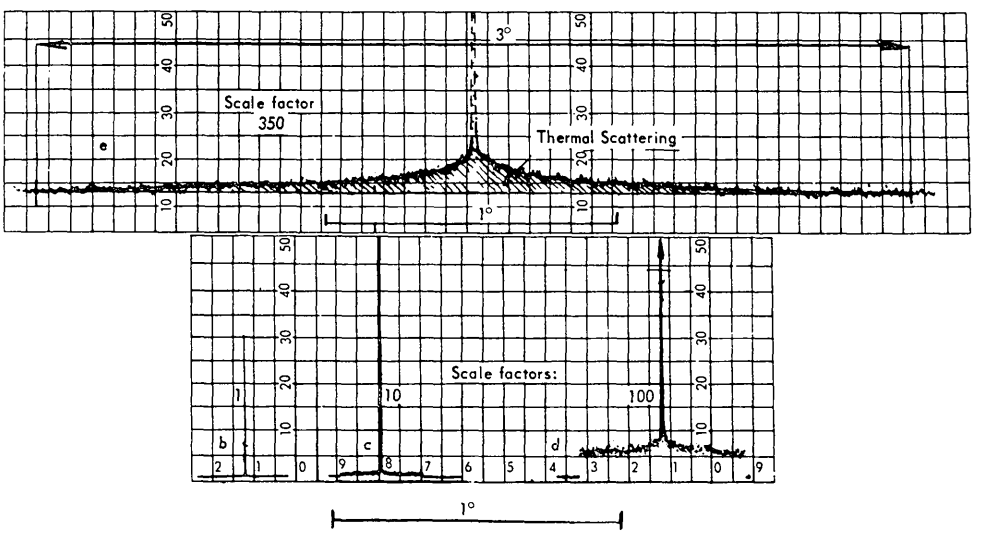

Fig. 5. Direct record of the thermal diffuse scattering intensity in relation to the Bragg peak intensity. (Reprinted with permission from Renninger, 1967.)

dominant TDS contribution not removed in background determinations should therefore arise from the portions of the acoustic branches close to the origin. There dispersion is low, the Debye spectrum approximation is good (for a given direction) and the velocity of sound determined from measurements of elastic constants should provide the information needed for calculation of the TDS. The TDS will therefore show anisotropy similar to that shown by the elastic tensor. Such anistropy is evident in Fig. 6, taken from Cole's (1952) plot of the TDS intensity in a reciprocal-lattice plane of AgCl. Though it is not at all a major point, for the experimental assessment of this anisotropy an instrumental σ-axis may sometimes be convenient.

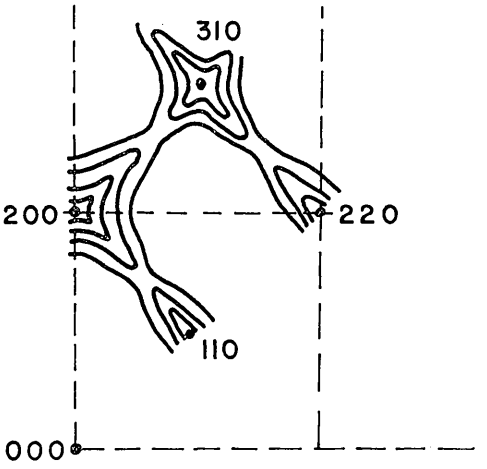

Fig. 6. Anisotropy of TDS shown by iso-scattering contours in reciprocal space of AgCl. (Reprinted with permission from Cole, 1953.)

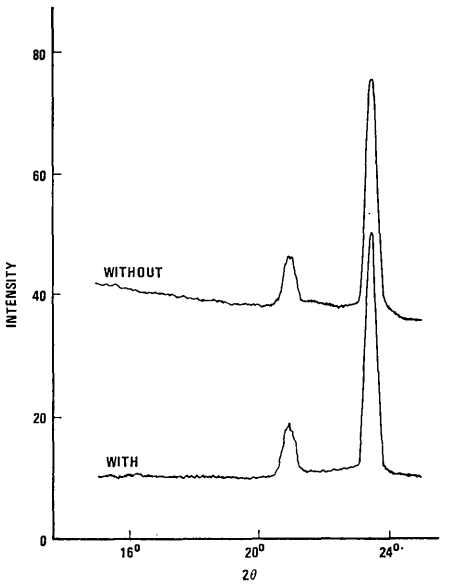

Fig. 7. Effect of diffracted-beam tunnel on background scattering with the instrument shown in Fig. 2. The specimen was a spherically shaped crystal of fluorapatite.

Finally, one would like to have an experimental method for spotchecking the accuracy of calculated TDS corrections. The need for such checking for each particular experiment arises because the calculated TDS correction depends strongly on the details of the particular experimental arrangement, *e.g.* counter aperture, specimen size and aspect presented to the incident beam, incident beam cross-fire, and distribution of intensity as a function of ray direction and cross-sectional position in the incident beam. It may often be possible to use the temperature dependence of the background slopes near the peak (but far enough away so that the tails of the Bragg peaks make a negligible contribution) for such an experimental verification. For example, in the one study (Nicklow & Young, 1964; 1966) where we have used this method we showed that our calculations were good to 15% and, hence our TDS correction was good to 1% of the Bragg intensity.

Incorporation of specimen-temperature control in the experimental design is therefore indicated by both points 1 and 4 of these TDS considerations. Obviously, it would be particularly convenient if specimen-temperature control were provided as an integral part of the diffraction experiment under the jurisdiction of, for example, the same on-line computer used to control the diffractometer.

Unnecessary other background

Because not all commercially available single-crystal diffractometers are properly designed in this respect, it is apparently worth re-emphasizing (see, for example, Young, 1965) that such things as unnecessarily large apertures and unenclosed beam paths reduce precision. They do so by permitting the measured background intensity to be increased without producing a compensating increase in Bragg-reflection intensity. One of the major sources of this additional background is air-scattering of X-rays from the incident-beam path. Such background is large at low 2θ angles because the detector then 'sees' more of the beam path. As one practical example, Fig. 7 shows the effect of removing the diffracted-beam tunnel from the instrument shown in Fig. 2. All other conditions were as they normally are during a data-collection run. It is obvious that the beam tunnel is an important feature in improving precision, even at fairly large angles.

Another important source of background is the white radiation present in unmonochromated X-ray beams. We can anticipate that Dr Kheiker (this conference) will cover this subject in detail. We restrict ourselves here to a few introductory comments about crystal monochromatization. Because the use of a crystal monochromator reduces the Bragg intensity while improving the signal-to-noise ratio, its use is not always indicated (Young, 1965). Further, its use may in-

troduce serious impediments to effective integration in reciprocal space, as we shall discuss later. However, a crystal monochromator's effect on reducing the background and improving the signal-to-noise ratio can be spectacular, as is shown by Fig. 8.

Counting statistics

Some ways of dealing with random variations to improve counting statistics are to be discussed in detail by Dr Diamond (this conference). We wish to point out two aspects of counting statistics that relate to equipment design and to scanning procedure.

The first is the matter of overall intensities. Obviously, the higher is the incident intensity then the shorter is the time required to count to a given statistical precision. We are interested in this time-saving both for itself and for its possible effect on the ultimately attainable precision through reduction of the opportunity for contributions from other sources of random error to build up. Rotating anode X-ray tubes are becoming increasingly popular as more people, such as Dr D. F. Koenig of Brookhaven National Laboratory (private communication, 1968), report good experience with them. However, for target atoms heavier than copper, in particular, there would seem to be a generally unexploited opportunity for us to increase the intensity of the characteristic radiation without increasing the heat load on the target. That is by increasing the high voltage applied to the tube. The intensity of the characteristic spectral line depends on the first power of the beam current but on a higher power (near $\frac{3}{2}$) of the *difference* between the applied potential and the excitation potential for the characteristic wavelength. Fig. 9 shows how the actual operational result with a Mo target and a constant heat load (100 watts) depends on applied voltage up to 50 kV, $\sim$ the maximum provided (or permitted) with most of today's diffraction equipment. Mental extrapolation from the Figure strongly suggests that a much higher applied voltage should be quite helpful. (The technical difficulties of operating X-ray diffraction tubes at voltages up to 100 kV are certainly not insuperable, for such was standard practice at the Cavendish Laboratory during the 1930's (Wilson, 1968).)

The second aspect of counting statistics is that of the signal-to-noise ratio, $\mathscr{S}$. For a single scan over a reflection profile on a linear background, the counting statistical standard error, σ, in the net intensity I_N is given by (see, for example, Young, 1965)

$$\frac{\sigma}{I_N} = \left[\frac{1+\frac{1+t}{\mathscr{S}}}{I_N}\right]^{1/2} \qquad (1)$$

where t is the ratio of time spent on the profile to that spent on background. It is therefore important that, for a given I_N, $\mathscr{S}$ should not be smaller than necessary. Excessive instrumental breadth in the profile simply diminishes $\mathscr{S}$. Similarly, background scans longer than necessary, such as from A to F rather than B to E in Fig. 10, also diminish $\mathscr{S}$. The $\mathscr{S}$ applicable to the integrated count collected during a scan is, obviously, some average of the signal-to-noise ratio at each point in the scan. One would like, then, to scan only the strongest part of the profile, *e.g.* from C to D or less, were it not for the severe truncation problem thereby introduced. (See Diamond, this conference, and Alexander & Smith (1962), for a profile-fitting scheme and a truncation-correction procedure, respectively, which might be applied here.)

From an equipment-design standpoint, $\mathscr{S}$ can be improved by reduction of the instrumental profile breadth through the use of X-ray tubes with small, high-brilliance focal spots. There are two practical lower limits on the desired focal spot size. One is that

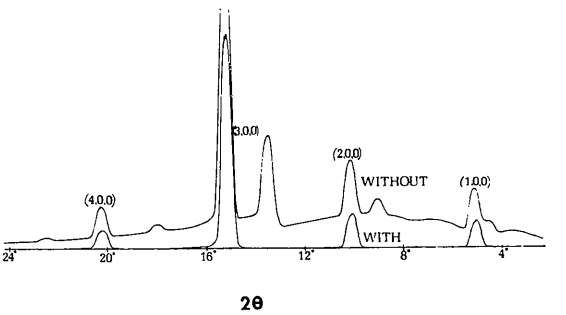

Fig. 8. Effect of crystal monochromator on $h00$ reflections of fluorapatite observed with Mo radiation.

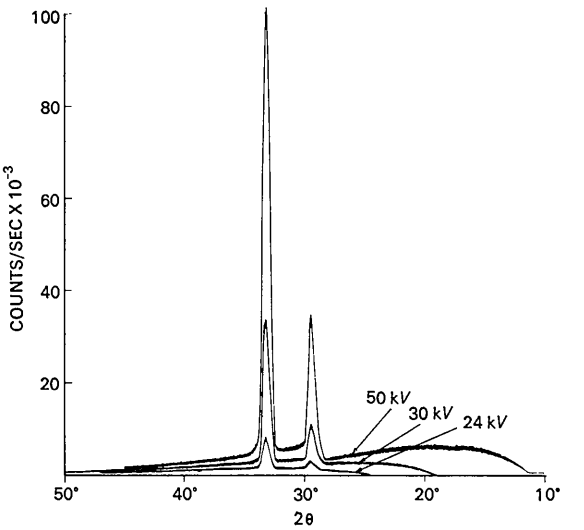

Fig. 9. Effect of increasing voltage applied to X-ray tube while keeping heat-load constant. (Mo-target sealed-off tube, 100 watts). Ratio of characteristic intensity to that of neighboring white radiation (corrected for counting losses at 50 keV) is 4·7 at 24 keV, 10·3 at 30 keV, and 23·0 at 50 keV.

the intensity available should not be reduced 'too much'. The other occurs at the point at which further reduction in focal spot size no longer produces significant reduction in the instrumental-profile breadth, as it is then primarily determined by other factors.

The use of crystal monochromators must certainly be considered in a discussion of control of $\mathscr{S}$ through equipment design. Crystal monochromators do always improve $\mathscr{S}$ by reducing the background more than the Bragg intensity. They can also improve $\mathscr{S}$ by reduction of the instrumental-profile breadth. However, as has been shown before (Young, 1965) the associated overall reduction of intensities will often impair rather than improve the counting statistics obtained in a given time. Attempts to compensate for the associated intensity loss by use of curved (focusing) crystal monochromators are not necessarily helpful. In fact, they could actually impair $\mathscr{S}$ (by requiring the use of larger apertures) while also tending to create reflection-overlap problems (Ladell & Spielberg, 1966) if the angle subtended at the specimen by the virtual source is large compared to the mosaic spread in the specimen. The high reflection efficiency of the new graphite monochromators, reported as high as 78% for one case with Mo radiation (Smith, 1968) seems to offer greater promise for the use of crystal monochromatization in single-crystal diffractometry.

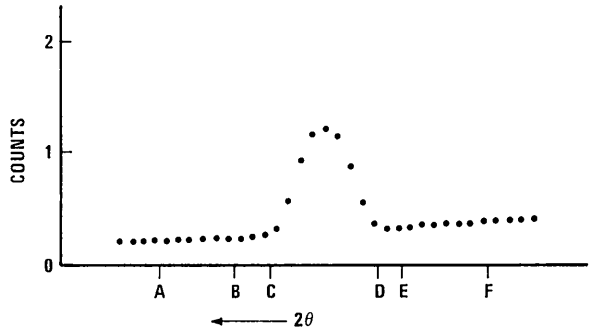

Fig. 10. Step-scanned reflection profile.

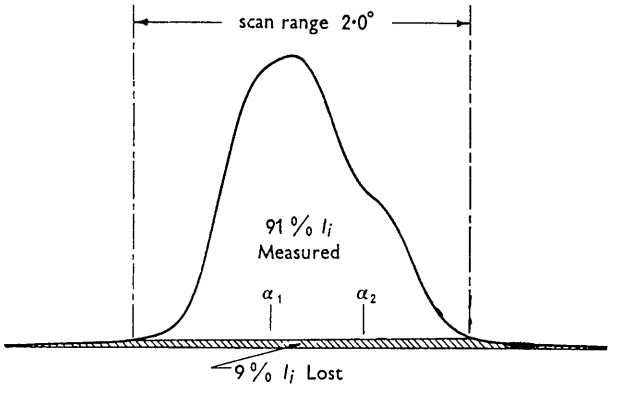

Fig. 11. Truncation effect. (Reprinted with permission from Alexander *et al.*, 1962.)

Effective integration

The problem of collecting an integrated intensity may be regarded as having both a geometric aspect and a weighting aspect, though the two are not entirely separable. In what we call the geometric aspect, the problem is that of detecting equally the intensity in all parts of the diffracted beam, of separating contributions from the various reflections (overlap), and of measuring all of the intensity including that in the tails of the reflection profile (truncation).

If the reflection profiles could be accurately predicted (see Diamond, this conference, for a discussion of such predictability), truncation corrections could be made as outlined by Alexander & Smith (1962) and scans could be kept short, thereby improving the signal-to-noise ratio, among other things. Fig. 11, taken from their paper, indicates something of the nature of the problem – actual profiles are not always simple. However, it does seem that a real possibility may exist for use of controlled truncation, followed by calculated truncation corrections, to reduce scanning times and, possibly, to improve precision by restricting measurement to parts of the scan where $\mathscr{S}$ is large.

Overlap of reflections can sometimes be a serious problem (Ladell & Spielberg, 1966), and exacerbates truncation problems. Overlap can be minimized by reduction of the instrumental profile breadth, b. The dispersion component of b can be much reduced by reducing the effective wavelength spread through crystal monochromatization, the component due to specimen mosaic spread can be reduced by use of an ω scan. The PAILRED instrument design exploits these two features to advantage.

The weighting aspect of effective integration is the requirement that each part of the specimen shall, except for losses in the specimen itself, receive equal illumination during the course of a scan. In many instruments not equipped with crystal monochromators, this aspect is attended by a design which lets each part of the crystal 'see' without obstruction each part of the X-ray source for equal times during the scan. When a crystal monochromator is used, two problems may arise: (1) the different parts of the specimen will receive radiation only from different parts of the source if the mosaic spread in the monochromator crystal is inadequate to permit each part of the specimen to 'see' equally well each part of the source reflected in the monochromator, (2) each point on the specimen receives radiation from a different set of points on the monochromator both at one time and in total. Fig. 12 is meant to help illustrate this point. It is assumed that the intrinsic diffraction profile of a mosaic block in the monochromator is narrow compared to the mosaic spread. In the Figure, $\beta - \beta'$ is the orientation difference

of two mosaic blocks which, let us say, represent the useful extremes. For example, these might correspond to the two 90%-height points (though >99% would be more appropriate for precision work) on a plot of quantity-of-mosaic-blocks as a function of orientation. We see that the active mosaic blocks are at different positions on the monochromator and reflect radiation from different parts of the target. Further, the two blocks may have differing reflection efficiencies for several reasons, one of which is difference in extinction. If, now, another point on the specimen is used the two corresponding 'useful extreme' mosaic block positions on the monochromator will be shifted along the surface by the difference in X coordinates of the specimen points. In these new positions the monochromator reflectivity may again be different. Without here going into the detail necessary to develop the points, one can perhaps accept as plausible the consequence that large (compared to the angle subtended by the source at the monochromator) mosaic spread and uniform reflectivity are important requirements of the monochromator if the weights given different parts of the specimen are not to differ, thereby preventing effective integration for determination of correct integrated intensities.

Many commonly used monochromator crystals do not meet these requirements. By way of example, Fig. 13 is a photograph of the beam from a doubly-bent LiF monochromator in use for powder diffractometry. Of course, much better crystals can be selected; the point is that individual selection is necessary.* Clearly, an operational test of the suitability of the crystal is needed. Here equipment design is to be considered again. If the monochromator mount permits controlled two-dimensional adjustment of the monochromator crystal parallel to its reflecting face, a 'good' portion of the crystal may be selected on the basis that small shifts in the monochromator crystal position then do not affect the integrated intensity measured for a particular specimen reflection.

Specimen change

Specimens may undergo change during examination due to annealing, radiation damage, continued slow chemical reaction, *etc.* We may anticipate that Dr Milledge (this conference) will discuss these matters in depth. We wish to develop some of the equipment-design implications.

If the change is not related to the incident flux, then the greater incident intensities from rotating-anode and higher-voltage X-ray tubes provide a partial solution. A concomitant need is that the detector dead-time be low enough so that the higher counting rates can actually be utilized. The new solid-state detectors such as Li-drifted Si and Li-drifted Ge show great promise in this regard. At the expense of high energy resolution, such detectors can operate with dead-times of a few nanoseconds.

If the specimen change is speeded by the X-ray flux then the approach must be to make more efficient use of the X-ray flux incident on the specimen. There are two parts to this, (1) preventing radiation of unused wavelengths from falling on the specimen and (2) detecting all diffracted photons. With ordinary X-ray sources, crystal monochromatization of the incident beam seems to be indicated as the method for eliminating unused wavelengths. It is in the second category, detection of all diffracted photons, that there seems presently to be the most promise for exciting new developments in the equipment for diffractometry.

Detection of all diffracted beams

In present single-crystal diffractometry attention is ordinarily fixed on the passage of a single reciprocal-lattice point through the surface of the Ewald sphere. But many reciprocal-lattice points pass at least partially into or out of the Ewald-sphere surface while the one point is passing through. Phillips (1964) has made good use of this 'nearly-simultaneous diffraction' to mount two or more detectors in position to make concurrent measures of such reflections. Arndt & Willis (1966) also report successful use of such a scheme. Plans for multi-cellular counters designed to detect reflections occurring anywhere in a large solid angle have been described (Cowan, MacIntyre & Thomas, 1965).

Li-drifted Ge detectors have been used at X-ray diffraction wavelengths with notable success: Giessen & Gordon (1968) have used the remarkable energy-resolution capability (*e.g.* 0·6 keV at 20,000 c/s) to produce X-ray diffraction powder patterns with a stationary detector and energy analysis of the white X-radiation diffracted onto it. Thomas (1968) is now exploiting

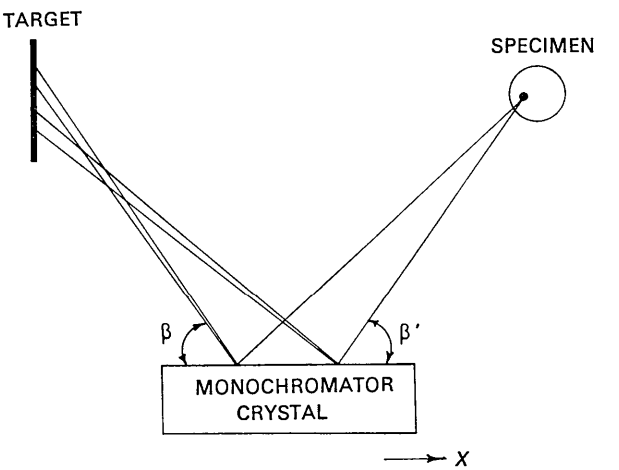

Fig. 12. Schematic representation of some geometric aspects of crystal-monochromator use.

* See comments by Azároff and Chandrasekhar following Witz's paper (B1.1).

the small sizes in which these Li-drifted Ge detectors can be used to mount many of them in a strip array which he will use to detect all of the reflections in one several-degree wide 2θ segment of a reciprocal-lattice layer. Using Weissenberg geometry and a computer to pre-calculate the proper location of the strip, he will know from the spindle angle the indices of the reflection detected by a particular counter.

Position-sensitive Li-drifted Ge detectors are now commercially available for use at gamma-ray energies (*e.g.* Nuclear Diodes, Inc., P.O. Box 135, Prairie View, Illinois 60069, U.S.A.). History suggests that, as happened with the scintillation counter, such devices will soon be effective at X-ray diffraction energies. In one design, a resistive strip on the back of the detector causes the relative amplitudes of the pulses detected at the two ends to reflect the position of the initiating event. The energy-resolution feature is said to be maintained. If such detectors live up to their promise, it takes little imagination for one to envisage a nearly 100%-efficient computer-operated diffractometer with no moving parts other than rotation of the crystal about one axis. Consider rotation-camera geometry with the film replaced by rings of one-dimensionally position-sensitive detectors placed where the layer lines would appear on the film when in place in the cylindrical cassette. One such detector might serve for a whole layer line if the technology of producing them in curved form can be mastered. (Epitaxic deposition methods may hold some promise here.) Otherwise, the ring could be a polygon, each straight-line segment of which was one detector. (It may be noted that such a configuration, with the detectors on the walls of a hollow cylinder and the specimen at its center, lends itself to cryogenic cooling.) The computer's task would then be to keep track of the rotation of the crystal in order to store counts from each detector location according to the appropriate Miller indices, both for Bragg-peak and background intensities. Finally, utilizing the energy-resolution feature one might simultaneously make use of the harmonic wavelengths present in the incident beam even if crystal-monochromatized. Such an arrangement would appear to represent the limit of getting the maximum (diffraction) information for a given X-ray exposure of the specimen.

Detectors position-sensitive in two dimensions have been reported (Cowan, MacIntyre & Thomas, 1965). Area-sensitive semiconductor detectors are also under development (*e.g.* Kalbitzer, Bader, Melzer & Stumpfi, 1967; Owen, 1968), also with energy resolution. It is intriguing to consider the possibilities of such detectors. With energy resolution capable of separating the various harmonics in a diffracted beam, such a detector could be used at the film position of a Laue camera to permit (with a large on-line computer) indexing of the reflections, including multiple orders, and to provide quantitative intensity information on each. With this flight of fancy one thus envisiges a quantitative diffractometer with no moving parts. Ten years from now this idea may appear foolish – or the diffractometer may be commercially available.

Data-collection strategy

The future of single-crystal diffractometry, as seen by this observer to be foreshadowed by the present, includes not only significant improvements, perhaps even radical changes, in equipment design but also, and perhaps with greater immediate reward, in data-collection strategy and with existing equipment.

Optimization of effort for the purposes of the study and validation of the data collected are the two aspects of strategy which we particularly wish to discuss here.

Optimization of effort

There are many different strategems in use for diffractometric data collection, each serving a different purpose. Often they are not ideally thought through, for the connection between ultimate purpose and the required strategem has often been quite unclear. Fortunately, that situation is changing, thanks in part to the recent literature.

The achievement, for a particular reflection, of the best counting statistics in a limited time, or of prechosen counting statistics subject to a maximum time limit, are requirements for which suitable strategems are easily determined. For example, a survey scan of each reflection permits determination of its approximate integrated intensity, I_N, and signal-to-noise ratio, $\mathscr{S}$. A computer (either on- or off-line) is then used to calculate, and to code into the control tape (or program) the required scan speed (or number of repetitions of the scan at one speed) required to produce the pre-chosen statistical precision as given by, for example, equation (1). The ratio of time-on-peak to time-on-background can also be programmed into the control structure at this time. [For the single-scan case of equation (1) the optimum value of this ratio is given by $t=(1+\mathscr{S})^{1/2}$.] The principal point to be made here is that some type of survey is needed, but it matters little whether the computer is off-line or on-line.

It has also been shown how the optimization in regard to statistics may be applied to the individual steps in a step-scanned profile (Wilson, Thomsen & Yap, 1965; Wilson, 1967).

Perhaps more interesting is the adjustment of relative emphasis put on each reflection in order to achieve minimum error in some crystal-structural property of interest. As Arndt & Willis (1966) point out, and as Killean (1967) has recently shown in detail, the error in electron density is minimized if equal time is devoted to scanning each reflection. An especially important paper is that by Shoemaker (1968) in which he develops quantitatively the previously missing, and much missed, connection between (1) the choice of structural parameter for which the errors are to be minimized and (2) the relative emphasis given to the determination of each reflection intensity. A rough knowledge of the

structure is required in advance, much as some survey information is needed if the counting statistics are to be preset. One easily remembered result applicable to many cases is that, unless an effectively infinite data collection time is to be used, Shoemaker finds that some reflections should not be measured at all!

Data validation

It is sometimes helpful to regard errors as being of three kinds: random errors, systematic errors, and blunders. Statistical treatments of random errors need no further discussion here. Of more interest are various tests of the collected data which can be made to detect errors of the last two kinds.

It is fairly common practice that a visual display, such as a strip-chart record or histogram, of the scanned profile is inspected for pathological character. Systematic errors such as interference from other reflections, overlap problems, and improper scan limits are among the factors subjectively adjudged in such visual inspection. Though difficult, it is not impossible and obviously will be standard operating procedure in the future for one to codify these various subjective judgments so that they may be carried out as objective tests by a computer. What is needed, then, is the detailed profile information such as is collected in a step-scanning procedure. Abrahams (Cetlin & Abrahams, 1963) has been using such a general procedure with an off-line computer for some years. An inconvenience is the large quantity of data output – at least 2 numbers for each of 50 to 100 data points for each reflection. Here an on-line computer is useful. Immediately following completion of a step-scan the computer can test the profile against the established criteria for normal character. If the profile meets the criteria, then all data except the net intensity, the signal-to-noise ratio, and the reflection indices, for example, can be discarded at once.

The matter of detecting blunders is easily addressed in automated data collection whether or not computer-controlled. If a σ-axis goniostat is in use, statistically significant multiple-reflection effects can be tested for at the same time. The strategy is that one collects the set of data twice, each time using only half of the counting time required for collection of the finally desired number of counts for each reflection. The two sets of data, each scaled to internal standards, may then be compared. If the two measures of a given reflection differ by more than, for example, 3 times the counting-statistical standard error, that reflection will then be set aside (either permanently or for later detailed study, as appropriate). Most of the reflections seriously compromised by errors such as scaler read-out errors, intermittent circuit malfunctions, *etc.* will thus be eliminated. Further, if the σ-axis is set differently for the two data sets, most of the reflections significantly compromised by avoidable multiple-reflection effects will also be eliminated. A particularly advantageous feature of the σ-axis here is that precisely the same set of control commands, whether on punched tape or in an on-line computer, is used for the two data sets, and thus another possible source of blunders is avoided.

Conclusions

In summary, we have tried to identify areas in which specified features of equipment design can make contributions in the area of precision determination of integrated intensities. These design features, many of which serve more than one purpose, include a σ-axis capability, low dead-time detectors, high voltage X-ray tubes, beam tunnels, suitably chosen and mounted crystal monochromators which need not be used, temperature control, and small (not micro), brilliant X-ray focal spots. We have pointed out advantages of multiple detectors and have tried to foresee a little of the exciting developments that may attend the successful use of extended detectors, *e.g.* diffractometers which have one or no moving parts and are far more efficient than present ones by virtue of detecting essentially all diffracted photons whatever their direction of travel. Many of these equipment design features and the functions to which they are applicable are summarized in Table 1.

We have particularly noted that there now seems to be considerable opportunity for improvement of experimental design through optimization of the data collection strategy within the context of a particular end to be served. Again, we feel compelled to mention Shoemaker's (1968) paper in this connection.

The background provided by the foregoing discourse affords a special opportunity for us to draw together here some thoughts about the use of on-line computers in single-crystal diffractometry.

On-line computers seem to us to be well used for purposes such as:

(1) Specimen-environment control as a part of the experiment.

(2) Initial data validation done to minimize required output from validation procedures based on, for example: (*a*) profile examination, and (*b*) comparison of sets of data that would be identical except for blunders and multiple-reflection effects.

(3) Implementation of data collection strategy based on reflection-by-reflection survey (thus saving the time involved in setting the angles a second time as would be required if an off-line computer were used) *e.g.* repeat scan until standard error is less than prechosen amount.

(4) Utilization of numerous or extended detectors.

An on-line computer is not purposefully used, we believe, to compensate for failures of mechanical maintenance or laboratory technique. (Even some protein crystals in the mother liquor may often remain fixed in position on the capillary wall. As for slipping goniometer heads, we have always found that routine maintenance of the gib adjustments eliminates this slippage.) Neither is much to be gained in most cases by

using an on-line computer to detect blunders on a scan-by-scan basis; so few occur that there is little lost if the reflections so affected are either re-examined later or, perhaps, simply omitted.

Finally, we would like to make some comments, based in part on our brief experience with one commercially available computer-controlled 4-circle diffractometer, about what we feel is required of an on-line computer. Though they need not be large, on-line computers should be programmable in a fairly high level language (preferably a commonly used one such as Fortran or Algol) through compilers which incorporate direct interrogation and control of the interface which, in turn, should include initially unused lines for the later control of other equipment, *e.g.* that for specimen-environment control, as part of the diffraction experiment. We would like to see the vendor of the composite apparatus take responsibility for the provision of this compiler; a particular operating program, though welcome on its own merits, is not a suitable substitute because it does not help the user to do his own programming and, thus, to take full advantage of the inherent flexibility of a computer-controlled instrument.

Grateful acknowledgement is made of many helpful conversations held during the formative period of this paper with many persons, and particularly Professor

Table 1. *Summary of purposes served by several points of experimental design*

Desirable aspects are indicated by '+', undesirable by '−'.

Problems and Purposes Served	Experimental Design Aspects														
	Hardware Design Features											Strategy-of-Use Features		
	σ-axis Rotation Capability	Crystal Monochromator: Ordinary Conditions	Crystal Monochromator: Special Selection and Mount	Crystal Monochromator: Rotation Axis	Beam Tunnels	Small, Brilliant Focal Spot	High Voltage X-Ray Tubes	Fast Detector	Temperature Control	Extended or Multiple Detectors	Store and Interpret Profile Information	Adjust Relative Time Per Reflection	Adjust Time per Point on Step-Scanned Profile
Multiple Reflection	++										+		
Extinction	+			+									
Crystal-Shape Anisotropy	++												
TDS	+	+	+			+			+				
Other Background		++	++		++	+							
Counting Statistics		±	+		+	+	+	+			+		
Effective Integration		−	+			+					+		
Specimen Change: With Time Only		−					+			++			
Specimen Change: With Irradiation		+	+							++			
Experimental Time		±					+			++		+	+
"Maximum" Information per Incident Photon		+	+							++			
Data Validation	+										+		
Optimization of Effort												++	+
On-line Computer Useful	+								+		+	+	+
On-line Computer Needed										+			+

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DISCUSSION

HERBSTEIN: In the early part of your talk you referred to the dangers of multiple reflexion, while, later, you dealt with the advantages of measurement of many reflexions simultaneously with the use of two-dimensional semi-conductor detectors. Is there a contradiction?

YOUNG: Not quite. For larger unit cells, simultaneous reflexions are unavoidable but, when they can be avoided, rotation about the scattering vector is the only systematic method.

JEFFERY: For smaller unit cells we deal with the problem of multiple reflexion when using equi-inclination cameras by displacing μ by $\frac{1}{2}°$.

ARNDT: I am not too hopeful about detector arrays. If we want a two-dimensional resolution of 1000×1000 (say) across the area of the detector, and also a range of levels to digitize energy, then the information required to be extracted and transferred to a computer is such that one wonders if there is at present a computer capable of dealing with it.

YOUNG: The amount of information to be handled may be quite manageable with linear rather than two-dimensional arrays.

ARNDT: You are aiming at recording the maximum number of reflexions for a minimum amount of X-ray exposure of the crystal: Linear arrays of semi-conductor detectors have to compete with photography without a layer-line screen, which is experimentally simpler when it is practicable. However, energy-discriminating semi-conductor detectors rapidly become easier to use as the quantum energy increases; these arrays may well be the answer for Mo $K\alpha$ and harder radiation, for which film is inefficient. Other three-dimensional data collection methods may be preferable when working with Cu $K\alpha$ and the softer radiations.